Chapter 1

The Schrödinger Equation

1.1 **(a)** F; **(b)** T; **(c)** T.

1.2 **(a)** $E_{\text{photon}} = h\nu = hc/\lambda =$(6.626 × 10^{-34} J s)(2.998 × 10^8 m/s)/(1064 × 10^{-9} m) = 1.867 × 10^{-19} J.

(b) E = (5 × 10^6 J/s)(2 × 10^{-8} s) = 0.1 J = n(1.867 × 10^{-19} J) and n = 5 × 10^{17}.

1.3 Use of $E_{\text{photon}} = hc/\lambda$ gives

$$E = \frac{(6.022\times10^{23})(6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m/s})}{300\times10^{-9}\text{ m}} = 399\text{ kJ}$$

1.4 **(a)** $T_{\max} = h\nu - \Phi =$

(6.626 × 10^{-34} J s)(2.998 × 10^8 m/s)/(200 × 10^{-9} m) – (2.75 eV)(1.602 × 10^{-19} J/eV) = 5.53 × 10^{-19} J = 3.45 eV.

(b) The minimum photon energy needed to produce the photoelectric effect is (2.75 eV)(1.602 × 10^{-19} J/eV) = $h\nu$ =hc/λ = (6.626 × 10^{-34} J s)(2.998 × 10^8 m/s)/λ and λ = 4.51 × 10^{-7} m = 451 nm.

(c) Since the impure metal has a smaller work function, there will be more energy left over after the electron escapes and the maximum T is larger for impure Na.

1.5 **(a)** At high frequencies, we have $e^{b\nu/T} >> 1$ and the -1 in the denominator of Planck's formula can be neglected to give Wien's formula.

(b) The Taylor series for the exponential function is $e^x = 1 + x + x^2/2! + \cdots$. For $x << 1$, we can neglect x^2 and higher powers to give $e^x - 1 \approx x$. Taking $x \equiv h\nu/kT$, we have for Planck's formula at low frequencies

$$\frac{a\nu^3}{e^{b\nu/T} - 1} = \frac{2\pi h\nu^3}{c^2(e^{h\nu/kT} - 1)} \approx \frac{2\pi h\nu^3}{c^2(h\nu/kT)} = \frac{2\pi\nu^2 kT}{c^2}$$

1.6 $\lambda = h/m\text{v} = 137h/mc =$ 137(6.626 × 10^{-34} J s)/(9.109 × 10^{-31} kg)(2.998 × 10^8 m/s) = 3.32 × 10^{-10} m = 0.332 nm.

1.7 Integration gives $x = -\frac{1}{2}gt^2 + (gt_0 + \mathsf{v}_0)t + c_2$. If we know that the particle had position x_0 at time t_0, then $x_0 = -\frac{1}{2}gt_0^2 + (gt_0 + \mathsf{v}_0)t_0 + c_2$ and $c_2 = x_0 - \frac{1}{2}gt_0^2 - \mathsf{v}_0 t_0$. Substitution of the expression for c_2 into the equation for x gives $x = x_0 - \frac{1}{2}g(t-t_0)^2 + \mathsf{v}_0(t-t_0)$.

1.8 $-(\hbar/i)(\partial\Psi/\partial t) = -(\hbar^2/2m)(\partial^2\Psi/\partial x^2) + V\Psi$. For $\Psi = ae^{-ibt}e^{-bmx^2/\hbar}$, we find $\partial\Psi/\partial t = -ib\Psi$, $\partial\Psi/\partial x = -2bm\hbar^{-1}x\Psi$, and $\partial^2\Psi/\partial x^2 = -2bm\hbar^{-1}\Psi - 2bm\hbar^{-1}x(\partial\Psi/\partial x)$ $= -2bm\hbar^{-1}\Psi - 2bm\hbar^{-1}x(-2bm\hbar^{-1}x\Psi) = -2bm\hbar^{-1}\Psi + 4b^2m^2\hbar^{-2}x^2\Psi$. Substituting into the time-dependent Schrödinger equation and then dividing by Ψ, we get $-(\hbar/i)(-ib\Psi) = -(\hbar^2/2m)(-2bm\hbar^{-1} + 4b^2m^2\hbar^{-2}x^2)\Psi + V\Psi$ and $V = 2b^2mx^2$.

1.9 **(a)** F; **(b)** F. (These statements are valid only for stationary states.)

1.10 ψ satisfies the time-independent Schrödinger (1.19). $\partial\psi/\partial x = be^{-cx^2} - 2bcx^2e^{-cx^2}$; $\partial^2\psi/\partial x^2 = -2bcxe^{-cx^2} - 4bcxe^{-cx^2} + 4bc^2x^3e^{-cx^2} = -6bcxe^{-cx^2} + 4bc^2x^3e^{-cx^2}$. Equation (1.19) becomes $(-\hbar^2/2m)(-6bcxe^{-cx^2} + 4bc^2x^3e^{-cx^2}) + (2c^2\hbar^2x^2/m)bxe^{-cx^2} = Ebxe^{-cx^2}$. The x^3 terms cancel and $E = 3\hbar^2c/m =$
$3(6.626 \times 10^{-34}\text{ J s})^2 2.00(10^{-9}\text{ m})^{-2}/4\pi^2(1.00 \times 10^{-30}\text{ kg}) = 6.67 \times 10^{-20}$ J.

1.11 Only the time-dependent equation.

1.12 **(a)** $|\Psi|^2\,dx = (2/b^3)x^2e^{-2|x|/b}\,dx =$
$2(3.0 \times 10^{-9}\text{ m})^{-3}(0.90 \times 10^{-9}\text{ m})^2e^{-2(0.90\text{ nm})/(3.0\text{ nm})}(0.0001 \times 10^{-9}\text{ m}) = 3.29 \times 10^{-6}$.

(b) For $x \ge 0$, we have $|x| = x$ and the probability is given by (1.23) and (A.7) as $\int_0^{2\text{ nm}} |\Psi|^2\,dx = (2/b^3)\int_0^{2\text{ nm}} x^2e^{-2x/b}\,dx = (2/b^3)e^{-2x/b}(-bx^2/2 - xb^2/2 - b^3/4)|_0^{2\text{ nm}} =$ $-e^{-2x/b}(x^2/b^2 + x/b + 1/2)|_0^{2\text{ nm}} = -e^{-4/3}(4/9 + 2/3 + 1/2) + 1/2 = 0.0753$.

(c) Ψ is zero at $x = 0$, and this is the minimum possible probability density.

(d) $\int_{-\infty}^{\infty}|\Psi|^2\,dx = (2/b^3)\int_{-\infty}^{0} x^2e^{2x/b}\,dx + (2/b^3)\int_0^{\infty} x^2e^{-2x/b}\,dx$. Let $w = -x$ in the first integral on the right. This integral becomes $\int_{\infty}^{0} w^2e^{-2w/b}(-dw) = \int_0^{\infty} w^2e^{-2w/b}\,dw$, which equals the second integral on the right [see Eq. (4.10)]. Hence $\int_{-\infty}^{\infty}|\Psi|^2\,dx = (4/b^3)\int_0^{\infty} x^2e^{-2x/b}\,dx = (4/b^3)[2!/(b/2)^3] = 1$, where (A.8) in the Appendix was used.

1.13 The interval is small enough to be considered infinitesimal (since Ψ changes negligibly within this interval). At $t = 0$, we have $|\Psi|^2 \; dx = (32/\pi c^6)^{1/2} x^2 e^{-2x^2/c^2} dx =$ $[32/\pi(2.00 \text{ Å})^6]^{1/2}(2.00 \text{ Å})^2 e^{-2}(0.001 \text{ Å}) = 0.000216$.

1.14 $\int_a^b |\Psi|^2 \, dx = \int_{1.5000 \text{ nm}}^{1.5001 \text{ nm}} a^{-1} e^{-2x/a} \, dx = -e^{-2x/a}/2 \,|_{1.5000 \text{ nm}}^{1.5001 \text{ nm}} = (-e^{-3.0002} + e^{-3.0000})/2 =$ 4.978×10^{-6}.

1.15 **(a)** This function is not real and cannot be a probability density.

(b) This function is negative when $x < 0$ and cannot be a probability density.

(c) This function is not normalized (unless $b = \pi$) and can't be a probability density.

1.16 **(a)** There are four equally probable cases for two children: BB, BG, GB, GG, where the first letter gives the gender of the older child. The BB possibility is eliminated by the given information. Of the remaining three possibilities BG, GB, GG, only one has two girls, so the probability that they have two girls is 1/3.

(b) The fact that the older child is a girl eliminates the BB and BG cases, leaving GB and GG, so the probability is 1/2 that the younger child is a girl.

1.17 The 138 peak arises from the case $^{12}C^{12}CF_6$, whose probability is $(0.9889)^2 = 0.9779$. The 139 peak arises from the cases $^{12}C^{13}CF_6$ and $^{13}C^{12}CF_6$, whose probability is $(0.9889)(0.0111) + (0.0111)(0.9889) = 0.02195$. The 140 peak arises from $^{13}C^{13}CF_6$, whose probability is $(0.0111)^2 = 0.000123$. (As a check, these add to 1.) The 139 peak height is $(0.02195/0.9779)100 = 2.24$. The 140 peak height is $(0.000123/0.9779)100 = 0.0126$.

1.18 There are 26 cards, 2 spades and 24 nonspades, to be distributed between B and D. Imagine that 13 cards, picked at random from the 26, are dealt to B. The probability that every card dealt to B is a nonspade is $\frac{24}{26}\frac{23}{25}\frac{22}{24}\frac{21}{23}\cdots\frac{14}{16}\frac{13}{15}\frac{12}{14} = \frac{13(12)}{26(25)} = \frac{6}{25}$. Likewise, the probability that D gets 13 nonspades is $\frac{6}{25}$. If B does not get all nonspades and D does not get all nonspades, then each must get one of the two spades and the probability that each gets one spade is $1 - \frac{6}{25} - \frac{6}{25} = 13/25$. (A commonly given answer is: There are four possible outcomes, namely, both spades to B, both spades to D, spade 1 to B and spade 2 to D, spade 2 to B and spade 1 to D, so the probability that each gets one spade is 2/4 = 1/2. This answer is wrong, because the four outcomes are not all equally likely.)

1.19 **(a)** The Maxwell distribution of molecular speeds; **(b)** the normal (or Gaussian) distribution.

1.20 **(a)** Real; **(b)** imaginary; **(c)** real; **(d)** imaginary; **(e)** imaginary; **(f)** real; **(g)** real; **(h)** real; **(i)** real.

1.21 **(a)** A point on the x axis three units to the right of the origin.

(b) A point on the y axis one unit below the origin.

(c) A point in the second quadrant with x coordinate –2 and y coordinate +3.

1.22 $\dfrac{1}{i}=\dfrac{1}{i}\dfrac{i}{i}=\dfrac{i}{i^2}=\dfrac{i}{-1}=-i$

1.23 **(a)** $i^2=-1$. **(b)** $i^3=ii^2=i(-1)=-i$. **(c)** $i^4=(i^2)^2=(-1)^2=1$.

(d) $i^*i=(-i)i=1$.

(e) $(1+5i)(2-3i)=2+10i-3i-15i^2=17+7i$.

(f) $\dfrac{1-3i}{4+2i}=\dfrac{1-3i}{4+2i}\dfrac{4-2i}{4-2i}=\dfrac{4-14i-6}{16+8i-8i+4}=\dfrac{-2-14i}{20}=-0.1-0.7i$.

1.24 **(a)** –4 **(b)** $2i$; **(c)** $6-3i$; **(d)** $2e^{i\pi/5}$.

1.25 **(a)** 1, 90°; **(b)** 2, $\pi/3$;

(c) $z=-2e^{i\pi/3}=2(-1)e^{i\pi/3}$. Since –1 has absolute value 1 and phase π, we have $z=2e^{i\pi}e^{i\pi/3}=2e^{i(4\pi/3)}=re^{i\theta}$, so the absolute value is 2 and the phase is 4π/3 radians.

(d) $|z|=(x^2+y^2)^{1/2}=[1^2+(-2)^2]^{1/2}=5^{1/2}$; $\tan\theta=y/x=-2/1=-2$ and $\theta=-63.4° = 296.6° = 5.176$ radians.

1.26 On a circle of radius 5. On a line starting from the origin and making an angle of 45° with the positive x axis.

1.27 **(a)** $i=1e^{i\pi/2}$; **(b)** $-1=1e^{i\pi}$;

(c) Using the answers to Prob. 1.25(d), we have $5^{1/2}e^{5.176i}$;

(d) $r=[(-1)^2+(-1)^2]^{1/2}=2^{1/2}$; $\theta=180°+45°=225°=3.927$ rad; $2^{1/2}e^{3.927i}$.

1.28 **(a)** Using Eq. (1.36) with $n = 3$, we have $e^{i\cdot 0}=1$, $e^{i(2\pi/3)}=\cos(2\pi/3)+i\sin(2\pi/3)=-0.5+i\sqrt{3}/2$, and $e^{i(4\pi/3)}=-0.5-i\sqrt{3}/2$.

(b) We see that ω in (1.36) satisfies $\omega\omega^* = e^0 = 1$, so the nth roots of 1 all have absolute value 1. When k in (1.36) increases by 1, the phase increases by $2\pi/n$.

1.29 $\dfrac{e^{i\theta} - e^{-i\theta}}{2i} = \dfrac{\cos\theta + i\sin\theta - [\cos(-\theta) + i\sin(-\theta)]}{2i} = \dfrac{\cos\theta + i\sin\theta - (\cos\theta - i\sin\theta)}{2i} = \sin\,\theta,$

where (2.14) was used.

$\dfrac{e^{i\theta} + e^{-i\theta}}{2} = \dfrac{\cos\theta + i\sin\theta + [\cos(-\theta) + i\sin(-\theta)]}{2} = \dfrac{\cos\theta + i\sin\theta + \cos\theta - i\sin\theta}{2} = \cos\,\theta.$

1.30 **(a)** From $f = ma$, 1 N = 1 kg m/s^2.

(b) 1 J = 1 kg m^2/s^2.

1.31 $F = \dfrac{Q_1 Q_2}{4\pi\varepsilon_0 r^2} = \dfrac{2(1.602\times 10^{-19}\ \text{C})79(1.602\times 10^{-19}\ \text{C})}{4\pi(8.854\times 10^{-12}\ \text{C}^2/\text{N-m}^2)(3.00\times 10^{-13}\ \text{m})^2} = 0.405$ N,

where 2 and 79 are the atomic numbers of He and Au.

1.32 **(a)** $4x\sin(3x^4) + 2x^2(12x^3)\cos(3x^4) = 4x\sin(3x^4) + 24x^5\cos(3x^4)$.

(b) $(x^3 + x)\,|_1^2 = (8+2) - (1+1) = 8$.

1.33 **(a)** T; **(b)** F; **(c)** F; **(d)** T; **(e)** F; **(f)** T.

Chapter 2

The Particle in a Box

2.1 **(a)** The auxiliary equation is $s^2 + s - 6 = 0$ and $s = [-1 \pm \sqrt{1+24}]/2 = 2$ and –3. So $y = c_1 e^{2x} + c_2 e^{-3x}$.

(b) Setting $x = 0$ and $y = 0$, we get $0 = c_1 + c_2$ (Eq. 1). Differentiation of y gives $y' = 2c_1 e^{2x} - 3c_2 e^{-3x}$. Setting $x = 0$ and $y' = 1$, we have $1 = 2c_1 - 3c_2$ (Eq. 2). Subtracting twice Eq. 1 from Eq. 2, we get $1 = -5c_2$ and $c_2 = -0.2$. Equation 1 then gives $c_1 = 0.2$.

2.2 For $y'' + py' + qy = 0$, the auxiliary equation is $s^2 + ps + q = 0 = (s - s_1)(s - s_2)$, where s_1 and s_2 are the roots. Comparison with Eq. (2.8) shows that $s_1 = 2 + i$ and $s_2 = 2 - i$, so the auxiliary equation is $0 = (s - 2 - i)(s - 2 + i) = s^2 - 4s + 5$. Therefore $p = -4$ and $q = 5$. The differential equation is $y'' - 4y' + 5y = 0$.

2.3 **(a)** The quadratic formula gives the solutions of the auxiliary equation $s^2 + ps + q = 0$ [Eq. (2.7)] as $s = (-p \pm \sqrt{p^2 - 4q})/2$. To have equal roots of the auxiliary equation requires that $p^2 - 4q = 0$. Setting $q = p^2/4$ in the differential equation (2.6), we have $y'' + py' + (p^2/4)y = 0$ (Eq. 1). The auxiliary-equation solution is $s = -p/2$. Thus we must show that $y_2 = xe^{-px/2}$ is the second solution. Differentiation gives $y_2' = e^{-px/2} - pxe^{-px/2}/2$ and $y_2'' = -pe^{-px/2} + p^2 xe^{-px/2}/4$. Substitution in Eq. (1) gives the left side of Eq. (1) as $-pe^{-px/2} + p^2 xe^{-px/2}/4 + pe^{-px/2} - p^2 xe^{-px/2}/2 + p^2 xe^{-px/2}/4$, which equals zero and completes the proof.

(b) The auxiliary equation $s^2 - 2s + 1 = (s-1)^2 = 0$ has roots $s = 1$ and $s = 1$. From part (a), the solution is $y = c_1 e^x + c_2 xe^x$.

2.4 In comparing Eqs. (1.8) and (2.2), y in (2.2) is replaced by x, and x in (2.2) is replaced by t. Therefore x and its derivatives in (1.8) must occur to the first power to have a linear differential equation. **(a)** Linear; **(b)** linear; **(c)** nonlinear; **(d)** nonlinear; **(e)** linear.

2.5 **(a)** F; **(b)** F; **(c)** T; **(d)** F (only solutions that meet certain conditions such as being continuous are allowed as stationary-state wave functions); **(e)** T.

2.6 **(a)** Maximum at $x = l/2$. Minimum at $x = 0$ and $x = l$, where the ends of the box are at $x = 0$ and l.

(b) Maximum at $l/4$ and $3l/4$. Minimum at 0, $l/2$, and l.

(c) Minimum at 0, $l/3$, $2l/3$, and l. Maximum at $l/6$, $l/2$, $5l/6$.

2.7 **(a)** $\int_0^{l/4} |\psi|^2\, dx = (2/l)\int_0^{l/4} \sin^2(n\pi x/l)\, dx = (2/l)[x/2 - (l/4n\pi)\sin(2n\pi x/l)]\,|_0^{l/4} =$ $1/4 - (1/2n\pi)\sin(n\pi/2)$, where (A.2) in the Appendix was used.

(b) The $(1/2n\pi)$ factor in the probability makes the probability smaller as n increases, and the maximum probability will occur for the smallest value of n for which the sine factor is negative. This value is $n = 3$.

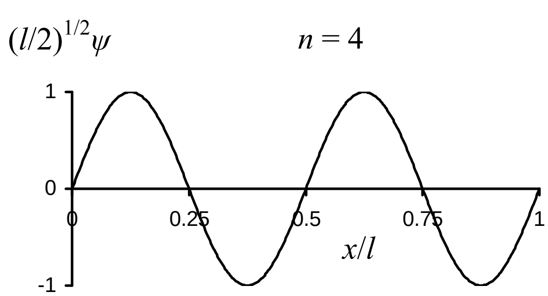
(c) 0.25.

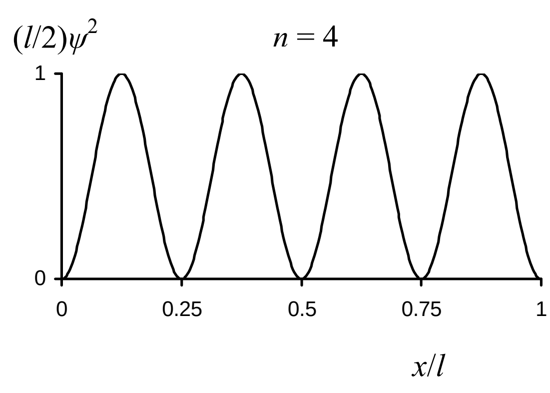
(d) The correspondence principle, since in classical mechanics the probability is uniform throughout the box.

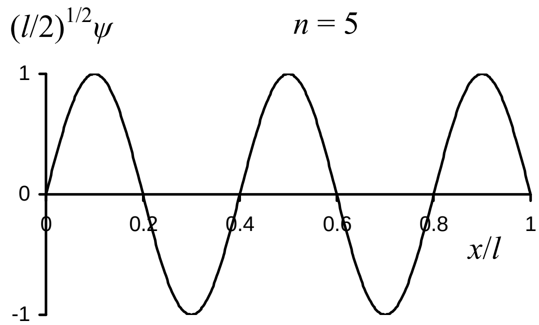
2.8 **(a)** The probability is $|\psi|^2\, dx = (2/l)\sin^2(\pi x/l)\, dx = (1/\text{Å})\sin^2(\pi \cdot 0.600/2)\cdot(0.001\ \text{Å})$ $= 6.55 \times 10^{-4}$. The number of times the electron is found in this interval is about $10^6(6.55 \times 10^{-4}) = 655$.

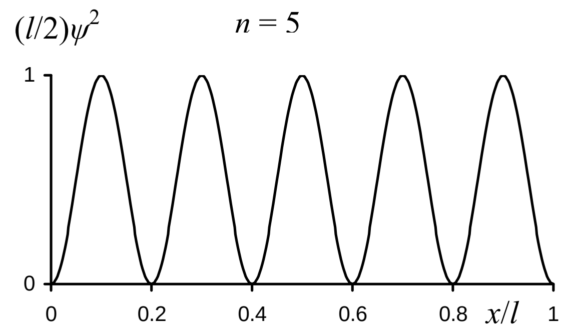
(b) The probability ratio for the two intervals is $\sin^2[\pi(1.00/2.00)]\big/\sin^2[\pi(0.700/2.00)] = 1.260$ and about $1.260(126) = 159$ measurements will be in the specified interval.

2.9 **(a)** The number of interior nodes is one less than n.









(b) $\psi^2 = (2/l)\sin^2(4\pi x/l)$ and $d(\psi^2)/dx = (4/l)(4\pi/l)\sin(4\pi x/l)\cos(4\pi x/l)$.
At $x = l/2$, $d(\psi^2)/dx = (4/l)(4\pi/l)\sin(2\pi)\cos(2\pi) = 0$.

2.10 **(a)** $E_{\text{upper}} - E_{\text{lower}} = (2^2 - 1^2)h^2/8ml^2 =$
$3(6.626 \times 10^{-34}\text{ J s})^2/8(9.109 \times 10^{-31}\text{ kg})(1.0 \times 10^{-10}\text{ m})^2 = 1.81 \times 10^{-17}$ J.
(b) $|\Delta E| = h\nu = hc/\lambda$ and $\lambda = hc/|\Delta E| =$
$(6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^8\text{ m/s})/(1.81 \times 10^{-17}\text{ J}) = 1.10 \times 10^{-8}\text{ m} = 110$ Å.
(c) Ultraviolet.

2.11 $E = n^2h^2/8ml^2$ and $n = (8mE)^{1/2}l/h$. We have $E = m\text{v}^2/2$ = ½(0.001 kg)(0.01 m/s)^2 = 5×10^{-8} J, so $n = [8(0.001\text{ kg})(5 \times 10^{-8}\text{ J})]^{1/2}(0.01\text{ m})/(6.626 \times 10^{-34}\text{ J s}) = 3 \times 10^{26}$.

2.12 $E_{\text{upper}} - E_{\text{lower}} = h\nu = (5^2 - 2^2)h^2/8ml^2$ and $l = (21h/8m\nu)^{1/2} =$
$[21(6.626 \times 10^{-34}\text{ J s})/8(9.1 \times 10^{-31}\text{ kg})(6.0 \times 10^{14}\text{ s}^{-1})]^{1/2} = 1.78 \times 10^{-9}\text{ m} = 1.78$ nm.

2.13 $E_{\text{upper}} - E_{\text{lower}} = h\nu = (n^2 - 1^2)h^2/8ml^2$, so $n^2 - 1 = 8ml^2\nu/h = 8ml^2c/\lambda h =$
$8(9.109 \times 10^{-31}\text{ kg})(2.00 \times 10^{-10}\text{ m})^2(2.998 \times 10^8\text{ m/s})/[(8.79 \times 10^{-9}\text{ m})(6.626 \times 10^{-34}\text{ J s})]$
$= 15$. So $n^2 = 16$ and $n = 4$.

2.14 $h\nu = (n_b^2 - n_a^2)h^2/8ml^2$, so ν is proportional to $n_b^2 - n_a^2$. For n = 1 to 2, $n_b^2 - n_a^2$ is 3 and for n = 2 to 3, $n_b^2 - n_a^2$ is 5. Hence for the 2 to 3 transition, $\nu = (5/3)(6.0 \times 10^{12}\text{ s}^{-1}) =$
$10 \times 10^{12}\text{ s}^{-1}$.

2.15 $h\nu = (n_b^2 - n_a^2)h^2/8ml^2$, so $n_b^2 - n_a^2 = 8ml^2\nu/h =$
$8(9.109 \times 10^{-31}\text{ kg})(0.300 \times 10^{-9}\text{ m})^2(5.05 \times 10^{15}\text{ s}^{-1})/(6.626 \times 10^{-34}\text{ J s}) = 5.00$.
The squares of the first few positive integers are 1, 4, 9, 16, 25,…, and the only two integers whose squares differ by 5 are 2 and 3.

2.16 $\nu = h^{-1}(E_{\text{upper}} - E_{\text{lower}}) = h^{-1}(h^2/8ml^2)(n_u^2 - n_\ell^2) = (h/8ml^2)k,$ where k is an integer.

For $n_u - n_\ell = 1$ and $n_\ell = 1, 2, 3, \ldots,$ we get the following k values:

$k = 2^2 - 1^2 = 3;\ k = 3^2 - 2^2 = 5;\ k = 4^2 - 3^2 = 7;\ k = 9, 11, 13, 15,$ etc.

For $n_u - n_\ell = 3$ and $n_\ell = 1, 2, 3, \ldots,$ we get

$k = 4^2 - 1^2 = 15;\ k = 5^2 - 2^2 = 21;\quad k = 6^2 - 3^2 = 27;\ k = 33, 39,$ etc.

For $n_u - n_\ell = 5$ and $n_\ell = 1, 2, 3, \ldots,$ we get $k = 35, 45, 55,$ etc.

The smallest k that corresponds to two different transitions is $k = 15$ for the 1 to 4 transition and the 7 to 8 transition.

2.17 Each double bond consists of one sigma and one pi bond, so the two double bonds have 4 pi electrons. With two pi electrons in each particle-in-a-box level, the 4 pi electrons occupy the lowest two levels, n = 1 and n = 2. The highest-occupied to lowest-vacant transition is from n = 2 to n = 3, so $|\Delta E| = h\nu = hc/\lambda = (3^2 - 2^2)h^2/8ml^2$ and

$$\lambda = \frac{8ml^2c}{5h} = \frac{8(9.109\times10^{-31}\text{ kg})(7.0\times10^{-10}\text{ m})^2(2.998\times10^8\text{ m/s})}{5(6.626\times10^{-34}\text{ J s})} = 3.2\times10^{-7}\text{ m} =$$

320 nm

2.18 Outside the box, $\psi = 0$. Inside the box, ψ is given by (2.15) as $\psi = a\cos[\hbar^{-1}(2mE)^{1/2}x] + b\sin[\hbar^{-1}(2mE)^{1/2}x]$. Continuity requires that $\psi = 0$ at $x = -l/2$ and at $x = l/2$, the left and right ends of the box. Using (2.14), we thus have

$0 = a\cos[\hbar^{-1}(2mE)^{1/2}l/2] - b\sin[\hbar^{-1}(2mE)^{1/2}l/2]$ [Eq. (1)]

$0 = a\cos[\hbar^{-1}(2mE)^{1/2}l/2] + b\sin[\hbar^{-1}(2mE)^{1/2}l/2]$ [Eq. (2)].

Adding Eqs. (1) and (2) and dividing by 2, we get $0 = a\cos[\hbar^{-1}(2mE)^{1/2}l/2]$, so

either $a = 0$ or $\cos[\hbar^{-1}(2mE)^{1/2}l/2] = 0$ [Eq. (3)].

Subtracting Eq. (1) from (2) and dividing by 2, we get $0 = b\sin[\hbar^{-1}(2mE)^{1/2}l/2]$, so

either $b = 0$ or $\sin[\hbar^{-1}(2mE)^{1/2}l/2] = 0$ [Eq. (4)].

If a = 0, then b cannot be 0 (because this would make ψ = 0), so if a = 0, then $\sin[\hbar^{-1}(2mE)^{1/2}l/2] = 0$ [Eq. (5)] and $\psi = b\sin[\hbar^{-1}(2mE)^{1/2}x]$. To satisfy Eq. (5), we must have $[\hbar^{-1}(2mE)^{1/2}l/2] = k\pi$, where k is an integer. The wave functions and energies when a = 0 are

$\psi = b\sin[2k\pi x/l]$ and $E = (2k)^2h^2/8ml^2$, where k = 1, 2, 3,…. [Eq. (6)]

(For reasons discussed in Chapter 2, k = 0 is not allowed and negative values of k do not give a different ψ.)

If $b = 0$, then a cannot be 0 (because this would make $\psi = 0$), so if $b = 0$, then $\cos[\hbar^{-1}(2mE)^{1/2} l/2] = 0$ [Eq. (7)] and $\psi = a\cos[\hbar^{-1}(2mE)^{1/2} x]$. To satisfy Eq. (7), we must have $[\hbar^{-1}(2mE)^{1/2} l/2] = (2j+1)\pi/2$, where j is an integer. The wave functions and energies when $b = 0$ are

$\psi = a\cos[(2j+1)\pi x/l]$ and $E = (2j+1)^2 h^2/8ml^2$, where j = 0, 1, 2, 3,… [Eq. (8)]
(As discussed in Chapter 2, negative values of j do not give a different ψ.)

In Eq. (8), $2j + 1$ takes on the values 1, 3, 5,…; in Eq. (6), $2k$ takes on the values 2, 4, 6,… . Therefore $E = n^2h^2/8ml^2$, where n = 1, 2, 3,…, as we found with the origin at the left end of the box. Also, the wave functions in Eqs. (6) and (8) are the same as with the origin at the left end, as can be verified by sketching a few of them.

2.19 Using square brackets to denote the dimensions of a quantity and M, L, T to denote the dimensions mass, length, and time, we have $[E] = \mathrm{ML^2T^{-2}} = [h]^a[m]^b[l]^c = [E]^a\mathrm{T}^a\mathrm{M}^b\mathrm{L}^c = (\mathrm{ML^2T^{-2}})^a\mathrm{T}^a\mathrm{M}^b\mathrm{L}^c = \mathrm{M}^{a+b}\mathrm{L}^{2a+c}\mathrm{T}^{-a}$. In order to have the same dimensions on each side of the equation, the powers of M, L, and T must match. So $1 = a + b$, $2 = 2a + c$, $-2 = -a$. We get $a = 2$, $b = 1 - a = -1$, and $c = 2 - 2a = -2$.

2.20 From Eqs. (1.20) and (2.30), $\Psi = e^{-iEt/\hbar}(c_1 e^{i(2mE)^{1/2}x/\hbar} + c_2 e^{-i(2mE)^{1/2}x/\hbar})$.

2.21 **(a)** Let $r \equiv (2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}$ and $s \equiv (2m/\hbar^2)^{1/2}E^{1/2}$. Then $\psi_{\mathrm{I}} = Ce^{rx}$ and $\psi_{\mathrm{II}} = A\cos sx + B\sin sx$. We have $\psi_{\mathrm{I}}' = Cre^{rx}$ and $\psi_{\mathrm{II}}' = -sA\sin sx + sB\cos sx$. The condition $\psi_{\mathrm{I}}'(0) = \psi_{\mathrm{II}}'(0)$ gives $Cr = sB$, so $B = Cr/s = Ar/s = A(V_0 - E)^{1/2}/E^{1/2}$, since $C = A$, as noted a few lines before Eq. (2.33).

(b) $\psi_{\mathrm{III}} = Ge^{-rx}$ and $\psi_{\mathrm{III}}' = -rGe^{-rx}$. From (a), $\psi_{\mathrm{II}}' = -sA\sin sx + s(Ar/s)\cos sx$. The relations $\psi_{\mathrm{II}}'(l) = \psi_{\mathrm{III}}''(l)$ and $\psi_{\mathrm{II}}(l) = \psi_{\mathrm{III}}(l)$ give $-sA\sin sl + rA\cos sl = -rGe^{-rl}$ and $A\cos sl + (Ar/s)\sin sl = Ge^{-rl}$. Dividing the first equation by the second, we get

$$\frac{-s\sin sl + r\cos sl}{\cos sl + rs^{-1}\sin sl} = -r$$ and $2rs\cos sl = (s^2 - r^2)\sin sl$. Substitution for r and s gives

$2(2m/\hbar^2)(V_0E - E^2)^{1/2}\cos[(2mE)^{1/2}l/\hbar] = (2m/\hbar^2)(2E - V_0)\sin[(2mE)^{1/2}l/\hbar]$, which is (2.33).

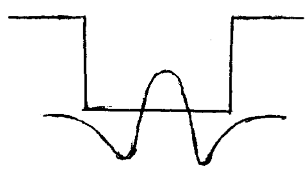
2.22 **(a)** As $V_0 \to \infty$, $2E$ on the left side of (2.33) can be neglected compared with V_0, and E^2 on the right side can be neglected to give $\tan[(2mE)^{1/2}l/\hbar] = -2(V_0E)^{1/2}/V_0 = -2(E/V_0)^{1/2}$. The right side of this equation goes to 0 as $V_0 \to \infty$, so $\tan[(2mE)^{1/2}l/\hbar] = 0$. This equation is satisfied when $(2mE)^{1/2}l/\hbar = n\pi$, where n is an integer. Solving for E, we get $E = n^2h^2/8ml^2$. (Zero and negative values of n are excluded for the reasons discussed in Sec. 2.2.)

(b) ψ_{I} and ψ_{III} are given by the equations preceding (2.32). In ψ_{I}, x is negative, and in ψ_{III}, x is positive. As $V_0 \to \infty$, ψ_{I} and ψ_{III} go to 0. To have ψ be continuous, ψ in (2.32) must be zero at $x = 0$ and at $x = l$, and we get (2.23) as the wave function inside the box.

2.23 $V_0 = (15.0 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV}) = 2.40 \times 10^{-18}$ J. $b = (2mV_0)^{1/2} l/\hbar =$ $[2(9.109 \times 10^{-31} \text{ kg})(2.40 \times 10^{-18} \text{ J})]^{1/2} 2\pi(2.00 \times 10^{-10} \text{ m})/(6.626 \times 10^{-34} \text{ J s}) = 3.97$ and $b/\pi = 1.26$. Then $N - 1 < 1.26 \le N$, so $N = 2$.

2.24 With $b = 3.97$, use of a spreadsheet to calculate the left side of (2.35) for increments of 0.005 in ε shows that it changes sign between the ε values 0.265 and 0.270 and between 0.900 and 0.905. Linear interpolation gives $\varepsilon \equiv E/V_0 = 0.268$ and 0.903, and $E =$ 0.268(15.0 eV) = 4.02 eV and 13.5 eV.

2.25



2.26 **(a)** The definition (2.34) shows that $b > 0$; hence $b/\pi > 0$. If the number N of bound states were 0, then we would have the impossible result that $b/\pi \le 0$. Hence N cannot be 0 and there is always at least one bound state.

(b) The Schrödinger equation is $\psi'' = -(2m/\hbar^2)(E - V)\psi$. Since V is discontinuous at $x = 0$, the Schrödinger equation shows that ψ'' must be discontinuous at $x = 0$.

2.27 $\varepsilon = E/V_0 =$ (3.00 eV)/(20.0 eV) = 0.150. Equation (2.35) becomes $-0.700\tan(0.387b) - 0.714 = 0$, so $\tan(0.387b) = -1.02$. From the definition (2.34), b cannot be negative, so $0.387b = -0.795 + \pi = 2.35$ and $b = 6.07$. (Addition of integral multiples of π to 2.35 gives $0.387b$ values that also satisfy Eq. (2.35), but these larger b values correspond to wells with larger l values and larger values of N, the number of bound levels; see Eq. (2.36). In these wider wells, the 3.00 eV level is not the lowest level.) Equation (2.34) gives $l = b\hbar/(2mV_0)^{1/2}$ =

$$\frac{6.07(6.626\times10^{-34} \text{ J s})}{2\pi[2(9.109\times10^{-31} \text{ kg})(20.0 \text{ eV})(1.602\times10^{-19} \text{ J/eV})]^{1/2}} = 2.65 \times 10^{-10} \text{ m} = 0.265 \text{ nm}.$$

2.28 Equation (2.36) gives $2\pi < (2mV_0)^{1/2}l/\hbar \le 3\pi$, so $l > 2\pi\hbar/(2mV_0)^{1/2}$ = $(6.626 \times 10^{-34}\text{ J s})/[2(9.109 \times 10^{-31}\text{ kg})(2.00 \times 10^{-18}\text{ J})]^{1/2} = 3.47 \times 10^{-10}\text{ m} = 3.47$ Å. Also, $l \le (3\pi/2\pi)$ (3.47 Å) = 5.20 Å.

2.29 **(a)** From Eq. (2.36), an increase in V_0 increases b/π, which increases the number N of bound states.

(b) An increase in l increases b/π, which increases the number N of bound states.

2.30 **(a)** From $\psi_{\text{I}}(0) = \psi_{\text{II}}(0)$, $\psi_{\text{II}}(l) = \psi_{\text{III}}(l)$, and $E = 0$, we get $C = b$ (Eq. 1) and $al + b = Ge^{-(2m/\hbar^2)^{1/2}V_0^{1/2}l}$ (Eq. 2). The conditions $\psi_{\text{I}}'(0) = \psi_{\text{II}}'(0)$ and $\psi_{\text{II}}'(l) = \psi_{\text{III}}'(l)$ give $C(2m/\hbar^2)^{1/2}V_0^{1/2} = a$ (Eq. 3) and $a = -(2m/\hbar^2)^{1/2}V_0^{1/2}Ge^{-(2m/\hbar^2)^{1/2}V_0^{1/2}l}$ (Eq. 4).

(b) If $C > 0$, then Eqs. 1 and 3 give $b > 0$ and $a > 0$. Equation 4 then gives $G < 0$ and Eq. 2 gives $G > 0$, which is a contradiction. If $C < 0$, then Eqs. 1 and 3 give $b < 0$ and $a < 0$. Equation 4 then gives $G > 0$ and Eq. 2 gives $G < 0$, which is a contradiction. Hence $C = 0$.

(c) With $C = 0$, Eqs. 1 and 3 give $b = 0$ and $a = 0$. Hence $\psi_{\text{II}} = 0$.

2.31 Although essentially no molecules have enough kinetic energy to overcome the electrostatic-repulsion barrier according to classical mechanics, quantum mechanics allows nuclei to tunnel through the barrier, and there is a significant probability for nuclei to come close enough to undergo fusion.

2.32 **(a)** F; **(b)** F; **(c)** T (Fig. 2.3 shows ψ' is discontinuous at the ends of the box.); **(d)** F; **(e)** T; **(f)** F (See Fig. 2.4.); **(g)** T; **(h)** F; **(i)** T.

Chapter 3

Operators

3.1 **(a)** $g = \hat{A}f = (d/dx)\cos(x^2+1) = -2x\sin(x^2+1)$;
(b) $\hat{A}f = \hat{5}\sin x = 5\sin x$;
(c) $\hat{A}f = \sin^2 x$;
(d) $\exp(\ln x) = e^{\ln x} = x$;
(e) $(d^2/dx^2)\ln 3x = (d/dx)3[1/(3x)] = -1/x^2$;
(f) $(d^2/dx^2 + 3x\,d/dx)(4x^3) = 24x + 36x^3$;
(g) $(\partial/\partial y)[\sin(xy^2)] = 2xy\cos(xy^2)$.

3.2 **(a)** Operator; **(b)** function; **(c)** function; **(d)** operator; **(e)** operator; **(f)** function.

3.3 $\hat{A} = 3x^2 \cdot + 2x(d/dx)$.

3.4 $\hat{1}$, (d/dx), (d^2/dx^2).

3.5 **(a)** Some possibilities are $(4/x)\times$ and d/dx.
(b) $(x/2)\times$, $(1/4)(\quad)^2$.
(c) $(1/x^2)\times$, $(4x)^{-1}\,d/dx$, $(1/12)\,d^2/dx^2$.

3.6 To prove that two operators are equal, we must show that they give the same result when they operate on an arbitrary function. In this case, we must show that $(\hat{A}+\hat{B})f$ equals $(\hat{B}+\hat{A})f$. Using the definition (3.2) of addition of operators, we have $(\hat{A}+\hat{B})f = \hat{A}f + \hat{B}f$ and $(\hat{B}+\hat{A})f = \hat{B}f + \hat{A}f = \hat{A}f + \hat{B}f$, which completes the proof.

3.7 We have $(\hat{A}+\hat{B})f = \hat{C}f$ for all functions f, so $\hat{A}f + \hat{B}f = \hat{C}f$ and $\hat{A}f = \hat{C}f - \hat{B}f$. Hence $\hat{A} = \hat{C} - \hat{B}$.

3.8 **(a)** $(d^2/dx^2)x^2x^3 = (d/dx)5x^4 = 20x^3$;
(b) $x^2(d^2/dx^2)x^3 = x^2(6x) = 6x^3$;
(c) $(d^2/dx^2)[x^2 f(x)] = (d/dx)(2xf + x^2 f') = 2f + 4xf' + x^2 f''$;

(d) $x^2(d^2/dx^2)f = x^2 f''$.

3.9 $\hat{A}\hat{B}f = x^3(d/dx)f = x^3 f'$, so $\hat{A}\hat{B} = x^3\, d/dx$. Also $\hat{B}\hat{A}f = (d/dx)(x^3 f) = 3x^2 f + x^3 f'$, so $\hat{B}\hat{A} = 3x^2 \cdot + x^3\, d/dx$

3.10 $[(\hat{A}\hat{B})\hat{C}]f = (\hat{A}\hat{B})(\hat{C}f) = \hat{A}[\hat{B}(\hat{C}f)]$, where (3.3) was used twice; first with $\hat{A}$ and $\hat{B}$ in (3.3) replaced by $\hat{A}\hat{B}$ and $\hat{C}$, respectively, and then with *f* in (3.3) replaced with the function $\hat{C}f$. Also, $[\hat{A}(\hat{B}\hat{C})]f = \hat{A}[(\hat{B}\hat{C})f] = \hat{A}[\hat{B}(\hat{C}f)]$, which equals $[(\hat{A}\hat{B})\hat{C}]f$.

3.11 **(a)** $(\hat{A}+\hat{B})^2 f = (\hat{A}+\hat{B})(\hat{A}+\hat{B})f = (\hat{A}+\hat{B})(\hat{A}f + \hat{B}f) = \hat{A}(\hat{A}f + \hat{B}f) + \hat{B}(\hat{A}f + \hat{B}f)$ (Eq. 1), where the definitions of the product and the sum of operators were used. If we interchange $\hat{A}$ and $\hat{B}$ in this result, we get $(\hat{B}+\hat{A})^2 f = \hat{B}(\hat{B}f + \hat{A}f) + \hat{A}(\hat{B}f + \hat{A}f)$. Since $\hat{A}f + \hat{B}f = \hat{B}f + \hat{A}f$, we see that $(\hat{A}+\hat{B})^2 f = (\hat{B}+\hat{A})^2 f$.

(b) If $\hat{A}$ and $\hat{B}$ are linear, Eq. 1 becomes $(\hat{A}+\hat{B})^2 f = \hat{A}^2 f + \hat{A}\hat{B}f + \hat{B}\hat{A}f + \hat{B}^2 f$. If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $(\hat{A}+\hat{B})^2 f = \hat{A}^2 f + 2\hat{A}\hat{B}f + \hat{B}^2 f$.

3.12 $[\hat{A},\ \hat{B}]f = (\hat{A}\hat{B} - \hat{B}\hat{A})f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$ and $[\hat{B},\ \hat{A}]f = (\hat{B}\hat{A} - \hat{A}\hat{B})f = \hat{B}\hat{A}f - \hat{A}\hat{B}f = -[\hat{A},\ \hat{B}]f$.

3.13 **(a)** $[\sin z,\ d/dz]f(z) = (\sin z)(d/dz)f(z) - (d/dz)[(\sin z)f(z)] =$
$(\sin z)f' - (\cos z)f - (\sin z)f' = -(\cos z)f$, so $[\sin z,\ d/dz] = -\cos z$.

(b) $[d^2/dx^2,\ ax^2+bx+c]f = (d^2/dx^2)[(ax^2+bx+c)f] - (ax^2+bx+c)(d^2/dx^2)f$
$= (d/dx)[(2ax+b)f + (ax^2+bx+c)f'] - (ax^2+bx+c)f''$
$= 2af + 2(2ax+b)f' + (ax^2+bx+c)f'' - (ax^2+bx+c)f'' = 2af + (4ax+2b)f'$,
so $[d^2/dx^2,\ ax^2+bx+c] = 2a + (4ax+2b)(d/dx)$.

(c) $[d/dx,\ d^2/dx^2]f = (d/dx)(d^2/dx^2)f - (d^2/dx^2)(d/dx)f = f''' - f''' = 0\cdot f$ so $[d/dx,\ d^2/dx^2] = 0$.

3.14 **(a)** Linear; **(b)** nonlinear; **(c)** linear; **(d)** nonlinear; **(e)** linear.

3.15 $[A_n(x)\,d^{(n)}/dx^{(n)} + A_{n-1}(x)\,d^{(n-1)}/dx^{(n-1)} + \cdots + A_1(x)\,d/dx + A_0(x)]y(x) = g(x)$

3.16 Given: $\hat{A}(f+g)=\hat{A}f+\hat{A}g,\ \hat{A}(cf)=c\hat{A}f,\ \hat{B}(f+g)=\hat{B}f+\hat{B}g,\ \hat{B}(cf)=c(\hat{B}f).$

Prove: $\hat{A}\hat{B}(f+g)=\hat{A}\hat{B}f+\hat{A}\hat{B}g,\ \hat{A}\hat{B}(cf)=c\hat{A}\hat{B}f.$

Use of the given equations gives $\hat{A}\hat{B}(f+g)=\hat{A}(\hat{B}f+\hat{B}g)=\hat{A}(\hat{B}f)+\hat{A}(\hat{B}g)=$ $\hat{A}\hat{B}f+\hat{A}\hat{B}g,$ since $\hat{B}f$ and $\hat{B}g$ are functions; also, $\hat{A}\hat{B}(cf)=\hat{A}(c\hat{B}f)=c\hat{A}(\hat{B}f)=c\hat{A}\hat{B}f.$

3.17 We have

$$\begin{aligned}
\hat{A}(\hat{B}+\hat{C})f &= \hat{A}(\hat{B}f+\hat{C}f) && \text{(defn. of sum of ops. } \hat{B} \text{ and } \hat{C}\text{)}\\
&= \hat{A}(\hat{B}f)+\hat{A}(\hat{C}f) && \text{(linearity of } \hat{A}\text{)}\\
&= \hat{A}\hat{B}f+\hat{A}\hat{C}f && \text{(defn. of op. prod.)}\\
&= (\hat{A}\hat{B}+\hat{A}\hat{C})f && \text{(defn. of sum of ops. } \hat{A}B \text{ and } \hat{A}\hat{C}\text{)}
\end{aligned}$$

Hence $\hat{A}(\hat{B}+\hat{C})=\hat{A}\hat{B}+\hat{A}\hat{C}.$

3.18 **(a)** Using first (3.9) and then (3.10), we have $\hat{A}(bf+cg)=\hat{A}(bf)+\hat{A}(cg)=b\hat{A}f+c\hat{A}g.$

(b) Setting $b=1$ and $c=1$ in (3.94), we get (3.9). Setting $c=0$ in (3.94), we get (3.10).

3.19 **(a)** Complex conjugation, since $(f+g)^*=f^*+g^*$ but $(cf)^*=c^*f^*\neq cf^*.$

(b) $(\ \ )^{-1}(d/dx)(\ \ )^{-1}$, since $(\ \ )^{-1}(d/dx)(\ \ )^{-1}cf=(\ \ )^{-1}(d/dx)c^{-1}f^{-1}=$
$(\ \ )^{-1}[c^{-1}(-f^{-2})f']=-cf^2/f'$ and $c(\ \ )^{-1}(d/dx)(\ \ )^{-1}f=c(\ \ )^{-1}(d/dx)f^{-1}=$
$-c(\ \ )^{-1}(f^{-2}f')=-cf^2/f'$, but
$(\ \ )^{-1}(d/dx)(\ \ )^{-1}(f+g)=(\ \ )^{-1}(d/dx)(f+g)^{-1}=-(\ \ )^{-1}[(f+g)^{-2}(f'+g')]=$
$-(f+g)^2(f'+g')^{-1}\neq(\ \ )^{-1}(d/dx)(\ \ )^{-1}f+(\ \ )^{-1}(d/dx)(\ \ )^{-1}g=-f^2/f'-g^2/g'.$

3.20 **(a)** This is always true since it is the definition of the sum of operators.

(b) Only true if $\hat{A}$ is linear.

(c) Not generally true; for example, it is false for differentiation and integration. It is true if $\hat{A}$ is multiplication by a function.

(d) Not generally true. Only true if the operators commute.

(e) Not generally true.

(f) Not generally true.

(g) True, since $fg=gf$.

(h) True, since $\hat{B}g$ is a function.

3.21 **(a)** $\hat{T}_h[f(x)+g(x)]=f(x+h)+g(x+h)=\hat{T}_hf(x)+\hat{T}_hg(x).$

Also, $\hat{T}_h[cf(x)]=cf(x+h)=c\hat{T}_hf(x).$ So $\hat{T}_h$ is linear.

(b) $(\hat{T}_1\hat{T}_1 - 3\hat{T}_1 + 2)x^2 = (x+2)^2 - 3(x+1)^2 + 2x^2 = -2x+1.$

3.22 $e^{\hat{D}}f(x) = (1+\hat{D}+\hat{D}^2/2!+D^3/3!+\cdots)f(x) = f(x)+f'(x)+f''(x)/2!+f'''(x)/3!+\cdots.$ $\hat{T}_1 f(x) = f(x+1).$ The Taylor series (4.85) in Prob. 4.1 with x changed to z gives $f(z) = f(a) + f'(a)(z-a)/1! + f''(a)(z-a)^2/2! + \cdots.$ Letting $h \equiv z-a,$ the Taylor series becomes $f(a+h) = f(a) + f'(a)h/1! + f''(a)h^2/2! + \cdots.$ Changing a to x and letting $h=1,$ we get $f(x+1) = f(x) + f'(x)/1! + f''(x)/2! + \cdots,$ which shows that $e^{\hat{D}}f = \hat{T}_1 f.$

3.23 **(a)** $(d^2/dx^2)e^x = e^x$ and the eigenvalue is 1.

(b) $(d^2/dx^2)x^2 = 2$ and x^2 is not an eigenfunction of d^2/dx^2.

(c) $(d^2/dx^2)\sin x = (d/dx)\cos x = -\sin x$ and the eigenvalue is –1.

(d) $(d^2/dx^2)3\cos x = -3\cos x$ and the eigenvalue is –1.

(e) $(d^2/dx^2)(\sin x + \cos x) = -(\sin x + \cos x)$ so the eigenvalue is –1.

3.24 **(a)** $(\partial^2/\partial x^2 + \partial^2/\partial y^2)(e^{2x}e^{3y}) = 4e^{2x}e^{3y} + 9e^{2x}e^{3y} = 13e^{2x}e^{3y}.$ The eigenvalue is 13.

(b) $(\partial^2/\partial x^2 + \partial^2/\partial y^2)(x^3y^3) = 6xy^3 + 6x^3y.$ Not an eigenfunction.

(c)
$(\partial^2/\partial x^2 + \partial^2/\partial y^2)(\sin 2x \cos 4y) = -4\sin 2x\cos 4y - 16\sin 2x \cos 4y = -20\sin 2x\cos 4y.$
The eigenvalue is $-20.$

(d) $(\partial^2/\partial x^2 + \partial^2/\partial y^2)(\sin 2x + \cos 3y) = -4\sin 2x - 9\cos 3y.$ Not an eigenfunction,

3.25 $-(\hbar^2/2m)(d^2/dx^2)g(x) = kg(x)$ and $g''(x) + (2m/\hbar^2)kg(x) = 0.$ This is a linear homogenous differential equation with constant coefficients. The auxiliary equation is $s^2 + (2m/\hbar^2)k = 0$ and $s = \pm i(2mk)^{1/2}/\hbar.$ The general solution is $g = c_1 e^{i(2mk)^{1/2}x/\hbar} + c_2 e^{-i(2mk)^{1/2}x/\hbar}.$ If the eigenvalue k were a negative number, then $k^{1/2}$ would be a pure imaginary number; that is, $k^{1/2} = ib,$ where b is real and positive. This would make $ik^{1/2}$ a real negative number and the first exponential in g would go to ∞ as $x \to -\infty$ and the second exponential would go to ∞ as $x \to \infty.$ Likewise, if k were an imaginary number ($k = a + bi = re^{i\theta},$ where a and b are real and b is nonzero), then $k^{1/2}$ would have the form $c + id,$ and $ik^{1/2}$ would have the form $-d + ic,$ where c and d are real. This would make the exponentials go to infinity as x goes to plus or minus infinity. Hence to keep g finite as $x \to \pm\infty,$ the eigenvalue k must be real and nonnegative, and the allowed eigenvalues are all nonnegative numbers.

3.26 $(\int dx)f = \int f\ dx = kf$. Differentiation of both sides of this equation gives $(d/dx)\int f\ dx = f = kf'$. So $df/dx = k^{-1}f$ and $(1/f)df = k^{-1}dx$. Integration gives $\ln f = k^{-1}x + c$ and $f = e^c e^{x/k} = Ae^{x/k}$, where A is a constant and k is the eigenvalue. To prevent the eigenfunctions from becoming infinite as $x \to \pm\infty$, k must be a pure imaginary number. (Strictly speaking, $Ae^{x/k}$ is an eigenfunction of $\int dx$ only if we omit the arbitrary constant of integration.)

3.27 $d^2 f/dx^2 + 2df/dx = kf$ and $f'' + 2f' - kf = 0$. The auxiliary equation is $s^2 + 2s - k = 0$ and $s = -1 \pm (1+k)^{1/2}$. So $f = Ae^{[-1+(1+k)^{1/2}]x} + Be^{[-1-(1+k)^{1/2}]x}$, where A and B are arbitrary constants. To prevent the eigenfunctions from becoming infinite as $x \to \pm\infty$, the factors multiplying x must be pure imaginary numbers: $-1 \pm (1+k)^{1/2} = ci$, where c is an arbitrary real number. So $\pm(1+k)^{1/2} = 1 + ci$ and $1 + k = (1+ci)^2 = 1 + 2ic - c^2$ and $k = 2ic - c^2$.

3.28 **(a)** $\hat{p}_y^3 = (\hbar/i)^3(\partial/\partial y)^3 = i\hbar^3\,\partial^3/\partial y^3$;

(b) $\hat{x}\hat{p}_y - \hat{y}\hat{p}_x = x(\hbar/i)\partial/\partial y - y(\hbar/i)\partial/\partial x$;

(c) $[x(\hbar/i)\partial/\partial y]^2 f(x,\ y) = -\hbar^2(x\,\partial/\partial y)(x\,\partial f/\partial y) = -\hbar^2(x^2\,\partial^2 f/\partial y^2)$.
Hence $(\hat{x}\hat{p}_y)^2 = -\hbar^2(x^2\,\partial^2/\partial y^2)$.

3.29 $(\hbar/i)(dg/dx) = kg$ and $dg/g = (ik/\hbar)\,dx$. Integration gives $\ln g = (ik/\hbar)x + C$ and $g = e^{ikx/\hbar}e^C = Ae^{ikx/\hbar}$, where C and A are constants. If k were imaginary $(k = a + bi$, where a and b are real and b is nonzero), then $ik = ia - b$, and the $e^{-bx/\hbar}$ factor in g makes g go to infinity as x goes to minus infinity if b is positive or as x goes to infinity if b is negative. Hence b must be zero and $k = a$, where a is a real number.

3.30 **(a)** $[\hat{x},\ \hat{p}_x]f = (\hbar/i)[x\,\partial/\partial x - (\partial/\partial x)x]f = (\hbar/i)[x\,\partial f/\partial x - (\partial/\partial x)(xf)] =$
$(\hbar/i)[x\,\partial f/\partial x - f - x\,\partial f/\partial x] = -(\hbar/i)f$, so $[\hat{x},\ \hat{p}_x] = -(\hbar/i)$.

(b) $[\hat{x},\ \hat{p}_x^2]f = (\hbar/i)^2[x\,\partial^2/\partial x^2 - (\partial^2/\partial x^2)x]f = -\hbar^2[x\,\partial^2 f/\partial x^2 - (\partial^2/\partial x^2)(xf)] =$
$-\hbar^2[x\,\partial^2 f/\partial x^2 - x\,\partial^2 f/\partial x^2 - 2\,\partial f/\partial x] = 2\hbar^2\,\partial f/\partial x$. Hence $[\hat{x},\ \hat{p}_x^2] = 2\hbar^2\,\partial/\partial x$.

(c) $[\hat{x},\ \hat{p}_y]f = (\hbar/i)[x\,\partial/\partial y - (\partial/\partial y)x]f = (\hbar/i)[x\,\partial f/\partial y - x(\partial f/\partial y)] = 0$, so $[\hat{x},\ \hat{p}_y] = 0$.

(d) $[\hat{x},\ \hat{V}(x, y, z)]f = (xV - Vx)f = 0$.

(e) Let $A \equiv -\hbar^2/2m$. Then $[\hat{x},\ \hat{H}]f =$
$\left\{x[A(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V] - [A(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V]x\right\}f =$

$A[x\,\partial^2 f/\partial x^2 + x\,\partial^2 f/\partial y^2 + x\partial^2 f/\partial z^2 - x\,\partial^2 f/\partial x^2 - 2\partial f/\partial x - x\,\partial^2 f/\partial y^2 - x\,\partial^2 f/\partial z^2] +$
$xAVf - AVxf = -2A\,\partial f/\partial x = (\hbar^2/m)\partial f/\partial x,$ so $[\hat{x},\ \hat{H}] = (\hbar^2/m)\partial/\partial x.$

(f) $[\hat{x}\hat{y}\hat{z},\ \hat{p}_x^2]f =$
$-\hbar^2[xyz\,\partial^2 f/\partial x^2 - (\partial^2/\partial x^2)(xyzf)] = -\hbar^2[xyz\,\partial^2 f/\partial x^2 - xyz\,\partial^2 f/\partial x^2 - 2yz\,\partial f/\partial x] =$
$2\hbar^2 yz\,\partial f/\partial x,$ so $[\hat{x}\hat{y}\hat{z},\ \hat{p}_x^2] = 2\hbar^2 yz\,\partial/\partial x.$

3.31 $$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)$$

3.32 $\hat{H} = -(\hbar^2/2m)\nabla^2 + c(x^2+y^2+z^2),$ where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2.$

3.33 **(a)** $\int_0^2 |\Psi(x,t)|^2\,dx$;

(b) $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^2 |\Psi(x,y,z,t)|^2\,dx\,dy\,dz$;

(c) $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^2 |\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)|^2\,dx_1\,dy_1\,dz_1\,dx_2\,dy_2\,dz_2$.

3.34 **(a)** $|\psi|^2\,dx$ is a probability and probabilities have no units. Since dx has SI units of m, the SI units of ψ are $\mathrm{m}^{-1/2}$.

(b) To make $|\psi|^2\,dx\,dy\,dz$ dimensionless, the SI units of ψ are $\mathrm{m}^{-3/2}$.

(c) To make $|\psi|^2\,dx_1\,dy_1\,dz_1\cdots dx_n\,dy_n\,dz_n$ dimensionless, the SI units of ψ are $\mathrm{m}^{-3n/2}$.

3.35 Let the x, y, and z directions correspond to the order used in the problem to state the edge lengths. The ground state has $n_x\,n_y\,n_z$ quantum numbers of 111. The first excited state has one quantum number equal to 2. The quantum-mechanical energy decreases as the length of a side of the box increases. Hence in the first excited state, the quantum-number value 2 is for the direction of the longest edge, the z direction. Then
$$h\nu = \frac{h^2}{8m}\left(\frac{1^2}{a^2}+\frac{1^2}{b^2}+\frac{2^2}{c^2}\right) - \frac{h^2}{8m}\left(\frac{1^2}{a^2}+\frac{1^2}{b^2}+\frac{1^2}{c^2}\right)$$
$$\nu = \frac{3h}{8mc^2} = \frac{3(6.626\times10^{-34}\ \mathrm{J\ s})}{8(9.109\times10^{-31}\ \mathrm{kg})(6.00\times10^{-10}\ \mathrm{m})^2} = 7.58\times10^{14}\ \mathrm{s}^{-1}$$

3.36 **(a)** Use of Eqs. (3.74) and (A.2) gives $\int_{2.00\text{ nm}}^{3.00\text{ nm}}\int_{1.50\text{ nm}}^{2.00\text{ nm}}\int_0^{0.40\text{ nm}} |\psi|^2\,dx\,dy\,dz =$
$\int_0^{0.40\text{ nm}}(2/a)\sin^2(\pi x/a)\,dx\int_{1.50\text{ nm}}^{2.00\text{ nm}}(2/b)\sin^2(\pi y/b)\,dy\int_{2.00\text{ nm}}^{3.00\text{ nm}}(2/c)\sin^2(\pi z/c)\,dz =$

$$\left[\frac{x}{a}-\frac{\sin(2\pi x/a)}{2\pi}\right]\Bigg|_0^{0.40\text{ nm}}\left[\frac{y}{b}-\frac{\sin(2\pi y/b)}{2\pi}\right]\Bigg|_{1.50\text{ nm}}^{2.00\text{ nm}}\left[\frac{z}{c}-\frac{\sin(2\pi z/c)}{2\pi}\right]\Bigg|_{2.00\text{ nm}}^{3.00\text{ nm}} =$$

$$\left[\frac{0.40}{1.00}-\frac{\sin(2\pi\cdot 0.40/1.00)}{2\pi}\right]\left[\frac{2.00-1.50}{2.00}-\frac{\sin(2\pi\cdot 2.00/2.00)-\sin(2\pi\cdot 1.50/2.00)}{2\pi}\right]\times$$

$$\left[\frac{3.00-2.00}{5.00}-\frac{\sin(2\pi\cdot 3.00/5.00)-\sin(2\pi\cdot 2.00/5.00)}{2\pi}\right] =$$

$(0.3065)(0.09085)(0.3871) = 0.0108.$

(b) The *y* and *z* ranges of the region include the full range of *y* and *z*, and the *y* and *z* factors in ψ are normalized. Hence the *y* and *z* integrals each equal 1. The *x* integral is the same as in part (a), so the probability is 0.3065.

(c) The same as (b), namely, 0.3065.

3.37 $\hat{p}_x = -i\hbar\,\partial/\partial x.$ **(a)** $\partial(\sin kx)/\partial x = k\cos kx,$ so ψ is not an eigenfunction of $\hat{p}_x$.

(b) $\hat{p}_x^2\psi_{(3.73)} = -\hbar^2(\partial^2/\partial x^2)\psi_{(3.73)} = -\hbar^2(-1)(n_x\pi/a)^2\psi_{(3.73)}$, where $\psi_{(3.73)}$ is given by Eq. (3.73). The eigenvalue is $h^2n_x^2/4a^2$, which is the value observed if p_x^2 is measured.

(c) $\hat{p}_z^2\psi_{(3.73)} = -\hbar^2(\partial^2/\partial z^2)\psi_{(3.73)} = -\hbar^2(-1)(n_z\pi/c)^2\psi_{(3.73)}$ and the observed value is $h^2n_z^2/4c^2$.

(d) $\hat{x}\psi_{(3.73)} = x\psi_{(3.73)} \neq (\text{const.})\psi_{(3.73)}$, so ψ is not an eigenfunction of $\hat{x}$.

3.38 Since $n_y = 2,$ the plane $y = b/2$ is a nodal plane within the box; this plane is parallel to the *xz* plane and bisects the box. With $n_z = 3,$ the function $\sin(3\pi z/c)$ is zero on the nodal planes $z = c/3$ and $z = 2c/3;$ these planes are parallel to the *xy* plane.

3.39 **(a)** $|\psi|^2$ is a maximum where $|\psi|$ is a maximum. We have $|\psi| = |f(x)||g(y)||h(z)|.$ For $n_x = 1,$ $|f(x)| = (2/a)^{1/2}|\sin(\pi x/a)|$ is a maximum at $x = a/2.$ Also, $|g(y)|$ is a maximum at $y = b/2$ and $|h(z)|$ is a maximum at $z = c/2.$ Therefore $|\psi|$ is a maximum at the point $(a/2,\ b/2,\ c/2),$ which is the center of the box.

(b) $|f(x)| = (2/a)^{1/2}|\sin(2\pi x/a)|$ is a maximum at $x = a/4$ and at $x = 3a/4.$ $|g(y)|$ is a maximum at $y = b/2$ and $|h(z)|$ is a maximum at $z = c/2.$ Therefore $|\psi|$ is a maximum at the points $(a/4,\ b/2,\ c/2)$ and $(3a/4,\ b/2,\ c/2),$

3.40 When integrating over one variable, we treat the other two variables as constant; hence
$\int\int\int F(x)G(y)H(z)\,dx\,dy\,dz = \int\int\left[\int F(x)G(y)H(z)\,dx\right]dy\,dz = \int\int G(y)H(z)\left[\int F(x)\,dx\right]dy\,dz$

$= \left[\int F(x)\,dx\right]\int\left[\int G(y)H(z)\,dy\right]dz = \int F(x)\,dx \int H(z)\left[\int G(y)\,dy\right]dz =$
$\int F(x)\,dx \int G(y)\,dy \int H(z)\,dz$.

3.41 If the ratio of two edge lengths is exactly an integer, we have degeneracy. For example, if $b = ka$, where k is an integer, then $n_x^2/a^2 + n_y^2/b^2 = (n_x^2 + n_y^2/k^2)/a^2$. The $(n_x,\ n_y,\ n_z)$ states $(1,\ 2k,\ n_z)$ and $(2,\ k,\ n_z)$ have the same energy.

3.42 With $V = 0$, we have $-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{\partial^2\psi}{\partial y^2} + \dfrac{\partial^2\psi}{\partial z^2}\right) = E\psi$. Assume $\psi(x,\ y,\ z) = F(x)G(y)H(z)$. Substitution into the Schrödinger equation followed by division by FGH, gives $-\dfrac{\hbar^2}{2m}\left(\dfrac{1}{F}\dfrac{d^2F}{dx^2} + \dfrac{1}{G}\dfrac{d^2G}{dy^2} + \dfrac{1}{H}\dfrac{d^2H}{dz^2}\right) = E$ and

$-\dfrac{\hbar^2}{2m}\left(\dfrac{1}{F}\dfrac{d^2F}{dx^2}\right) = E + \dfrac{\hbar^2}{2m}\left(\dfrac{1}{G}\dfrac{d^2G}{dy^2} + \dfrac{1}{H}\dfrac{d^2H}{dz^2}\right)$ (Eq. 1). Let $E_x \equiv -\dfrac{\hbar^2}{2m}\left(\dfrac{1}{F}\dfrac{d^2F}{dx^2}\right)$.

Then, since F is a function of x only, E_x is independent of y and z. But Eq. 1 shows E_x is equal to the right side of Eq. 1, which is independent of x, so E_x is independent of x. Hence E_x is a constant and $-(\hbar^2/2m)(d^2F/dx^2) = E_xF$. This is the same as the one-dimensional free-particle Schrödinger equation (2.29), so $F(x)$ and E_x are given by (2.30) and (2.31). By symmetry, G and H are given by (2.30) with x replaced by y and by z, respectively.

3.43 For a linear combination of eigenfunctions of $\hat{H}$ to be an eigenfunction of $\hat{H}$, the eigenfunctions must have the same eigenvalue. In this case, they must have the same value of $n_x^2 + n_y^2 + n_z^2$. The functions (a) and (c) are eigenfunctions of $\hat{H}$ and (b) is not.

3.44 In addition to the 11 states shown in the table after Eq. (3.75), the following 6 states have $E(8ma^2/h^2) < 15$:

$n_xn_yn_z$	123	132	213	231	312	321
$E(8ma^2/h^2)$	14	14	14	14	14	14

These 6 states and the 11 listed in the textbook give a total of 17 states. These 17 states have 6 different values of $E(8ma^2/h^2)$, and there are 6 energy levels.

3.45 **(a)** From the table after Eq. (3.75), there is only one state with this value, so the degree of degeneracy is 1, meaning this level is nondegenerate.

(b) From the table in the Prob. 3.44 solution, the degree of degeneracy is 6.

(c) The following $n_x n_y n_z$ values have $E(8ma^2/h^2) = 27;$ 115, 151, 511, 333. The degree of degeneracy is 4.

3.46 **(a)** These are linearly independent since none of them can be written as a linear combination of the others.

(b) Since $3x^2 - 1 = 3(x^2) - \frac{1}{8}(8),$ these are not linearly independent.

(c) Linearly independent.

(d) Linearly independent.

(e) Since $e^{ix} = \cos x + i\sin x,$ these are linearly dependent.

(f) Since $1 = \sin^2 x + \cos^2 x,$ these are linearly dependent.

(g) Linearly independent.

3.47 See the beginning of Sec. 3.6 for the proof.

3.48 **(a)** $\langle x\rangle = \int_0^c \int_0^b \int_0^a x\,|f(x)|^2|g(y)|^2|h(z)|^2\,dx\,dy\,dz =$ $\int_0^a x\,|f(x)|^2\,dx \int_0^b |g(y)|^2\,dy \int_0^c |h(z)|^2\,dz,$ where *f*, *g*, and *h* are given preceding Eq. (3.72). Since *g* and *h* are normalized, $\langle x\rangle = \int_0^a x\,|f(x)|^2\,dx = (2/a)\int_0^a x\sin^2(n_x\pi x/a)\,dx$ =

$$\frac{2}{a}\left[\frac{x^2}{4} - \frac{ax}{4n_x\pi}\sin(2n_x\pi x/a) - \frac{a^2}{8n_x^2\pi^2}\cos(2n_x\pi x/a)\right]\Bigg|_0^a = \frac{a}{2},$$ where Eq. (A.3) was used.

(b) By symmetry, $\langle y\rangle = b/2$ and $\langle z\rangle = c/2.$

(c) The derivation of Eq. (3.92) for the ground state applies to any state, and $\langle p_x\rangle = 0.$

(d) Since *g* and *h* are normalized,
$\langle x^2\rangle = \int_0^a x^2\,|f(x)|^2\,dx = (2/a)\int_0^a x^2\sin^2(n_x\pi x/a)\,dx =$

$$\frac{2}{a}\left[\frac{x^3}{6} - \left(\frac{ax^2}{4n_x\pi} - \frac{a^3}{8n_x^3\pi^3}\right)\sin(2n_x\pi\,x/a) - \frac{a^2x}{4n_x^2\pi^2}\cos(2n_x\pi\,x/a)\right]\Bigg|_0^a = \frac{a^2}{3} - \frac{a^2}{2n_x^2\pi^2},$$

where Eq. (A.4) was used. We have $\langle x\rangle^2 = a^2/4 \neq \langle x^2\rangle.$ Also,
$\langle xy\rangle = \int_0^c \int_0^b \int_0^a xy\,|f(x)|^2|g(y)|^2|h(z)|^2\,dx\,dy\,dz =$
$\int_0^a x\,|f(x)|^2\,dx \int_0^b y\,|g(y)|^2\,dy \int_0^c |h(z)|^2\,dz = \langle x\rangle\langle y\rangle.$

3.49 $\langle A+B\rangle = \int \Psi^*(\hat{A}+\hat{B})\Psi\,d\tau = \int \Psi^*(\hat{A}\Psi + \hat{B}\Psi)\,d\tau = \int \Psi^*\hat{A}\Psi\,d\tau + \int \Psi^*\hat{B}\Psi\,d\tau =$
$\langle A\rangle + \langle B\rangle.$ Also $\langle cB\rangle = \int \Psi^*(c\hat{B})\Psi\,d\tau = c\int \Psi^*\hat{B}\Psi\,d\tau = c\langle B\rangle.$

3.50 **(a)** Not acceptable, since it is not quadratically integrable. This is obvious from a graph or from $\int_{-\infty}^{\infty} e^{-2ax}\,dx = -(1/2a)e^{-2ax}\,|_{-\infty}^{\infty} = \infty$.

(b) This is acceptable, since it is single-valued, continuous, and quadratically integrable when multiplied by a normalization constant. See Eqs. (4.49) and (A.9).

(c) This is acceptable, since it is single-valued, continuous, and quadratically integrable when multiplied by a normalization constant. See Eqs. (4.49) and (A.10) with $n = 1$.

(d) Acceptable for the same reasons as in (b).

(e) Not acceptable since it is not continuous at $x = 0$.

3.51 Given: $i\hbar\,\partial\Psi_1/\partial t = \hat{H}\Psi_1$ and $i\hbar\,\partial\Psi_2/\partial t = \hat{H}\Psi_2$. Prove that $i\hbar\,\partial(c_1\Psi_1 + c_2\Psi_2)/\partial t = \hat{H}(c_1\Psi_1 + c_2\Psi_2)$. We have $i\hbar\,\partial(c_1\Psi_1 + c_2\Psi_2)/\partial t =$ $i\hbar[\partial(c_1\Psi_1)/\partial t + \partial(c_2\Psi_2)/\partial t] = c_1 i\hbar\partial\Psi_1/\partial t + c_2 i\hbar\partial\Psi_2/\partial t = c_1\hat{H}\Psi_1 + c_2\hat{H}\Psi_2 =$ $\hat{H}(c_1\Psi_1 + c_2\Psi_2)$, since $\hat{H}$ is linear.

3.52 (a) An inefficient C++ program is

```
#include <iostream>
using namespace std;
int main() {
  int  m, i, j, k, nx, ny, nz, L[400], N[400], R[400], S[400];
  i=0;
  for (nx=1; nx<8; nx=nx+1) {
    for (ny=1; ny<8; ny=ny+1) {
      for (nz=1; nz<8; nz=nz+1) {
        m=nx*nx+ny*ny+nz*nz;
        if (m>60)
          continue;
        i=i+1;
        L[i]=m;
        N[i]=nx;
        R[i]=ny;
        S[i]=nz;
      }
    }
  }
  for (k=3; k<61; k=k+1) {
    for (j=1; j<=i; j=j+1) {
      if (L[j]==k)
        cout<<N[j]<< " "<<R[j]<< " "<<S[j]<< " "<<L[j]<<endl;
    }
  }
  return 0;
```

```
}
```

A free integrated development environment (IDE) to debug and run C++ programs is Code::Blocks, available at www.codeblocks.org. For a Windows computer, downloading the file with mingw-setup.exe as part of the name will include the MinGW (GCC) compiler for C++. Free user guides and manuals for Code::Blocks can be found by searching the Internet.

Alternatively, you can run the program at ideone.com.

(b) One finds 12 states.

3.53 **(a)** T. **(b)** F. See the paragraph preceding the example at the end of Sec. 3.3.

(c) F. This is only true if f_1 and f_2 have the same eigenvalue.

(d) F. **(e)** F. This is only true if the two solutions have the same energy eigenvalue.

(f) F. This is only true for stationary states.

(g) F. **(h)** F. $x(5x) \neq (\text{const.})(5x)$.

(i) T. $\hat{H}\Psi = \hat{H}(e^{-iEt/\hbar}\psi) = e^{-iEt/\hbar}\hat{H}\psi = Ee^{-iEt/\hbar}\psi = E\Psi$.

(j) T. **(k)** T. **(l)** F.

(m) T. $\hat{A}^2 f = \hat{A}(\hat{A}f) = \hat{A}(af) = a\hat{A}f = a^2 f$, provided $\hat{A}$ is linear. Note that the definition of eigenfunction and eigenvalue in Sec. 3.2 specified that $\hat{A}$ is linear.

(n) F. **(o)** F.

Chapter 4

The Harmonic Oscillator

4.1 Taking $(d/dx)^m$ of (4.84) gives $f^{(m)}(x) = \sum_{n=0}^{\infty} c_n n(n-1)(n-2)\cdots(n-m+1)(x-a)^{n-m}$. The factors $n,\ (n-1),...$ make the terms with $n=0,\ n=1,\ldots,\ n=m-1$ vanish, so $f^{(m)}(x) = \sum_{n=m}^{\infty} c_n n(n-1)(n-2)\cdots(n-m+1)(x-a)^{n-m}$ (Eq. 1). (If this is too abstract for you, write the expansion as $f(x) = c_0 + c_1 x + c_2 x^2 + \cdots + c_k x^k + \cdots$ and do the differentiation.) With $x = a$ in Eq. 1, the $(x-a)^{n-m}$ factor makes all terms equal to zero except the term with $n = m,$ which is a constant. Equation (1) with $x = a$ gives $f^{(m)}(a) = c_m m(m-1)(m-2)\cdots(m-m+1) = c_m m!$ and $c_m = f^{(m)}(a)/m!$.

4.2 **(a)** $f(x) = \sin x,\ f'(x) = \cos x,\ f''(x) = -\sin x,\ f'''(x) = -\cos x,\ f^{(\text{iv})}(x) = \sin x, \ldots;$ $a = 0$ and $f(0) = \sin 0 = 0,\ f'(0) = \cos 0 = 1,\ f''(0) = 0,\ f'''(0) = -1,\ f^{(\text{iv})}(0) = 0, \ldots$. The Taylor series is $\sin x = 0 + x/1! + 0 - x^3/3! + 0 + x^5/5! + \cdots = \sum_{k=0}^{\infty}(-1)^k x^{2k+1}/(2k+1)!$.

(b) $\cos x = 1/1! - 3x^2/3! + 5x^4/5! - = 1 - x^2/2! + x^4/4! - \cdots = \sum_{k=0}^{\infty}(-1)^k x^{2k}/(2k)!$.

4.3 **(a)** We use (4.85) with $a = 0$. We have $f(x) = e^x$ and $f^{(n)}(x) = e^x$. $f^{(n)}(0) = e^0 = 1$. So $e^x = 1 + x/1! + x^2/2! + x^3/3! + \cdots = \sum_{n=0}^{\infty} x^n/n!$.

(b) $e^{i\theta} = 1 + (i\theta)/1! + (i\theta)^2/2! + (i\theta)^3/3! + (i\theta)^4/4! + (i\theta)^5/5! + \cdots =$
$1 - \theta^2/2! + \theta^4/4! - \cdots + i(\theta/1! - \theta^3/3! + \theta^5/5! - \cdots) = \cos\theta + i\sin\theta.$

4.4 From (4.22) and (4.28), $dx/dt = 2\pi\nu A\cos(2\pi\nu t + b)$ and $T = 2m\pi^2\nu^2 A^2\cos^2(2\pi\nu t + b)$. From (4.22) and (4.27), $V = 2\pi^2\nu^2 mA^2\sin^2(2\pi\nu t + b)$. Then $T + V = 2\pi^2\nu^2 mA^2$, since $\sin^2\theta + \cos^2\theta = 1$.

4.5 **(a)** Let $y = \sum_{n=0}^{\infty} c_n x^n$. Then $y' = \sum_{n=0}^{\infty} nc_n x^{n-1}$ and $y'' = \sum_{n=0}^{\infty} n(n-1)c_n x^{n-2}$. Since the first two terms in the y'' sum are zero, we have $y'' = \sum_{n=2}^{\infty} n(n-1)c_n x^{n-2}$. Let $j \equiv n-2$. Then $y'' = \sum_{j=0}^{\infty}(j+2)(j+1)c_{j+2}x^j = \sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}x^n$. Substitution in the differential equation gives

$\sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}x^n - \sum_{n=0}^{\infty}n(n-1)c_nx^n - 2\sum_{n=0}^{\infty}nc_nx^n + 3\sum_{n=0}^{\infty}c_nx^n = 0$.

We have $\sum_{n=0}^{\infty}[(n+2)(n+1)c_{n+2} + (3-n-n^2)c_n]x^n = 0$. Setting the coefficient of x^n equal to zero, we have $c_{n+2} = (n^2+n-3)c_n/[(n+2)(n+1)]$.

(b) The recursion relation of (a) with $n=0$ gives $c_2 = -3c_0/2$ and with $n=2$ gives $c_4 = 3c_2/12 = c_2/4 = (-3c_0/2)/4 = -3c_0/8$. With $n=1$ and $n=3$ in the recursion relation, we get $c_3 = -c_1/6$ and $c_5 = 9c_3/20 = 9(-c_1/6)/20 = -3c_1/40$.

4.6 **(a)** Odd; **(b)** even; **(c)** odd; **(d)** neither; **(e)** even; **(f)** odd; **(g)** neither; **(h)** even.

4.7 Given: $f(-x) = f(x)$, $g(-x) = g(x)$, $h(-x) = -h(x)$, $k(-x) = -k(x)$. Let $p(x) \equiv f(x)g(x)$. We have $p(-x) = f(-x)g(-x) = f(x)g(x) = p(x)$, so the product of two even functions is an even function. Let $q(x) \equiv h(x)k(x)$. Then $q(-x) = h(-x)k(-x) = -h(x)[-k(x)] = h(x)k(x) = q(x)$, so the product of two odd functions is an even function. Let $r(x) = f(x)h(x)$. Then $r(-x) \equiv f(-x)h(-x) = f(x)[-h(x)] = -f(x)h(x) = -r(x)$.

4.8 **(a)** Given: $f(x) = f(-x)$. Differentiation of this equation gives $f'(x) = df(-x)/dx = f'(-x)[d(-x)/dx] = -f'(-x)$, so f' is an odd function.

(b) Differentiation of $f(x) = -f(-x)$ gives $f'(x) = -(-1)f'(-x) = f'(-x)$.

(c) Differentiation of $f(x) = f(-x)$ gives $f'(x) = -f'(-x)$, as in (a). Putting $x = 0$ in this equation, we get $f'(0) = -f'(0)$, so $2f'(0) = 0$ and $f'(0) = 0$.

4.9 $\langle T\rangle = \int \psi^*\hat{T}\psi\, d\tau = -(\hbar^2/2m)\int_{-\infty}^{\infty}(\alpha/\pi)^{1/2}e^{-\alpha x^2/2}(d^2/dx^2)e^{-\alpha x^2/2}\,dx =$
$-(\hbar^2/2m)(\alpha/\pi)^{1/2}\int_{-\infty}^{\infty}e^{-\alpha x^2/2}(\alpha^2x^2-\alpha)e^{-\alpha x^2/2}\,dx =$
$-(\hbar^2/2m)(\alpha/\pi)^{1/2}2\int_0^{\infty}(\alpha^2x^2-\alpha)e^{-\alpha x^2}\,dx =$
$-(\hbar^2/m)(\alpha/\pi)^{1/2}[\alpha^2(1/4)(\pi^{1/2}/\alpha^{3/2}) - \alpha(1/2)(\pi/\alpha)^{1/2}] = \hbar^2\alpha/4m =$
$\hbar^2(2\pi\nu m/\hbar)/4m = h\nu/4$, where (A.9) and (A.10) were used.
$\langle V\rangle = \int \psi^*\hat{V}\psi\, d\tau = (\alpha/\pi)^{1/2}\int_{-\infty}^{\infty}e^{-\alpha x^2/2}(2\pi^2\nu^2mx^2)e^{-\alpha x^2/2}\,dx =$
$(\alpha/\pi)^{1/2}2\int_0^{\infty}(2\pi^2\nu^2mx^2)e^{-\alpha x^2}dx = 4\pi^{3/2}\alpha^{1/2}\nu^2m(1/4)(\pi^{1/2}/\alpha^{3/2}) = \pi^2\nu^2m/\alpha =$
$\pi^2\nu^2m/(2\pi\nu m\hbar^{-1}) = h\nu/4 = \langle T\rangle$.

4.10 From (4.54), $1 = |c_1|^2\int_{-\infty}^{\infty}x^2e^{-\alpha x^2}\,dx = 2|c_1|^2\int_0^{\infty}x^2e^{-\alpha x^2}\,dx = 2|c_1|^2\frac{1}{4}\pi^{1/2}/\alpha^{3/2}$, where (4.49) and (A.10) with $n = 1$ were used. We get $|c_1| = 2^{1/2}\alpha^{3/4}\pi^{-1/4}$. From (4.56),

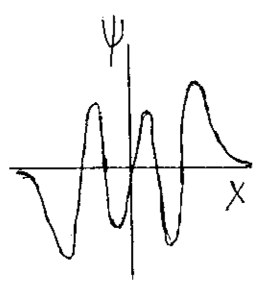
$1 = |c_0|^2 \int_{-\infty}^{\infty} (1 - 4\alpha x^2 + 4\alpha^2 x^4) e^{-\alpha x^2}\, dx = 2|c_0|^2 \int_0^{\infty} (1 - 4\alpha x^2 + 4\alpha^2 x^4) e^{-\alpha x^2}\, dx$
$= 2|c_0|^2 [2^{-1}(\pi/\alpha)^{1/2} - 4\alpha(1/4)\pi^{1/2}/\alpha^{3/2} + 4\alpha^2(3/8)\pi^{1/2}/\alpha^{5/2}] = 2|c_0|^2 (\pi/\alpha)^{1/2}$
where (A.9) and (A.10) were used. Hence $|c_0| = 2^{-1/2}(\alpha/\pi)^{1/4}$.

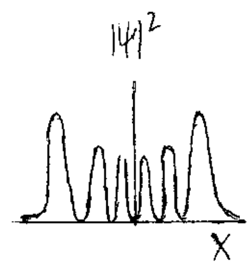
4.11 From (4.47), $\psi_3 = (c_1 x + c_3 x^3) e^{-\alpha x^2/2}$. From (4.46), $c_3 = [2\alpha(1-3)/6]c_1 = -2\alpha c_1/3$. So $\psi_3 = c_1[x - (2/3)\alpha x^3] e^{-\alpha x^2/2}$. We have
$1 = |c_1|^2 2\int_0^{\infty} [x^2 - (4/3)\alpha x^4 + (4/9)\alpha^2 x^6] e^{-\alpha x^2}\, dx =$
$2|c_1|^2 [(1/2^2)\pi^{1/2}/\alpha^{3/2} - (4/3)\alpha(3/2^3)\pi^{1/2}/\alpha^{5/2} + (4/9)\alpha^2(15/2^4)\pi^{1/2}/\alpha^{7/2}] =$
$|c_1|^2 \pi^{1/2}\alpha^{-3/2}/3$ and $|c_1| = 3^{1/2}\alpha^{3/4}\pi^{-1/4}$. Then
$\psi_3 = 3^{1/2}\alpha^{3/4}\pi^{-1/4}[x - (2/3)\alpha x^3] e^{-\alpha x^2/2}$.

4.12 From (4.47), $\psi_4 = e^{-\alpha x^2}(c_0 + c_2 x^2 + c_4 x^4)$. From (4.46) with $v = 4$,
$c_2 = 2\alpha(-4)c_0/2 = -4\alpha c_0$ and
$c_4 = 2\alpha(2-4)c_2/(3\cdot 4) = -\alpha c_2/3 = -\alpha(-4\alpha c_0)/3 = 4\alpha^2 c_0/3$. Then
$\psi_4 = c_0 e^{-\alpha x^2}(1 - 4\alpha x^2 + 4\alpha^2 x^4/3)$.

4.13 At the maxima in the probability density $|\psi|^2$, we have $\partial|\psi|^2/\partial x = 0$. From (4.54), $0 = c_1^2(\partial/\partial x)(x^2 e^{-\alpha x^2}) = c_1^2(2x - 2\alpha x^3)e^{-\alpha x^2}$, so $0 = x - \alpha x^3 = x(1 - \alpha x^2)$. The solutions are $x = 0$ and $x = \pm\alpha^{-1/2}$. From Fig. 4.4b, $x = 0$ is a minimum in probability density, so the maxima are at $x = \pm\alpha^{-1/2}$.

4.14 The wave function is an odd function with five nodes, one of which is at the origin.





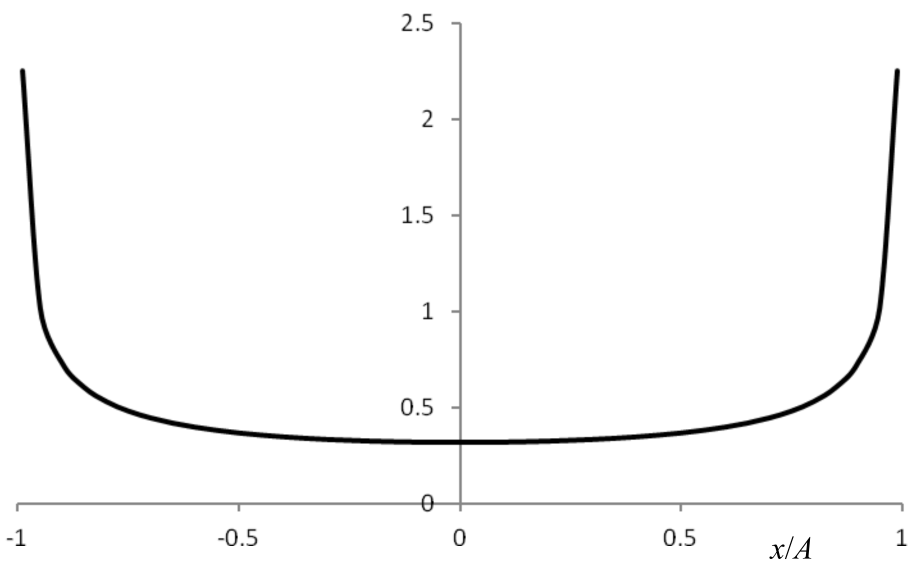
Alternatively, one could take -1 times the ψ function graphed above.

4.15 $\langle x\rangle = \int \psi^* \hat{x}\psi\, d\tau = \int_{-\infty}^{\infty} x\,|\psi_{\text{v}}|^2\, dx$. The wave function ψ_{v} is either even or odd, so $|\psi_{\text{v}}|^2$ is an even function. Hence $x\,|\psi_{\text{v}}|^2$ is an odd function and $\int_{-\infty}^{\infty} x\,|\psi_{\text{v}}|^2\, dx = 0.$ The result $\langle x\rangle = 0$ is obvious from the graphs of $|\psi|^2$ that correspond to Fig. 4.4.

4.16 **(a)** T. **(b)** T. **(c)** F (since ψ can be multiplied by –1 and remain a valid wave function). **(d)** T. **(e)** T.

4.17 *Similarities*: The number of nodes between the boundary points is zero for the ground state and increases by one for each increase in the quantum number. The quantum numbers are integers. There is a zero-point energy. The shapes of corresponding wave functions are similar. If the origin is placed at the center of the box, the wave functions alternate between being even or odd as the quantum number increases. The energy levels are nondegenerate. There are an infinite number of bound-state energy levels
Differences: The energy levels are equally spaced for the harmonic oscillator (ho) but unequally spaced for the particle in a box (pib). For the ho, there is some probability for the particle to be found in the classically forbidden region, but this probability is zero for the pib.

4.18 **(a)** $t = (2\pi\nu)^{-1}[\sin^{-1}(x/A) - b]$ and $dt/dx = (2\pi\nu)^{-1}A^{-1}[1-(x/A)^2]^{-1/2}$, so $dt = (2\pi\nu A)^{-1}[1-(x/A)^2]^{-1/2}\,dx.$ The period is $1/\nu$, so the probability that the particle is found between x and $x+dx$ is $2\nu\, dt = (\pi A)^{-1}[1-(x/A)^2]^{-1/2}\,dx.$
(b) At $x = \pm A,$ the classical probability density is infinite.
(c)



For high values of the quantum number v, the outer peaks in $|\psi|^2$ are much higher than the inner peaks, and the highest probability density is near the classical turning points of the motion, as is true for the classical probability density graphed above. This is in accord with the correspondence principle.

4.19 For $x \ge 0,$ the Hamiltonian operator is the same as that of the harmonic oscillator. Hence the solutions of the Schrödinger equation for $x \ge 0$ are the functions (4.42), where the coefficients obey the recursion relation (4.39). To make ψ quadratically integrable, ψ must go to zero as $x \to \infty.$ This boundary condition then restricts the solutions to the harmonic-oscillator functions (4.47). Since V is infinite for $x < 0$, ψ must be zero for $x < 0$ (as for the particle in a box). The condition that ψ be continuous then requires that $\psi = 0$ at $x = 0$. The even harmonic-oscillator functions in (4.47) are not zero at the origin, so these are eliminated. Hence the well-behaved solutions are the harmonic oscillator wave functions with $\text{v} = 1,\ 3,\ 5,...,$ and $E = (\text{v} + \frac{1}{2})h\nu$ with $\text{v} = 1,\ 3,\ 5,....$ If we define $n \equiv (\text{v} - 1)/2$, then $E = (2n + \frac{3}{2})h\nu$, with $n = 0,\ 1,\ 2,....$

4.20 **(a)** The time-independent Schrödinger equation (3.47) is
$-(\hbar^2/2m)(\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2) + (\frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2)\psi = E\psi.$
The Hamiltonian operator is the sum of terms that each involve only one coordinate, so we try a separation of variables, taking $\psi = f(x)g(y)h(z).$ Substitution of this ψ into the Schrödinger equation followed by division by fgh gives

$$-\frac{\hbar^2}{2m}\left(gh\frac{d^2 f}{dx^2} + fh\frac{d^2 g}{dy^2} + fg\frac{d^2 h}{dz^2}\right) + (\tfrac{1}{2}k_x x^2 + \tfrac{1}{2}k_y y^2 + \tfrac{1}{2}k_z z^2)fgh = Efgh$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{f}\frac{d^2 f}{dx^2} + \frac{1}{g}\frac{d^2 g}{dy^2} + \frac{1}{h}\frac{d^2 h}{dz^2}\right) + \tfrac{1}{2}k_x x^2 + \tfrac{1}{2}k_y y^2 + \tfrac{1}{2}k_z z^2 = E \qquad \text{(Eq. 1)}$$

$$E_x \equiv -\frac{\hbar^2}{2m}\frac{1}{f}\frac{d^2 f}{dx^2} + \tfrac{1}{2}k_x x^2 = E + \frac{\hbar^2}{2m}\left(\frac{1}{g}\frac{d^2 g}{dy^2} + \frac{1}{h}\frac{d^2 h}{dz^2}\right) - \tfrac{1}{2}k_y y^2 - \tfrac{1}{2}k_z z^2 \qquad \text{(Eq. 2)}$$

Since f is a function of x only, the defined quantity E_x is independent of y and z. Since E_x equals the right side of the last equation and x does not appear on this side, E_x is independent of x. Therefore E_x is a constant. Multiplication of the E_x definition by f gives $-(\hbar^2/2m)(d^2 f/dx^2) + \frac{1}{2}k_x x^2 f = E_x f$, which is the same as the one-dimensional harmonic-oscillator (ho) Schrödinger equation (4.32) [see also (4.26)] with ψ replaced by f, k replaced by k_x, and E replaced by E_x. Hence $f(x)$ is the one-dimensional ho wave function (4.47) with v replaced by v_x, and E_x is given by (4.45) and (4.23) as $E_x = (\text{v}_x + \frac{1}{2})h\nu_x,\ \nu_x = (1/2\pi)(k_x/m)^{1/2}.$ Since x, y, and z occur symmetrically, $g(y)$ and $h(z)$ are ho functions with y and z as the variable. Equations 1 and 2 give,

$E = E_x + E_y + E_z = (\mathrm{v}_x + \frac{1}{2})h\nu_x + (\mathrm{v}_y + \frac{1}{2})h\nu_y + (\mathrm{v}_z + \frac{1}{2})h\nu_z$, where $\mathrm{v}_x = 0, 1, 2, \ldots$, $\mathrm{v}_y = 0, 1, 2, \ldots$ $\mathrm{v}_z = 0, 1, 2, \ldots$

(b) When the k's are equal, we have $\nu_x = \nu_y = \nu_z \equiv \nu$ and $E = (\mathrm{v}_x + \mathrm{v}_y + \mathrm{v}_z + \frac{3}{2})h\nu$. The lowest energy level is 000 and is nondegenerate, where the numbers give the values of the quantum numbers v_x, v_y, v_z. The next-lowest level is threefold degenerate, consisting of the states 100, 010, and 001. The next level is sixfold degenerate and has the states 200, 020, 200, 110, 101, 011. The next level is tenfold degenerate and has the states 300, 030, 003, 111, 210, 201, 012, 021, 102, 120.

4.21 **(a)** $H_0 = (-1)^0 e^{z^2} e^{-z^2} = 1$. $H_1 = (-1)e^{z^2}(d/dz)e^{-z^2} = -e^{z^2}(-2ze^{-z^2}) = 2z$.
$H_2 = e^{z^2}(-2e^{-z^2} + 4z^2 e^{-z^2}) = 4z^2 - 2$,
$H_3 = -e^{z^2}(4ze^{-z^2} + 8ze^{-z^2} - 8z^3 e^{-z^2}) = 8z^3 - 12z$.

(b) For $n = 0$, $zH_0 = z$ and $\frac{1}{2}H_1 = z$.
For $n = 1$, $zH_1 = 2z^2$ and $H_0 + \frac{1}{2}H_2 = 1 + 2z^2 - 1 = 2z^2$.
For $n = 2$, $zH_2 = 4z^3 - 2z$ and $2H_1 + \frac{1}{2}H_3 = 4z + 4z^3 - 6z = 4z^3 - 2z$.

(c) For $\mathrm{v} = 0$, (4.86) is $\psi_0 = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$, as in (4.53). For $\mathrm{v} = 1$, (4.86) is $\psi_1 = (2 \cdot 1!)^{-1/2} (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} (2\alpha^{1/2} x) = 2^{1/2} \alpha^{3/4} \pi^{-1/4} x e^{-\alpha x^2/2}$, as in (4.55). Finally, $\psi_2 = (2^2 \cdot 2!)^{-1/2} (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} [4(\alpha^{1/2} x)^2 - 2] = 2^{-1/2} (\alpha/\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$ as in (4.57).

4.22 For very large $|x|$, the first term in parentheses in (4.32) can be neglected compared with the second term, and (4.32) becomes $\psi'' - \alpha^2 x^2 \psi = 0$. With $\psi = e^{-\alpha x^2/2}$, we have $\psi'' - \alpha^2 x^2 \psi = -\alpha e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\alpha x^2/2} - \alpha^2 x^2 e^{-\alpha x^2/2} = -\alpha e^{-\alpha x^2/2}$. For very large $|x|$, $-\alpha e^{-\alpha x^2/2}$ is extremely close to zero, so $\psi = e^{-\alpha x^2/2}$ is an approximate solution for very large $|x|$.

4.23 **(a)** Let $x_r \equiv \alpha^{1/2} x$. Then Eq. (4.40) becomes

$$\psi/c_0 = e^{-x_r^2/2}\left(1 + \frac{c_2 x_r^2}{c_0 \alpha} + \frac{c_4 x_r^4}{c_0 \alpha^2} + \frac{c_6 x_r^6}{c_0 \alpha^3} + \cdots\right)$$

Let $E_r \equiv mE\hbar^{-2}/\alpha = E/h\nu$. Then Eq. (4.39) becomes $c_{n+2}/\alpha c_n = (2n + 1 - 2E_r)/[(n+1)(n+2)] \equiv f_n$, where f_n was defined as shown. We have $\dfrac{c_2}{\alpha c_0} = f_0$, $\dfrac{c_4}{c_0 \alpha^2} = \dfrac{c_4}{\alpha c_2}\dfrac{c_2}{\alpha c_0} = f_2 f_0$, $\dfrac{c_6}{\alpha^3 c_0} = \dfrac{c_6}{\alpha c_4}\dfrac{c_4}{\alpha c_2}\dfrac{c_2}{\alpha c_0} = f_4 f_2 f_0, \ldots$. Hence

$\psi / c_0 = e^{-x_r^2/2}\left(1 + f_0 x_r^2 + f_0 f_2 x_r^4 + f_0 f_2 f_4 x_r^6 + \cdots\right).$

We have $f_{2n-2} = (4n-4+1-2E_r)/[(2n-2+1)(2n-2+2) = (4n-3-2E_r)/(4n^2-2n)$.

A C++ program is

```
#include <iostream>
#include <cmath>
using namespace std;
int main () {
      int n;
      double er, xr, fac, sum, term, psi;
      label2: cout  <<  "Enter Er (enter 1000 to quit)";
      cin >> er;
      if (er > 999) {
        return 0;
      }
      for (xr=0; xr<=6; xr=xr+0.5)  {
        fac=exp(-xr*xr/2);
        sum=1;
        term=1;
        for (n=1; n<=9500; n=n+1)  {
           term=term*(4*n-3-2*er)*xr*xr/(4*n*n-2*n);
           if (fabs(fac*term) < 1e-15)  {
                goto label1;
          }
          sum=sum+term;
        }
        cout << "Did not converge";
        return 0;
        label1: psi=fac*sum;
        cout  <<  " xr =  "   << xr  << "  Psi =  "  << psi  << "  n =  " <<  n << endl;
      }
      goto label2;
}
```

(b) For $E_r = 0.499,\ 0.500,\ 0.501,$ the values of ψ/c_0 at $x_r = 4$ are 0.684869, 0.000335463, and –0.68198.

4.24 **(a)** With the harmonic-oscillator approximation for the molecular vibration, Eq. (4.61) gives the molecular vibration frequency as $\nu = 8.65\times10^{13}\ \text{s}^{-1}$. From (4.59), $k = 4\pi^2\nu^2\mu$ and $\mu = m_1m_2/(m_1+m_2)$. From Table A.3 in the Appendix,

$$\mu = \frac{1.008(34.97)\ \text{g}}{(1.008+34.97)}\frac{1}{6.022\times10^{23}} = 1.627\times10^{-24}\ \text{g}$$

So $k = 4\pi^2\nu^2\mu = 4\pi^2(8.65\times10^{13}\ \text{s}^{-1})^2(1.627\times10^{-27}\ \text{kg}) = 481$ N/m.

(b) $\frac{1}{2}h\nu = 0.5(6.626\times10^{-34}\ \text{J s})(8.65\times10^{13}\ \text{s}^{-1}) = 2.87\times10^{-20}$ J.

(c) From the last equation in (4.59), the force constant *k* of a molecule is found from the *U*(*R*) function. The electronic energy function *U* is found by repeatedly solving the electronic Schrödinger equation at fixed nuclear locations. The nuclear masses do not occur in the electronic Schrödinger equation, so the function *U* is independent of the nuclear masses and is the same for $^2H^{35}Cl$ as for $^1H^{35}Cl$. Hence *k* is the same for these two molecules. From the first equation in (4.59), $\nu_2/\nu_1 = (\mu_1/\mu_2)^{1/2}$, where 2 and 1 refer to $^2H^{35}Cl$ and $^1H^{35}Cl$, respectively. From Table A.3,

$$\mu_2 = \frac{2.014(34.97)\ \text{g}}{(2.014+34.97)}\frac{1}{6.022\times10^{23}} = 3.162\times10^{-24}\ \text{g}$$

So $\nu_2 = (\mu_1/\mu_2)^{1/2}\nu_1 = (1.627/3.162)^{1/2}(8.65\times10^{13}\ \text{s}^{-1}) = 6.20\times10^{13}\ \text{s}^{-1}$.

4.25 **(a)** Putting $\text{v}_2 = 1$ and $\text{v}_2 = 2$ in the result of Prob. 4.27b, we have $2885.98\ \text{cm}^{-1} = \tilde{\nu}_e - 2\tilde{\nu}_e x_e$ and $5667.98\ \text{cm}^{-1} = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e$. Subtracting twice the first equation from the second, we get $-103.98\ \text{cm}^{-1} = -2\tilde{\nu}_e x_e$ and $\tilde{\nu}_e x_e = 51.99\ \text{cm}^{-1}$. The first equation then gives $\tilde{\nu}_e = 2885.98\ \text{cm}^{-1} + 2(51.99\ \text{cm}^{-1}) = 2989.96\ \text{cm}^{-1}$. Also, $\nu_e = \tilde{\nu}_e c = (2989.96\ \text{cm}^{-1})(2.99792\times10^{10}\ \text{cm/s}) = 8.96366\times10^{13}\ \text{s}^{-1}$ and $\nu_e x_e = \tilde{\nu}_e x_e c = (51.99\ \text{cm}^{-1})(2.99792\times10^{10}\ \text{cm/s}) = 1.559\times10^{12}\ \text{s}^{-1}$.

(b) With $\text{v}_2 = 3$, the result of Prob. 4.27b becomes $\tilde{\nu}_{\text{light}} = 3\tilde{\nu}_e - 12\tilde{\nu}_e x_e = 3(2989.96\ \text{cm}^{-1}) - 12(51.99\ \text{cm}^{-1}) = 8346.00\ \text{cm}^{-1}$.

4.26 **(a)** Using the harmonic-oscillator approximation, the energy difference between these two vibrational levels is $h\nu = h\tilde{\nu}c = (6.626\times10^{-34}\ \text{J s})(1359\ \text{cm}^{-1})(2.998\times10^{10}\ \text{cm/s}) = 2.70\times10^{-20}$ J. The Boltzmann distribution law (4.63) for these nondegenerate levels gives $N_1/N_0 = \exp[(-2.70\times10^{-20}\ \text{J})/(1.381\times10^{-23}\ \text{J/K})(298\ \text{K})] = 0.0014$ at 25°C and $N_1/N_0 = \exp[(-2.70\times10^{-20}\ \text{J})/(1.381\times10^{-23}\ \text{J/K})(473\ \text{K})] = 0.016$ at 200°C.

(b) $h\nu = h\tilde{\nu}c =$ (6.626 × 10^{-34} J s)(381 cm^{-1})(2.998 × 10^{10} cm/s) = 7.57 × 10^{-21} J.
$N_1/N_0 = \exp[(-7.57\times10^{-21}\text{ J})/(1.381\times10^{-23}\text{ J/K})(298\text{ K})] = 0.16$ at 25°C and
$N_1/N_0 = \exp[(-7.57\times10^{-21}\text{ J})/(1.381\times10^{-23}\text{ J/K})(473\text{ K})] = 0.31$ at 200°C.

4.27 **(a)**
$\nu_{\text{light}} = (E_2 - E_1)/h = h^{-1}\left\{(\text{v}_2+\tfrac{1}{2})h\nu_e - (\text{v}_2+\tfrac{1}{2})^2 h\nu_e x_e - \left[(\text{v}_1+\tfrac{1}{2})h\nu_e - (\text{v}_1+\tfrac{1}{2})^2 h\nu_e x_e\right]\right\} =$
$(\text{v}_2 - \text{v}_1)\nu_e + \nu_e x_e[(\text{v}_1^2 - \text{v}_2^2) + (\text{v}_1 - \text{v}_2)]$ (Eq. 1). Use of the selection rule $\text{v}_2 - \text{v}_1 = 1$ gives $\nu_{\text{light}} = \nu_e + \nu_e x_e[\text{v}_1^2 - (\text{v}_1+1)^2 - 1] = \nu_e - 2\nu_e x_e(\text{v}_1+1)$.
(b) Putting $\text{v}_1 = 0$ in Eq. 1 of part (a), we get $\nu_{\text{light}} = \text{v}_2\nu_e - \nu_e x_e(\text{v}_2^2 + \text{v}_2)$.

4.28 The Taylor series (4.85) of Prob. 4.1 with $x = R$, $f(x) = U(R)$, and $a = R_e$ gives
$U(R) = U(R_e)/0! + U'(R_e)(R-R_e)/1! + U''(R_e)(R-R_e)^2/2! + U'''(R_e)(R-R_e)^3/3! + \cdots$.
Since R_e occurs at the minimum in the $U(R)$ curve, we have $U'(R_e) = 0$. From (4.59), $U''(R_e) = k$. The zero of potential energy can be chosen wherever we please, so we can take $U(R_e) = 0$, as in Fig. 4.6. Neglecting the $(R-R_e)^3$ term and higher terms, we thus have $U(R) \approx \tfrac{1}{2}k(R-R_e)^2 = \tfrac{1}{2}kx^2$, where $x \equiv R - R_e$.

4.29 **(a)** Putting $R = \infty$ and then $R = R_e$ in the Morse function, we get $U(\infty) = D_e$ and $U(R_e) = 0$. So $U(\infty) - U(R_e) = D_e$.
(b) From (4.59), $k_e = U''(R_e)$. For the Morse function,
$U' = 2D_e[1 - e^{-a(R-R_e)}]ae^{-a(R-R_e)} = 2aD_e[e^{-a(R-R_e)} - e^{-2a(R-R_e)}]$ and
$U'' = 2aD_e[-ae^{-a(R-R_e)} + 2ae^{-2a(R-R_e)}]$. Then $k_e = U''(R_e) = 2aD_e(-a+2a) = 2a^2D_e$, so $a = (k_e/2D_e)^{1/2}$.

4.30 We begin by finding combinations of *m, l*, and $\hbar$ that have dimensions of energy and of length. The reduced energy and *x* coordinate are $E_r \equiv E/A$ and $x_r \equiv x/B$.
Let $A = m^a l^b \hbar^c$. Using (4.71) and (4.70), we have
$[\text{A}] = \text{ML}^2\text{T}^{-2} = [m^a l^b \hbar^c] = \text{M}^a\text{L}^b(\text{ML}^2\text{T}^{-1})^c = \text{M}^{a+c}\text{L}^{b+2c}\text{T}^{-c}$, so
$a + c = 1$, $b + 2c = 2$, $-c = -2$. Hence $c = 2$, $a = -1$, $b = -2$ and $E_r = E/(\hbar^2/ml^2)$.
Let $B = m^d l^e \hbar^f$. We have $[B] = \text{L} = \text{M}^d\text{L}^e(\text{ML}^2\text{T}^{-1})^f = \text{M}^{d+f}\text{L}^{e+2f}T^{-f}$, so
$d + f = 0$, $e + 2f = 1$, $-f = 0$. Hence, $f = 0$, $d = 0$, $e = 1$, and $x_r = x/l$, as is obvious without doing the detailed analysis. From (4.78) and (4.79), $\psi_r = \psi B^{1/2} = \psi l^{1/2}$ and $\psi'' = \psi_r'' B^{-5/2} = l^{-5/2}\psi_r''$. The Schrödinger equation $-(\hbar^2/2m)\psi'' = E\psi$ becomes

$-(\hbar^2/2m)l^{-5/2}\psi_r'' = (\hbar^2/ml^2)E_r l^{-1/2}\psi_r$ or $\psi_r'' = -2E_r\psi_r$. To put this equation in the form of Eq. (4.66) and the first equation in (4.82), we define $G_r \equiv -2E_r$ to give $\psi_r'' = G_r\psi_r$. The formula in cell B7 and the cells below it in Fig. 4.9 becomes =-2*B3. There is no penetration into the classically forbidden region, so we omit steps (c) and (d) at the end of Sec. 4.4. The variable $x_r = x/l$ runs from 0 to 1. We take the interval s_r as 0.01. We enter 0.0001 in C8. The ψ_r formulas in column C are the same as in Fig. 4.9. The Solver is set to make C107 equal to zero by varying B3. The lowest three $E_r = 4\pi^2 E/(h^2/ml^2)$ eigenvalues are found to be 4.9348021805, 19.7392075201, and 44.41320519866. (For maximum accuracy, use the Options button in the Solver to reduce the Precision to 10^{-14}.) These E_r values correspond to E values of h^2/ml^2 times 0.12499999949, 0.4999999675, and 1.124999630, as compared with the true values of h^2/ml^2 times $n^2/8 =$ 0.125, 0.500, and 1.125.

4.31 **(a)** As in Prob. 4.30, we take combinations of *m, l*, and $\hbar$ that have dimensions of energy and of length; the reduced energy and *x* coordinate are $E_r \equiv E/A = E/(\hbar^2/ml^2)$ and $x_r \equiv x/B = x/l$. The Schrödinger equation is $-(\hbar^2/2m)\psi'' + K(\hbar^2/ml^2)\psi = E\psi$, where $K = 20$ in regions I and III of Fig. 2.5, and $K = 0$ in region II. From (4.78) and (4.79), $\psi_r = \psi B^{1/2} = \psi l^{1/2}$ and $\psi'' = \psi_r'' B^{-5/2} = l^{-5/2}\psi_r''$. The Schrödinger equation becomes $-(\hbar^2/2m)l^{-5/2}\psi_r'' + K(\hbar^2/ml^2)l^{-1/2}\psi_r = (\hbar^2/ml^2)E_r l^{-1/2}\psi_r$ or $\psi_r'' = (2K - 2E_r)\psi_r$. The bound-state reduced energies are less than 20, so the maximum reduced energy we are interested in is 20. For reduced energies less than 20, the classically forbidden regions are regions I and III in Fig. 2.5. Reasonable starting and ending points are 1.5 units into each of the classically forbidden regions, so we shall take x_r to run from –1.5 to 2.5. A reasonable interval is $s_r = 0.02$ or 0.01. For greater accuracy, we shall use 0.01. The *K* value for regions I and III is entered into cell B2 of Fig. 4.9. In column B, x_r values in regions I (from –1.5 to 0) and III (from 1 to 2.5) contain the formula 2*B2-2*B3 and x_r values in region II (from 0 to 1) contain the formula -2*B3. The ψ_r formulas in column C are the same as in Fig. 4.9. The Solver is set to make C407 equal to zero by varying B3. The Options button in the Solver is used to set the Precision at 10^{-8}. The bound-state $E_r = 4\pi^2 E/(h^2/ml^2)$ eigenvalues are found to be 2.772515720011 and 10.6051190761. (A value of 20.213299 is also obtained, but the graph shows that the solution for this energy does not go to zero asymptotically in the forbidden region.)

(b) The spreadsheet of part (a) is modified by changing cell B2 from 20 to 50. The Solver gives the E_r values 3.3568218287, 13.256836483275, 29.003101429782, and 47.66519784181.

(c) Substitution of $V_0 = 20\hbar^2/ml^2$ in (2.34) for b gives $b = 6.3245553203$ and $b/\pi = 2.0132,$ so there are three bound states. The Solver shows the roots of Eq. (2.35) to be $\varepsilon = 0.1407215,\ 0.5375806,\ 0.9995981.$ From (2.34), $E_r = \varepsilon V_{0,r} = 20\varepsilon =$ $2.814429,\ 10.75161,\ 19.99196.$ The eigenvalues found in (a) are rather inaccurate, indicating that we need to go further into the classically forbidden regions and decrease the interval. For $V_0 = 50\hbar^2/ml^2$, one finds $b = 10$;
$\varepsilon = 0.06827142,\ 0.26951445,\ 0.58904615,\ 0.9628693;$
$E_r = 50\varepsilon = 3.413571,\ 13.47572,\ 29.452308,\ 48.143464.$
The eigenvalues in (b) are rather inaccurate.

4.32 We begin by finding combinations of m, c, and $\hbar$ that have dimensions of energy and of length. c has dimensions of energy divided by length[4], so $[c] = \mathrm{ML^2T^{-2}/L^4} = \mathrm{MT^{-2}L^{-2}}$. The reduced energy and x coordinate are $E_r \equiv E/A$ and $x_r \equiv x/B.$
Let $A = m^a\hbar^b c^d$. Using (4.71) and (4.70), we have
$[\mathrm{A}] = \mathrm{ML^2T^{-2}} = [\,m^a\hbar^b c^d\,] = \mathrm{M}^a(\mathrm{ML^2T^{-1}})^b(\mathrm{MT^{-2}L^{-2}})^d = \mathrm{M}^{a+b+d}\mathrm{L}^{2b-2d}\mathrm{T}^{-b-2d}$, so
$a + b + d = 1,\ 2b - 2d = 2,\ -b - 2d = -2$. Adding twice the third equation to the second, we get $-6d = -2$ and $d = \frac{1}{3}$. Then $b = \frac{4}{3}$ and $a = -\frac{2}{3}$. So $E_r = E/A = E/m^{-2/3}\hbar^{4/3}c^{1/3}$.
Let $B = m^e\hbar^f c^g$. We have
$[B] = \mathrm{L} = \mathrm{M}^e(\mathrm{ML^2T^{-1}})^f(\mathrm{MT^{-2}L^{-2}})^g = \mathrm{M}^{e+f+g}\mathrm{L}^{2f-2g}\mathrm{T}^{-f-2g}$, so
$e + f + g = 0,\ 2f - 2g = 1,\ -f - 2g = 0$. Subtracting the third equation from the second, we get $f = \frac{1}{3}$. Then $g = -\frac{1}{6}$ and $e = -\frac{1}{6}$. So $x_r = x/B = x/m^{-1/6}\hbar^{1/3}c^{-1/6}$. The Schrödinger equation is $-(\hbar^2/2m)\psi'' + cx^4\psi = E\psi$. From (4.78) and (4.79), $\psi_r = \psi B^{1/2}$ and $\psi'' = \psi_r'' B^{-1/2}B^{-2} = B^{-1/2}m^{1/3}\hbar^{-2/3}c^{1/3}\psi_r''$. The Schrödinger equation becomes $-(\hbar^2/2m)B^{-1/2}m^{1/3}\hbar^{-2/3}c^{1/3}\psi_r'' + cx_r^4 m^{-2/3}\hbar^{4/3}c^{-2/3}B^{-1/2}\psi_r = m^{-2/3}\hbar^{4/3}c^{1/3}E_r B^{-1/2}\psi_r$ and $\psi_r'' = (2x_r^4 - 2E_r)\psi_r = G_r\psi_r$, where $G_r \equiv 2x_r^4 - 2E_r$. Let us find eigenvalues with $E_r \le 10.$ Setting this maximum E_r equal to V_r, we have $10 = x_r^4$ and the classically allowed region is bounded by $x_r = \pm 1.78$. We shall start well into the classically forbidden region at $x_r = -3.5$ and go to $x_r = +3.5$ in steps of 0.05. Cell B7 of Fig. 4.9 contains the formula 2*A7^4-2*B3 and this is copied to other column B cells. With 0.001 in cell C8, a suitable Precision (set by clicking the Solver Options button) is 0.1. The Solver gives the lowest three eigenvalues as
$E_r \equiv E/m^{-2/3}\hbar^{4/3}c^{1/3} = 0.667986133,\ 2.39364258,\ 4.69678795.$

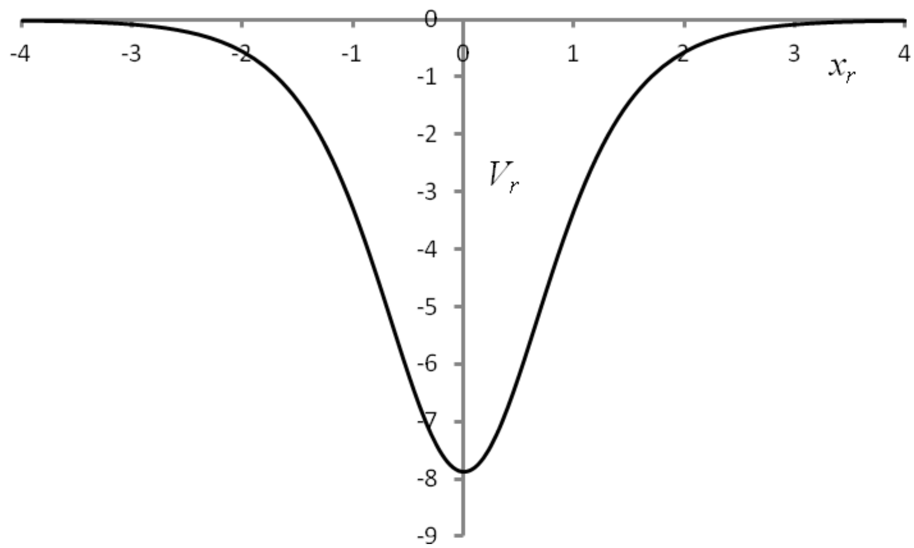
4.33 Proceeding similarly as in Prob. 4.32, we have $[a] = \mathrm{ML^2T^{-2}/L^8} = \mathrm{MT^{-2}L^{-6}}$. $E_r \equiv E/A$ and $x_r \equiv x/B.$ Let $A = m^b\hbar^c a^d$. Then $[A] = \mathrm{ML^2T^{-2}} = [\,m^b\hbar^c a^d\,] =$

$M^b(ML^2T^{-1})^c(MT^{-2}L^{-6})^d = M^{b+c+d}L^{2c-6d}T^{-c-2d}$, so $b+c+d=1,\ 2c-6d=2,\ -c-2d=-2$. $d=\frac{1}{5},\ c=\frac{8}{5},\ b=-\frac{4}{5}$. $E_r = E/A = E/m^{-4/5}\hbar^{8/5}a^{1/5}$. Let $B = m^e\hbar^f a^g$. We have $[B] = L = M^e(ML^2T^{-1})^f(MT^{-2}L^{-6})^g = M^{e+f+g}L^{2f-6g}T^{-f-2g}$, so $e+f+g=0,\ 2f-6g=1,\ -f-2g=0$. $g=-\frac{1}{10},\ f=\frac{1}{5},\ e=-\frac{1}{10}$. $x_r = x/B = x/m^{-1/10}\hbar^{1/5}a^{-1/10}$. The Schrödinger equation is $-(\hbar^2/2m)\psi'' + ax^8\psi = E\psi$. From (4.78) and (4.79), $\psi_r = \psi B^{1/2}$ and $\psi'' = \psi_r'' B^{-1/2}B^{-2} = B^{-1/2}m^{1/5}\hbar^{-2/5}a^{1/5}\psi_r''$. The Schrödinger equation becomes $-(\hbar^2/2m)B^{-1/2}m^{1/5}\hbar^{-2/5}a^{1/5}\psi_r'' + ax_r^8 m^{-4/5}\hbar^{8/5}a^{-4/5}B^{-1/2}\psi_r = m^{-4/5}\hbar^{8/5}a^{1/5}E_r B^{-1/2}\psi_r$ and $\psi_r'' = (2x_r^8 - 2E_r)\psi_r = G_r\psi_r$, where $G_r \equiv 2x_r^8 - 2E_r$. Let us find eigenvalues with $E_r \le 10$. Setting this maximum E_r equal to V_r, we have $10 = x_r^8$ and the classically allowed region is bounded by $x_r = \pm 1.33$. We shall start well into the classically forbidden region at $x_r = -3$ and go to $x_r = +3$ in steps of 0.02. Cell B7 of Fig. 4.9 contains the formula 2*A7^8-2*B3 and this is copied to other column B cells. With 0.001 in cell C8, a suitable Precision (set by clicking the Solver Options button) is 0.1. The Solver gives the lowest three eigenvalues as $E_r = E/A = E/m^{-4/5}\hbar^{8/5}a^{1/5}$ = 0.70404876, 2.731532, 5.884176.

4.34 Proceeding similarly as in Prob. 4.32, we have $[b] = ML^2T^{-2}/L = MT^{-2}L$. $E_r \equiv E/A$ and $x_r \equiv x/B$. Let $A = m^a\hbar^c b^d$. Then $[A] = ML^2T^{-2} = [m^a\hbar^c b^d] = M^a(ML^2T^{-1})^c(MT^{-2}L)^d = M^{a+c+d}L^{2c+d}T^{-c-2d}$, so $a+c+d=1,\ 2c+d=2,\ -c-2d=-2$. $d=\frac{2}{3},\ c=\frac{2}{3}\ a=-\frac{1}{3}$. So $E_r = E/A = E/m^{-1/3}\hbar^{2/3}b^{2/3}$. Let $B = m^e\hbar^f b^g$. We have $[B] = L = M^e(ML^2T^{-1})^f(MT^{-2}L)^g = M^{e+f+g}L^{2f+g}T^{-f-2g}$, so $e+f+g=0,\ 2f+g=1,\ -f-2g=0$ and $g=-\frac{1}{3},\ f=\frac{2}{3},\ e=-\frac{1}{3}$. $x_r = x/B = x/m^{-1/3}\hbar^{2/3}b^{-1/3}$. The Schrödinger equation is $-(\hbar^2/2m)\psi'' + bx\psi = E\psi$. From (4.78) and (4.79), $\psi_r = \psi B^{1/2}$ and $\psi'' = \psi_r'' B^{-1/2}B^{-2} = B^{-1/2}m^{2/3}\hbar^{-4/3}b^{2/3}\psi_r''$. The Schrödinger equation becomes $-(\hbar^2/2m)B^{-1/2}m^{2/3}\hbar^{-4/3}b^{2/3}\psi_r'' + bx_r m^{-1/3}\hbar^{2/3}b^{-1/3}B^{-1/2}\psi_r = m^{-1/3}\hbar^{2/3}b^{2/3}E_r B^{-1/2}\psi_r$ and $\psi_r'' = (2x_r - 2E_r)\psi_r = G_r\psi_r$, where $G_r \equiv 2x_r - 2E_r$. Let us find eigenvalues with $E_r \le 8$. Setting this maximum E_r equal to V_r, we have $8 = x_r$ and the classically allowed region is $0 \le x_r \le 8$. We shall go from $x_r = 0$ to 10 in steps of 0.05. Cell B7 of Fig. 4.9 contains the formula 2*A7-2*B3 and this is copied to other column B cells. The Solver gives the lowest four eigenvalues as 1.85575706, 3.24460719, 4.38167006, 5.38661153.

4.35 **(a)** Let $E_r \equiv E/A$. a has dimensions of length, and just as $A = \hbar^2/ml^2$ in Prob. 4.30, we have $A = \hbar^2/ma^2$ here. Hence, $V_r = V/A = -31.5/(e^{x_r} + e^{-x_r})^2$, where $x_r \equiv x/a$.

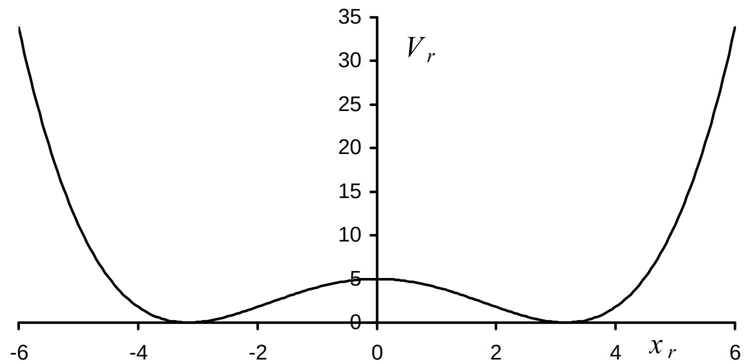
(b)



(c) For $E_r = -0.1$, the boundaries of the classically allowed region are where $V_r = E_r = -0.1$. The table used to make the graph in (b) shows that $V_r = -0.1$ at $x_r \approx \pm 2.9$. We shall go from $x_r = -7$ to 7 in steps of 0.05. (Use of too small a range for x can give erroneous results. For example going from -4 to 4 gives only 3 states instead of 4. Also, the value of the highest energy level found varies significantly with the size of the range.) Setting $E_r = -0.1$, we get a function with 4 nodes interior to the boundary points, indicating that there are 4 states below $E_r = -0.1$. These are found to be $E_r = E/(\hbar^2/ma^2) = -6.125000942$, -3.1250035, -1.125005, and -0.1226. For the lowest state the Solver might say that it could not find a solution, but the appearance of the wave function shows that the Solver has found a good solution; you could improve it by varying by hand the last digit of the Solver's value. If we go from -8 to 8 in steps of 0.05, the highest energy level is improved to -0.1241.

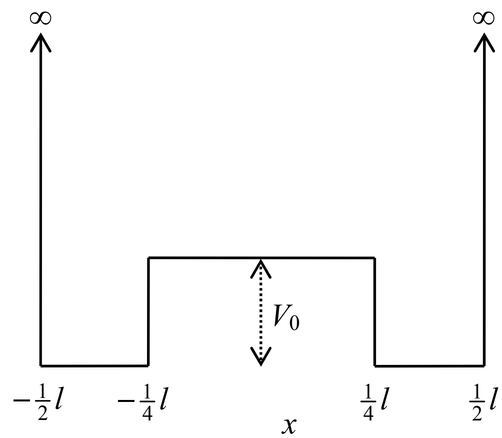
4.36 **(a)** $V_r = V/A = (\frac{1}{4}b^2 \cdot a^{-1}m^{-1/2}b^{-3/2}\hbar - bx^2 + ab^{3/2}m^{1/2}\hbar^{-1}x^4)/m^{-1/2}b^{1/2}\hbar =$ $1/(4a) - b^{1/2}m^{1/2}\hbar^{-1}x^2 + abm\hbar^{-2}x^4 = 1/(4a) - x_r^2 + ax_r^4$, where we used the expression for c given in the statement of this problem, (4.73) with k replaced by b, and $x = x_rB =$ $m^{-1/4}b^{-1/4}\hbar^{1/2}x_r$.

(b)



(c) The graph gives $x_r = \pm 4.9$ at $E_r = V_r = 10,$ and these are the boundary points of the classically allowed region. We shall go from $x_r = -6.5$ to 6.5 in steps of 0.05. We modify the spreadsheet of Fig. 4.9 by changing the formulas in column B to correspond to $2V_r - 2E_r$ with $a = 0.05.$ Putting $E_r = 10$ in the spreadsheet gives a function with 12 nodes, indicating that 12 states have energies below 10. One finds the following E_r values: 0.97336479758, 0.97339493833903, 2.7958839769, 2.79920822, 4.315510072, 4.4214678772594, 5.3827766596746, 5.9746380026562, 6.8331392725971, 7.7437224213536, 8.7368315651332, 9.7948731480794, where the number of interior nodes goes from 0 to 11.

4.37 **(a)** The potential-energy function is



As in the particle in a box (Prob. 4.30) $E_r = E/(\hbar^2/ml^2)$, $x_r = x/l$. x_r goes from -0.5 to 0.5. We shall take $s_r = 0.01$. A cell is designated to contain the value of $V_{0,r}$. The column B cells contain the formula for $2V_r - 2E_r$, where V_r is 0 for $-0.5 \le x_r \le -0.25$ and for $0.25 \le x_r \le 0.5$; and is $V_{0,r}$ for $-0.25 < x_r < 0.25$. One finds $E_r = E/(\hbar^2/ml^2)$ = 5.7400863, 20.216046, 44.798915, 79.459117. The wave functions closely resemble those of a particle in a box (pib). This is because the bound-state energies are all substantially greater than V_0, so V_0 is only a small perturbation on the pib potential energy.

(b) With $V_{0,r}$ changed to 100, one finds $E_r = E/(\hbar^2/ml^2)$ = 44.4763188, 44.7856494, 113.73536239, 142.13947708.

(c) With $V_{0,r} = 1000$, we get $E_r =$ 63.869414269, 63.869414294, 254.025267141, 254.025267989. The first two states have wave functions that look like particle-in-box $n = 0$ functions in the left and right quarters of the well with ψ being small in the central region, and the next two wave functions resemble $n = 1$ functions in these two quarters. The energies of these states are well below V_0. In the limit $V_0 \to \infty$, we would have two boxes with infinitely high walls.

4.38 **(a)** 0.4999996, 1.4999973, 2.4999903, 3.4999765, 4.4999621, 5.5000081; 11.7121. The range –5 to 5 was chosen as appropriate for reduced energies less than 5. For $E_r = 11.5$, the classically allowed region is found from $0.5x_r^2 = 11.5$ and $x_r = \pm 4.8$. At $x_r = \pm 5$, we are not far enough into the classically forbidden region to approximate ψ as zero. If we redo things with the range taken from –6.5 to 6.5 with $s_r = 0.1$, we get 11.49921.

(b) 0.499747, 1.498209, 2.493505, 3.483327, 4.465124, 5.436066. The larger s_r value reduces the accuracy.

(c) 0.500391, 1.506079, 2.541116, 3.664184, 4.954083.

4.39 **(a)** The usual mathematical convention is that $-x^2 + x^2 = 0$. Hence one would expect 0 as the result.

(b) Excel gives 50. Certain other spreadsheets give 0.

4.40 **(b)** x2 can be misinterpreted as a cell reference, so x2 is not allowed as the name of a parameter.

4.41 Put $n = 1$ in (4.67). Since $\psi_0 = 0$, (4.67) shows that ψ_2 is proportional to ψ_1. With $n = 2$, (4.67) shows that ψ_3 contains only terms linear in ψ_2 and ψ_1, and since ψ_2 is proportional to ψ_1, ψ_3 is proportional to ψ_1. With $n = 2$, (4.67) shows that ψ_4 contains only terms linear in ψ_3 and ψ_2 and since both of these are proportional to ψ_1, ψ_4 is proportional to ψ_1. And so on.

4.42 For the $v = 0$ state with $E_r = 0.5$, the boundaries of the classically allowed region are found from $0.5 = 0.5x_r^2$ and thus are $x_r = \pm 1$. The probability of being in the classically forbidden region is $2\int_{-5}^{-1} |\psi_r|^2 \, dx_r$. We square the normalized ψ_r column E values to get $|\psi_r|^2$ values in column F. We approximate this probability by $2\sum |\psi_r|^2 \, (0.1)$, where the sum uses the column F values from –5 to –1. Since the value at –1 is at the boundary of the allowed and forbidden regions, we shall include one-half the $|\psi_r|^2$ value at –1 in the sum. We get 0.16 as the probability of being in the classically forbidden region. For the $E_r = 1.5$ state, the boundaries of the classically allowed region satisfy $1.5 = 0.5x_r^2$ and $x_r = \pm 1.73$. Taking twice the sum from –5 to –1.7 for this state, we get 0.12 as the probability of being in the classically forbidden region. This is smaller than 0.16, in accord with the correspondence principle.

4.43 **(a)** With this notation, (4.85) becomes

$$f(x_n + s) = f(x_n) + f'(x_n)s + \tfrac{1}{2} f''(x_n)s^2 + \tfrac{1}{6} f'''(x_n)s^3 + \tfrac{1}{24} f^{(\text{iv})}(x_n)s^4 + \tfrac{1}{120} f^{(\text{v})}(x_n)s^5 + \cdots$$

(b) Replacement of s by $-s$ gives

$$f(x_n - s) = f(x_n) - f'(x_n)s + \tfrac{1}{2} f''(x_n)s^2 - \tfrac{1}{6} f'''(x_n)s^3 + \tfrac{1}{24} f^{(\text{iv})}(x_n)s^4 - \tfrac{1}{120} f^{(\text{v})}(x_n)s^5 + \cdots$$

Addition of these two equations and neglect of s^6 and higher powers gives

$$f(x_n + s) + f(x_n - s) \approx 2f(x_n) + f''(x_n)s^2 + \tfrac{1}{12} f^{(\text{iv})}(x_n)s^4$$

Use of the notation of (4.65) with ψ replaced by f followed by the replacement of f by ψ gives

$$f_{n+1} \approx -f_{n-1} + 2f_n + f_n'' s^2 + \tfrac{1}{12} f_n^{(\text{iv})} s^4 \tag{4.87}$$

$$\psi_{n+1} \approx -\psi_{n-1} + 2\psi_n + \psi_n'' s^2 + \tfrac{1}{12} \psi_n^{(\text{iv})} s^4 \tag{4.88}$$

(c) Replacement of f in (4.87) with ψ'' and multiplication by s^2 gives

$$\psi_{n+1}'' s^2 \approx -\psi_{n-1}'' s^2 + 2\psi_n'' s^2 + \psi_n^{(\text{iv})} s^4 + \tfrac{1}{12} \psi_n^{(\text{vi})} s^6$$

Neglecting the s^6 term, we get

$$\psi_n^{(\text{iv})} s^4 \approx \psi_{n+1}'' s^2 + \psi_{n-1}'' s^2 - 2\psi_n'' s^2$$

Use of $\psi'' = G\psi$ in this last equation gives

$$\psi_n^{(\text{iv})} s^4 \approx G_{n+1}\psi_{n+1} s^2 + G_{n-1}\psi_{n-1} s^2 - 2G_n\psi_n s^2 \tag{4.89}$$

Substitution of (4.89) and $\psi'' = G\psi$ into (4.88) gives

$$\psi_{n+1} \approx -\psi_{n-1} + 2\psi_n + G_n\psi_n s^2 + \tfrac{1}{12}\left[G_{n+1}\psi_{n+1} s^2 + G_{n-1}\psi_{n-1} s^2 - 2G_n\psi_n s^2\right]$$

Solving this last equation for ψ_{n+1}, we get Eq. (4.67).

4.44 Let $B = m^d k^e \hbar^f$. Then (4.70) and (4.71) give

$$[B] = \left[m^d k^e \hbar^f\right] = \text{M}^d \left(\text{MT}^{-2}\right)^e \left(\text{ML}^2\text{T}^{-1}\right)^f = \text{M}^{d+e+f}\text{L}^{2f}\text{T}^{-2e-f} = \text{L}$$

$$d + e + f = 0, \quad 2f = 1, \quad -2e - f = 0$$

$$f = \tfrac{1}{2}, \quad e = -\tfrac{1}{4}, \quad d = -\tfrac{1}{4}$$

$$B = m^{-1/4} k^{-1/4} \hbar^{1/2}$$

4.45 **(a)** From $-(\hbar^2/2m)\psi'' + V(x)\psi = E\psi$, we get $\psi''(a) = 0$ if $\psi(a) = 0$ and $V(a)$ is finite.

(b) Differentiation of the Schrödinger equation gives $-(\hbar^2/2m)\psi''' + V\psi' + V'\psi = E\psi'$. Then if both ψ and ψ' are zero at a and V' is finite at a, we get $\psi'''(a) = 0$. Further differentiation of the Schrödinger equation then shows all higher derivatives are zero at a.

4.46 **(a)** V is the same as in Prob. 4.33, except that c replaces a. From the Prob. 4.33 solution, $x_r = x/m^{-1/10}\hbar^{1/5}c^{-1/10}$, $E_r = E/A = E/m^{-4/5}\hbar^{8/5}c^{1/5}$ and $V_r = V/A = V/m^{-4/5}\hbar^{8/5}c^{1/5} = cx^8/m^{-4/5}\hbar^{8/5}c^{1/5} = cx_r^8(m^{-1/10}\hbar^{1/5}c^{-1/10})^8/m^{-4/5}\hbar^{8/5}c^{1/5} = x_r^8$. The classically allowed region has $E_r \ge V_r$, that is, $10 \ge x_r^8$, which gives $|x_r| \le 10^{1/8} = 1.33$ and $-1.33 \le x_r \le 1.33$.

(b) With these values of $x_{r,0}$, $x_{r,\max}$, and s_r, one finds that ψ oscillates between positive and negative values from one point to the next between –3 and –2.65 and between 2.65 and 3.

(c) $1-G_r s_r^2/12 = 1-(2V_r - 2E_r)s_r^2/12$. We have $V_r = x_r^8 = (\pm 2.65)^8 = 2432$; this is much greater than E_r, which is less than 10, so $1-G_r s_r^2/12 \approx 1-2V_r s_r^2/12 =$ $1-2(2430)(0.05)^2/12 = -0.01$. So for $|x_r| > 2.65$, the denominator in (4.67) is negative and ψ oscillates in sign from point to point.

(d) The spurious oscillations are eliminated with both of these choices.

4.47 Replace the last statement goto label1; with

```
z=0;
for (i=1; i<=m; i=i+1)  {
        z=z+p[i]*p[i]*s;
}
n=1/sqrt(z);
for (i=1; i <= m; i=i+1)  {
        p[i]=n*p[i];
        cout  <<  " xr =  " <<  x[i]  <<  "  psir =  "  <<  p[i]  <<  endl;
}
goto  label1;
```

Also add z and n to the list of double-precision variables in the sixth line of the program.

4.48 A C++ program is

```
include  <iostream>
using namespace std;
int main() {
   int m, nn, i;
   double x, s, E, p, q, y, g, h, ss, z, j, r;
   cout <<  " Enter initial xr  ";
   cin  >>  x;
   cout  <<   " Enter interval sr  ";
   cin  >>  s;
   cout  <<  " Enter number of intervals m  ";
   cin  >>  m;
   label1:
```

```
   cout  << " Enter Er (enter 1e10 to quit)  ";
   cin  >> E;
   if (E > 1e9) {
      cout  <<  "quitting ";
      return 0;
   }
   nn = 0;  p = 0;  q = 0.0001;
   y = x+ s;
   g = x*x - 2*E;
   h = y*y - 2*E;
   ss = s*s/12;
   for (i=1; i <= m-1; i=i+1)  {
      z=y+s;
      j=z*z - 2*E;
      r=(-p+2*q+10*h*q*ss+g*p*ss)/(1-j*ss);
      if(r*q < 0)
           nn = nn+1;
      p=q;  q=r;  x=y;  y=z;
      g=h;  h=j;
   }
   cout  << " Er=  " << E  << "  nodes =  " << nn << "  Psir(xm) =  "  << q  << endl;
   x = z - m*s;
   goto label1;
}
```

4.49 **(a)** From Prob. 2.23, $b = 3.97$. Use of the Solver to make the left side of (2.35) equal to zero subject to the constraints that $\varepsilon \le 1$ and $\varepsilon \ge 10^{-6}$ gives $\varepsilon = 0.2677$ and 0.9035. Then $E = \varepsilon(15.0 \text{ eV}) =$ 4.02 eV and 13.6 eV.

(b) When $E_r > V_{0r}$, we have $(V_{0r} - E_r)^{1/2} = i(E_r - V_{0r})^{1/2}$. Also, use of (2.14) gives

$$\tanh(ix) = \frac{e^{ix} - e^{-ix}}{e^{ix} + e^{-ix}} = \frac{\cos x + i\sin x - (\cos x - i\sin x)}{\cos x + i\sin x + (\cos x - i\sin x)} = \frac{2i\sin x}{2\cos x} = i\tan x$$

Thus we enter four formulas into the spreadsheet, corresponding to whether E_r is less or greater than V_{0r} and whether p is 1 or –1. We use the constraints in the Solver either that $E_r > V_{0r}$ or $10^{-5} \le E_r \le V_{0r}$. The values found in Prob. 4.37 can be used as initial values for the Solver. For $V_{0r} = 1$, the Solver gives 5.7503448, 20.23604266, 44.808373, 79.45920976, where the first and third numbers are for $p = -1$. For $V_{0r} = 100$, we get $E_{0r} = 45.80216565$, 46.10722291, 113.9380765, 143.353994. For $V_{0r} = 1000$, we get 66.399924233, 66.399924251, 263.9170623, 263.9170630. To get accurate values when two states lie very close together, use Options to change the Solver precision to a much smaller value than the default value. (Although $E_r = V_{0r}$ satisfies the equation, it is not a valid energy level.)

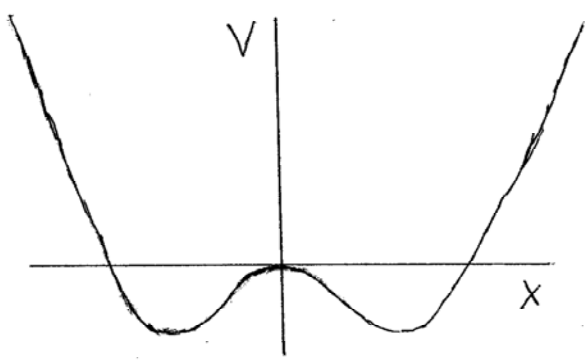
4.50 **(a)** Given: $\hat{A}f_i = k_i f_i$. Prove: $\hat{A}(cf_i) = k_i(cf_i)$. We have $\hat{A}(cf_i) = c\hat{A}f_i = ck_i f_i = k_i(cf_i)$, where we assumed that $\hat{A}$ is linear, as is true for quantum-mechanical operators corresponding to physical properties.

(b) The operator $(h\nu)^{-1}\hat{H}_{\text{ho}}$, where $\hat{H}_{\text{ho}}$ is the harmonic-oscillator Hamiltonian operator (4.30), has eigenvalues (4.45) divided by $h\nu$ and has the required eigenvalues.

(c) If we add a constant *a* to a linear operator, we add *a* to each of its eigenvalues. (See Prob. 4.52.) Hence the operator $(h\nu)^{-1}\hat{H}_{\text{ho}} + \frac{1}{2}$ has the desired eigenvalues.

4.51 **(a)** The wave function depends on one coordinate and is for a one-particle, one-dimensional system. The time-independent Schrödinger equation is $-(\hbar^2/2m)d^2(Ne^{-ax^4})/dx^2 + VNe^{-ax^4} = ENe^{-ax^4}$, so $-(\hbar^2/2m)(-12ax^2e^{-ax^4} + 16a^2x^6e^{-ax^4}) + Ve^{-ax^4} = Ee^{-ax^4}$, and $V(x) = E + (\hbar^2/2m)(-12ax^2 + 16a^2x^6)$. If we choose $V(0) = 0$, then we get $0 = E$ and $V(x) = (\hbar^2/m)(8a^2x^6 - 6ax^2)$.

(b) To aid in sketching *V*, we find its maxima and minima. We have $V' = (\hbar^2/m)(48a^2x^5 - 12ax) = 0$ and $x = 0$ and $x = \pm(4a)^{-1/4}$. Clearly *a* is positive (otherwise ψ would not be quadratically integrable). Evaluating V'', we find that it is negative at $x = 0$ and positive at $x = \pm(4a)^{-1/4}$. Hence, *V* is a local maximum at $x = 0$ and a local minimum at $x = \pm(4a)^{-1/4}$. For very large *x*, the x^2 term in *V* is negligible compared with the x^6 term and $V \approx (\hbar^2/m)8a^2x^6$. Thus *V* is positive for very large *x* and goes to ∞ as $x \to \pm\infty$. Also, *V* is an even function and is zero at $x = 0$. Combining this information, we have



(c) Because ψ has no nodes, it is the ground state. See the paragraph after Eq. (4.57).

4.52 Given: $\hat{H}\psi = E\psi$. Prove: $(\hat{H} + C)\psi = (E + C)\psi$. We have $(\hat{H} + C)\psi = \hat{H}\psi + C\psi = E\psi + C\psi = (E + C)\psi$.

4.53 **(a)** F.

(b) T.

(c) T, since the integrand is an odd function.

(d) T. This follows from the one-particle, one-dimensional Schrödinger equation.

(e) F.

(f) T, since ψ is an odd function and, as noted near the end of Sec. 4.2, ψ does not oscillate in the classically forbidden region).

(g) T.

Chapter 5

Angular Momentum

5.1 **(a)** No; **(b)** yes; **(c)** yes; **(d)** yes; **(e)** yes.

5.2 $[\hat{A},\ \hat{B}]f = (\hat{A}\hat{B} - \hat{B}\hat{A})f = \hat{A}\hat{B}f - \hat{B}\hat{A}f = -(\hat{B}\hat{A}f - \hat{A}\hat{B}f) = -[\hat{B},\ \hat{A}]f.$

$[\hat{A},\ \hat{A}^n]f = (\hat{A}\hat{A}^n - \hat{A}^n\hat{A})f = \hat{A}^{n+1}f - \hat{A}^{n+1}f = 0 = 0\cdot f$

$[k\hat{A},\ \hat{B}]f = (k\hat{A}\hat{B} - \hat{B}k\hat{A})f = k\hat{A}\hat{B}f - k\hat{B}\hat{A}f = k[\hat{A},\ \hat{B}]f$, since $\hat{B}$ is linear.

$[\hat{A},\ \hat{B}+\hat{C}]f = \hat{A}(\hat{B}+\hat{C})f - (\hat{B}+\hat{C})\hat{A}f = \hat{A}\hat{B}f - \hat{B}\hat{A}f + \hat{A}\hat{C}f - \hat{C}\hat{A}f = [\hat{A},\ \hat{B}]f + [\hat{A},\ \hat{C}]f$.

$[\hat{A},\ \hat{B}\hat{C}]f = \hat{A}\hat{B}\hat{C}f - \hat{B}\hat{C}\hat{A}f$. Also,

$[\hat{A},\ \hat{B}]\hat{C}f + \hat{B}[\hat{A},\ \hat{C}]f = (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{C}f + \hat{B}(\hat{A}\hat{C} - \hat{C}\hat{A})f = \hat{A}\hat{B}\hat{C}f - \hat{B}\hat{A}\hat{C}f + \hat{B}\hat{A}\hat{C}f - \hat{B}\hat{C}\hat{A}f$

$= \hat{A}\hat{B}\hat{C}f - \hat{B}\hat{C}\hat{A}f = [\hat{A},\ \hat{B}\hat{C}]f$.

The second identities in (5.3), (5.4), and (5.5) are proved similarly.

5.3 $[\hat{x},\ \hat{p}_x^3] = [\hat{x},\ \hat{p}_x\hat{p}_x^2] = \hat{p}_x[\hat{x},\ \hat{p}_x^2] + [\hat{x},\ \hat{p}_x]\hat{p}_x^2 = -i\hbar(\partial/\partial x)(2\hbar^2\partial/\partial x) + i\hbar(-\hbar^2\partial^2/\partial x^2) =$
$-3i\hbar^3(\partial^2/\partial x^2)$ where (5.6) and (5.7) were used.

5.4 From (5.11), $(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2$. From Prob. 4.9, $\langle V\rangle = \langle \frac{1}{2}kx^2\rangle = \frac{1}{4}h\nu$ so $\langle x^2\rangle = \frac{1}{2}h\nu k^{-1} = \frac{1}{2}h\nu/4\pi^2\nu^2 m = h/8\pi^2\nu m$. Figure 4.4a shows $\langle x\rangle = 0$. Equation (5.11) then gives $\Delta x = (h/8\pi^2\nu m)^{1/2}$. From Prob. 4.9, $\langle T\rangle = \langle (2m)^{-1}p_x^2\rangle = \frac{1}{4}h\nu$ and $\langle p_x^2\rangle = h\nu m/2$. Essentially the same reasoning that gave Eq. (3.92) gives $\langle p_x\rangle = 0$. Then $\Delta p_x = (h\nu m/2)^{1/2}$ and $\Delta x\,\Delta p_x = (h/8\pi^2\nu m)^{1/2}(h\nu m/2)^{1/2} = h/4\pi = \hbar/2$.

5.5 From (3.88),
$\langle x^2\rangle = (105/l^7)\int_0^l (x^6l^2 - 2lx^7 + x^8)\,dx = (105/l^7)(l^9/7 - l^9/4 + l^9/9) = 5l^2/12$ and
$\langle x\rangle = (105/l^7)\int_0^l (x^5l^2 - 2lx^6 + x^7)\,dx = (105/l^7)(l^8/6 - 2l^8/7 + l^8/8) = 5l/8$. Also,
$\hat{p}_x\psi = -i\hbar\,\partial\psi/\partial x = -i\hbar(105/l^7)^{1/2}(2lx - 3x^2)$ and $\hat{p}_x^2\psi = -\hbar^2(105/l^7)^{1/2}(2l - 6x)$. So
$\langle p_x\rangle = -i\hbar(105/l^7)\int_0^l (lx^2 - x^3)(2lx - 3x^2)\,dx = -i\hbar(105/l^7)\int_0^l (2l^2x^3 - 5lx^4 + 3x^5)\,dx =$
$-i\hbar(105/l^7)l^6(\frac{1}{2} - 1 + \frac{1}{2}) = 0$, which also follows by the reasoning used to get Eq. (3.92).
Then $\langle p_x^2\rangle = -\hbar^2(105/l^7)\int_0^l (lx^2 - x^3)(2l - 6x)\,dx = -\hbar^2(105/l^7)\int_0^l (2l^2x^2 - 8lx^3 + 6x^4)\,dx$

$= -(105\hbar^2/l^7)l^5(\frac{2}{3} - 2 + \frac{6}{5}) = 14\hbar^2/l^2$. So $(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{5}{12}l^2 - \frac{25}{64}l^2 = \frac{5}{192}l^2$ and $(\Delta p_x)^2 = 14\hbar^2/l^2$. We have $\Delta x\,\Delta p_x = (5/192)^{1/2}l(14^{1/2}\hbar/l) = (35/96)^{1/2}\hbar = 0.6038\hbar > \frac{1}{2}\hbar$.

5.6 If $\hat{A}\Psi = a\Psi$, then $\hat{A}^2\Psi = \hat{A}\hat{A}\Psi = \hat{A}a\Psi = a\hat{A}\Psi = a^2\Psi$ and $\langle A^2\rangle = \int \Psi^*\hat{A}^2\Psi\,d\tau = a^2\int\Psi^*\Psi\,d\tau = a^2$. Also $\langle A\rangle^2 = \left(\int\Psi^*\hat{A}\Psi\,d\tau\right)^2 = \left(a\int\Psi^*\Psi\,d\tau\right)^2 = a^2$. Then (5.11) gives $(\Delta A)^2 = 0$ and $\Delta A = 0$.

5.7 We have $(\hat{A} - \langle A\rangle)^2\Psi = (\hat{A} - \langle A\rangle)(\hat{A} - \langle A\rangle)\Psi = \hat{A}^2\Psi - 2\langle A\rangle\hat{A}\Psi + \langle A\rangle^2\Psi$, where Eqs. (3.11), (3.12), (3.10), and (3.2) were used. Then Eq. (5.10) becomes

$(\Delta A)^2 = \int(\Psi^*\hat{A}^2\Psi - 2\langle A\rangle\Psi^*\hat{A}\Psi + \Psi^*\langle A\rangle^2\Psi)\,d\tau$

$= \int\Psi^*\hat{A}^2\Psi\,d\tau - 2\langle A\rangle\int\Psi^*\hat{A}\Psi\,d\tau + \langle A\rangle^2\int\Psi^*\Psi\,d\tau =$

$\langle A^2\rangle - 2\langle A\rangle\langle A\rangle + \langle A\rangle^2\cdot 1 = \langle A^2\rangle - \langle A\rangle^2$.

5.8 The possible outcomes are HH, HT, TH, TT, where HT means the first coin showed heads and the second showed tails. The w values are 2, 1, 1, 0. We have $\langle w\rangle = (2+1+1+0)/4 = 1$. Alternatively, the probabilities for 2, 1, and 0 heads are $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$, respectively, and (3.81) gives $\langle w\rangle = \frac{1}{4}(2) + \frac{1}{2}(1) + \frac{1}{4}(0) = 1$. The w^2 values are 4, 1, 1, 0 and $\langle w^2\rangle = (4+1+1+0)/4 = 1.5$. We have $\sigma_w^2 = \langle w^2\rangle - \langle w\rangle^2 = 1.5 - 1^2 = 0.5$ and $\sigma_w = 2^{-1/2} = 0.707$.

5.9 **(a)** Vector; **(b)** vector; **(c)** scalar; **(d)** scalar; **(e)** vector; **(f)** scalar.

5.10 $|\mathbf{A}| = [3^2 + (-2)^2 + 6^2]^{1/2} = 7$, $|\mathbf{B}| = [(-1)^2 + 4^2 + 4^2]^{1/2} = 33^{1/2}$,

$\mathbf{A} + \mathbf{B} = (3-1)\mathbf{i} + (-2+4)\mathbf{j} + (6+4)\mathbf{k} = 2\mathbf{i} + 2\mathbf{j} + 10\mathbf{k}$,

$\mathbf{A} - \mathbf{B} = (3+1)\mathbf{i} + (-2-4)\mathbf{j} + (6-4)\mathbf{k} = 4\mathbf{i} - 6\mathbf{j} + 2\mathbf{k}$, $\mathbf{A}\cdot\mathbf{B} = 3(-1) + (-2)4 + 6(4) = 13$,

$$\mathbf{A}\times\mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ 3 & -2 & 6 \\ -1 & 4 & 4 \end{vmatrix} = (-8-24)\mathbf{i} - (12+6)\mathbf{j} + (12-2)\mathbf{k} = -32\mathbf{i} - 18\mathbf{j} + 10\mathbf{k}.$$

$\mathbf{A}\cdot\mathbf{B} = |\mathbf{A}||\mathbf{B}|\cos\theta = 13 = 7(33)^{1/2}\cos\theta$; $\cos\theta = 0.3232887$; $\theta = 1.2416$ rad $= 71.14°$.

5.11 Let the sides of the cube be 1 unit long and let the cube be placed with one corner at the origin and three of its edges lying on the positive *x*, *y*, and *z* axes, respectively. Then the center of the cube has (*x*, *y*, *z*) coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. If we imagine H_3 in the middle drawing of Fig. 12.5 to lie at the origin, then H_3 and H_4 have coordinates (0, 0, 0) and

(1, 1, 0), respectively. If we draw a vector from C at the center of the cube to H_3 and slide this vector so its tail is at the origin, this vector's tip has the coordinates $(0-\frac{1}{2},\ 0-\frac{1}{2},\ 0-\frac{1}{2}) = (-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$. The vector from C to H_4 has coordinates $(1-\frac{1}{2},\ 1-\frac{1}{2},\ 0-\frac{1}{2}) = (\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ when moved to bring its tail to the origin while preserving its direction. Calling these two vectors **A** and **B**, we have $|\mathbf{A}| = [(-\frac{1}{2})^2 + (-\frac{1}{2})^2 + (-\frac{1}{2})^2]^{1/2} = 3^{1/2}/2$, $|\mathbf{B}| = [(\frac{1}{2})^2 + (\frac{1}{2})^2 + (-\frac{1}{2})^2]^{1/2} = 3^{1/2}/2$, $\mathbf{A\cdot B} = (-\frac{1}{2})(\frac{1}{2}) + (-\frac{1}{2})(\frac{1}{2}) + (-\frac{1}{2})(-\frac{1}{2}) = -\frac{1}{4} = |\mathbf{A}||\mathbf{B}|\cos\theta = \frac{3}{4}\cos\theta$, so $\cos\theta = -\frac{1}{3}$ and $\theta = \arccos(-0.3333333) = 1.91063$ rad = 109.47°. This is the tetrahedral bond angle.

5.12 **(a)** Let the labels 1, 2, 3 distinguish the three Br atoms. Let the C atom lie at the origin, the C—H bond lie on the positive z axis, and the Br_1 atom lie in the xz plane with a positive x coordinate. Let α denote the HCBr angle and β denote the BrCBr angle. The angle made by the C—Br_1 bond and the negative z axis is $\pi - \alpha$. Let b denote the C—Br_1 bond length. A little trigonometry shows that the x, y, z coordinates of Br_1 are $b\sin(\pi-\alpha),\ 0,\ -b\cos(\pi-\alpha)$, respectively, and the x, y, z coordinates of Br_2 are $-\frac{1}{2}b\sin(\pi-\alpha),\ \frac{1}{2}\sqrt{3}b\sin(\pi-\alpha),\ -b\cos(\pi-\alpha)$. (The x and y coordinates of Br_2 are more easily found if the molecule is raised in the z direction to make the Br atoms lie in the xy plane; the line from the origin to atom Br_2 will then make a 30° angle with the y axis.) The dot product of the vectors that go from the origin at C to Br_1 and to Br_2 is [Eqs. (5.20) and (5.23)]: $b^2\cos\beta = -\frac{1}{2}b^2\sin^2(\pi-\alpha) + 0 + b^2\cos^2(\pi-\alpha)$. Hence $\cos\beta = -\frac{1}{2}\sin^2(\pi-\alpha) + \cos^2(\pi-\alpha) = 1 - 1.5\sin^2(\pi-\alpha)$ where $\cos^2\theta + \sin^2\theta = 1$ was used. We have $\sin(\pi-\alpha) = \sin\pi\cos\alpha - \cos\pi\sin\alpha = \sin\alpha$, so $\cos\beta = 1 - 1.5\sin^2\alpha$.

(b) $\cos(\angle\text{BrCBr}) = 1 - 1.5\sin^2(107.2°) = -0.36884$ and $\angle\text{BrCBr} = 111.6°$.

5.13 $\textbf{grad}\, f = \mathbf{i}(\partial f/\partial x) + \mathbf{j}(\partial f/\partial y) + \mathbf{k}(\partial f/\partial z) = (4x - 5yz)\mathbf{i} - 5xz\mathbf{j} + (2z - 5xy)\mathbf{k}$.
$\nabla^2 f = (\partial^2 f/\partial x^2 + \partial^2 f/\partial y^2 + \partial^2 f/\partial z^2) = 4 + 0 + 2 = 6.$

5.14 **(a)** $\text{div}[\textbf{grad}\, g(x,y,z)] = \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right)\cdot\left(\mathbf{i}\frac{\partial g}{\partial x} + \mathbf{j}\frac{\partial g}{\partial y} + \mathbf{k}\frac{\partial g}{\partial z}\right) = \frac{\partial^2 g}{\partial x^2} + \frac{\partial^2 g}{\partial y^2} + \frac{\partial^2 g}{\partial z^2}$

(b) $\nabla\cdot\mathbf{r} = \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right)\cdot(\mathbf{i}x + \mathbf{j}y + \mathbf{k}z) = \frac{\partial x}{\partial x} + \frac{\partial y}{\partial y} + \frac{\partial z}{\partial z} = 3$.

5.15 **(a)** Let $\mathbf{B}$ denote the vector. We have $|\mathbf{B}| = [3^2 + (-2)^2 + 0^2 + 1^2]^{1/2} = 14^{1/2}$.

(b) Let $\alpha, \beta, \gamma, \delta$ be the direction angles. Then $\cos\alpha = \mathbf{B}\bullet\mathbf{e}_1/|\mathbf{B}||\mathbf{e}_1| = (3, -2, 0, 1)\bullet(1, 0, 0, 0)\,/\,(14)^{1/2}(1) = 3/14^{1/2} = 0.80178$ and $\alpha = 0.6405$ rad $= 36.7°$. Next $\cos\beta = (3, -2, 0, 1)\bullet(0, 1, 0, 0)/14^{1/2} = -2/14^{1/2} = -0.53452$

and $\beta = 2.1347$ rad $= 122.3°$. Then $\cos\gamma = 0$ and $\gamma = \pi/2$ rad $= 90°$.
$\cos\delta = 1/14^{1/2} = 0.26726$ and $\delta = 1.300$ rad $= 74.5°$.

5.16 **(a)** No; **(b)** yes; **(c)** yes; **(d)** yes; see Eqs. (5.5) and (5.49).

5.17 $$\hat{L}_x^2 f = -\hbar^2\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\left(\sin\phi\frac{\partial f}{\partial\theta} + \cot\theta\cos\phi\frac{\partial f}{\partial\phi}\right)$$

$$\hat{L}_x^2 f = -\hbar^2\left(\begin{array}{l}\sin^2\phi\dfrac{\partial^2 f}{\partial\theta^2} - \sin\phi\cos\phi\csc^2\theta\dfrac{\partial f}{\partial\phi} + \sin\phi\cos\phi\cot\theta\dfrac{\partial^2 f}{\partial\theta\partial\phi} + \cot\theta\cos^2\phi\dfrac{\partial f}{\partial\theta}\\ + \cot\theta\cos\phi\sin\phi\dfrac{\partial^2 f}{\partial\phi\partial\theta} - \cot^2\theta\cos\phi\sin\phi\dfrac{\partial f}{\partial\phi} + \cot^2\theta\cos^2\phi\dfrac{\partial^2 f}{\partial\phi^2}\end{array}\right)$$

$$\hat{L}_y^2 f = -\hbar^2\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\left(\cos\phi\frac{\partial f}{\partial\theta} - \cot\theta\sin\phi\frac{\partial f}{\partial\phi}\right)$$

$$\hat{L}_y^2 f = -\hbar^2\left(\begin{array}{l}\cos^2\phi\dfrac{\partial^2 f}{\partial\theta^2} + \cos\phi\sin\phi\csc^2\theta\dfrac{\partial f}{\partial\phi} - \cos\phi\sin\phi\cot\theta\dfrac{\partial^2 f}{\partial\theta\partial\phi} + \cot\theta\sin^2\phi\dfrac{\partial f}{\partial\theta}\\ - \cot\theta\sin\phi\cos\phi\dfrac{\partial^2 f}{\partial\phi\partial\theta} + \cot^2\theta\sin\phi\cos\phi\dfrac{\partial f}{\partial\phi} + \cot^2\theta\sin^2\phi\dfrac{\partial^2 f}{\partial\phi^2}\end{array}\right)$$

$$\hat{L}_z^2 f = -\hbar^2\frac{\partial^2 f}{\partial\phi^2}$$

$$(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) f = -\hbar^2\left(\frac{\partial^2 f}{\partial\theta^2} + \cot\theta\frac{\partial f}{\partial\theta} + (\cot^2\theta + 1)\frac{\partial^2 f}{\partial\phi^2}\right),$$ where $\sin^2\beta + \cos^2\beta = 1$

was used. Use of $\cot^2\theta + 1 = \dfrac{\cos^2\theta}{\sin^2\theta} + 1 = \dfrac{\cos^2\theta + \sin^2\theta}{\sin^2\theta} = \dfrac{1}{\sin^2\theta}$ completes the proof.

5.18 $[\hat{L}_x^2, \hat{L}_y] = \hat{L}_x[\hat{L}_x, \hat{L}_y] + [\hat{L}_x, \hat{L}_y]\hat{L}_x = \hat{L}_x i\hbar\hat{L}_z + i\hbar\hat{L}_z\hat{L}_x = i\hbar(\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x) =$
$i\hbar(\hat{L}_x\hat{L}_z + \hat{L}_x\hat{L}_z + i\hbar\hat{L}_y) = i\hbar(2\hat{L}_x\hat{L}_z + i\hbar\hat{L}_y)$, where (5.48) was used.

5.19 **(a)** $r = (x^2 + y^2 + z^2)^{1/2} = (1 + 4 + 0)^{1/2} = 5^{1/2}$; $\cos\theta = z/r = 0$ and $\theta = 90°$;
$\tan\phi = y/x = 2$ and $\phi = \arctan 2 = 1.10715$ rad $= 63.435°$.

(b) $r = (1 + 0 + 9)^{1/2} = 10^{1/2}$; $\cos\theta = 3/10^{1/2} = 0.948683$ and $\theta = 0.32175$ rad $= 18.435°$;
$\tan\phi = 0$ and $\phi = 180°$ (the projection of **r** in the *xy* plane lies on the negative *x* axis).

(c) $r = (9 + 1 + 4)^{1/2} = 14^{1/2}$; $\cos\theta = -2/14^{1/2} = -0.534522$ and
$\theta = 2.13474$ rad $= 122.31°$; $\tan\phi = 1/3$ and $\phi = 0.321751$ rad $= 18.435°$.

(d) $r = (1 + 1 + 1)^{1/2} = 3^{1/2}$; $\cos\theta = -1/3^{1/2} = -0.57735$ and $\theta = 2.18628$ rad $= 125.26°$;
$\tan\phi = (-1)/(-1) = 1$ and $\phi = 225°$.

5.20 **(a)** $x = r\sin\theta\cos\phi = \sin(\pi/2)\cos\pi = -1$; $y = r\sin\theta\sin\phi = \sin(\pi/2)\sin\pi = 0$; $z = r\cos\theta = \cos(\pi/2) = 0$.

(b) $x = 2\sin(\pi/4)\cos 0 = 2^{1/2} = 1.414$; $y = 2\sin(\pi/4)\sin 0 = 0$; $z = 2\cos(\pi/4) = 1.414$.

5.21 **(a)** A sphere with center at the origin.

(b) A cone whose axis is the z axis.

(c) A half-plane perpendicular to the xy plane with edge being the z axis.

5.22 For points in the sphere, the angular coordinates go over their full ranges and r goes from 0 to R. So

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{R} r^2 \sin\theta\, dr\, d\theta\, d\phi = \int_0^{R} r^2\, dr \int_0^{\pi}\sin\theta\, d\theta \int_0^{2\pi} d\phi = \tfrac{1}{3}R^3(-\cos\theta)\big|_0^{\pi}\,(2\pi) = \tfrac{4}{3}\pi R^3.$$

5.23 From Fig. 5.6, $\cos\theta = m\hbar\big/[l(l+1)]^{1/2}\,\hbar = m\big/[l(l+1)]^{1/2}$. For $l = 2$, the possible m values are –2, –1, 0, 1, 2 corresponding to $\cos\theta = -2/6^{1/2},\ -1/6^{1/2},\ 0,\ 1/6^{1/2},\ 2/6^{1/2}$, respectively. Hence the possibilities are $\theta = 2.5261 \text{ rad} = 144.74°$, $\theta = 1.9913 \text{ rad} = 114.09°$, $\theta = 90°$, $\theta = 1.1503 \text{ rad} = 65.91°$, $\theta = 0.61548 \text{ rad} = 35.26°$.

5.24 **(a)** When the angle θ between the z axis and the **L** vector is smallest, then L_z has its largest possible value, which is $l\hbar$. We then have (Fig. 5.6)

$\cos\theta = L_z/|\mathbf{L}| = l\hbar/[l(l+1)]^{1/2}\hbar = l/[l(l+1)]^{1/2}$ and $\cos^2\theta = l/(l+1)$.

(b) As l increases, $l/(l+1)$ increases, coming closer and closer to 1, and θ decreases towards zero.

5.25 We have

$$\frac{d^2S}{d\theta^2} = \frac{d}{d\theta}\frac{dS}{d\theta} = -(1-w^2)^{1/2}\frac{d}{dw}\left[-(1-w^2)^{1/2}\frac{dG}{dw}\right]$$
$$= (1-w^2)\frac{d^2G}{dw^2} + (1-w^2)^{1/2}\,\tfrac{1}{2}(1-w^2)^{-1/2}(-2w)\frac{dG}{dw}$$
$$= (1-w^2)\frac{d^2G}{dw^2} - w\frac{dG}{dw}$$

5.26 **(a)** From (5.146), $S_{2,0} = (\tfrac{5}{2}\tfrac{2!}{2!})^{1/2} P_2^0(\cos\theta)$.

From (5.145), $P_2^0(w) = \dfrac{1}{8}\dfrac{d^2}{dw^2}(w^4 - 2w^2 + 1) = \tfrac{3}{2}w^2 - \tfrac{1}{2}$. So

$S_{2,0} = (\tfrac{5}{2})^{1/2}[\tfrac{3}{2}(\cos^2\theta) - \tfrac{1}{2}] = \tfrac{1}{4}(10)^{1/2}(3\cos^2\theta - 1)$.

(b) Equations (5.97) and (5.98) with j = 0, m = 0, l = 2 give $S_{2,0} = (a_0 + a_2\cos^2\theta)$ and $a_2 = \frac{-6}{2}a_0$, so $S_{2,0} = a_0(1-3\cos^2\theta)$. We have $1 = \int_0^\pi |S_{2,0}|^2 \sin\theta\, d\theta = |a_0|^2 \int_0^\pi (\sin\theta - 6\cos^2\theta\sin\theta + 9\cos^4\theta\sin\theta)\, d\theta$. Let $w \equiv \cos\theta$. Then $dw = -\sin\theta\, d\theta$ and $1 = |a_0|^2 \int_1^{-1}(-1+6w^2-9w^4)\, dw = |a_0|^2\ (2-4+\frac{18}{5}) = \frac{8}{5}|a_0|^2$, so $|a_0| = (5/8)^{1/2} = (10/16)^{1/2} = 10^{1/2}/4$ and $S_{2,0} = \frac{1}{4}10^{1/2}(1-3\cos^2\theta)$.

5.27 **(a)** From (5.99), $Y_3^0 = S_{3,0}(2\pi)^{-1/2}$. From (5.97), $S_{3,0} = a_1\cos\theta + a_3\cos^3\theta$. From (5.98) with j = 1, m = 0, l = 3, we have $a_3 = [(2-12)/6]a_1 = -\frac{5}{3}a_1$ so $S_{3,0} = a_1(\cos\theta - \frac{5}{3}\cos^3\theta)$. Then $1 = \int_0^\pi |S_{2,0}|^2 \sin\theta\, d\theta = |a_1|^2 \int_0^\pi (\sin\theta\cos^2\theta - \frac{10}{3}\cos^4\theta\sin\theta + \frac{25}{9}\cos^6\theta\sin\theta)\, d\theta$. Let $w \equiv \cos\theta$. Then $dw = -\sin\theta\, d\theta$ and $1 = |a_1|^2 \int_1^{-1}(-w^2 + \frac{10}{3}w^4 - \frac{25}{9}w^6)\, dw =$ $|a_1|^2\ (\frac{2}{3} - \frac{20}{15} + \frac{50}{63})\ =\ \frac{8}{63}|a_1|^2$ and $|a_1| = (63/8)^{1/2} = (126)^{1/2}/4 = 3(14)^{1/2}/4$. Then $S_{3,0} = [3(14)^{1/2}/4](\cos\theta - \frac{5}{3}\cos^3\theta)$, which differs by a factor –1 from Table 5.1. Finally, $Y_3^1 = [3(14)^{1/2}/4](\cos\theta - \frac{5}{3}\cos^3\theta)(2\pi)^{-1/2}$.

(b) From (5.99), $Y_3^1 = S_{3,1}(2\pi)^{-1/2}e^{i\phi}$. From (5.97), $S_{3,1} = \sin\theta(a_0 + a_2\cos^2\theta)$. Eq. (5.98) with j = 0, m = 1, l = 3 gives $a_2 = [(2-12)/2]a_0 = -5a_0$ so $S_{3,1} = a_0(1-5\cos^2\theta)\sin\theta$. Then $1 = \int_0^\pi |S_{3,1}|^2 \sin\theta\, d\theta = |a_0|^2 \int_0^\pi \sin^2\theta(1-10\cos^2\theta+25\cos^4\theta)\sin\theta\, d\theta$. Let $w \equiv \cos\theta$. Then $dw = -\sin\theta\, d\theta$ and $1 = |a_0|^2 \int_1^{-1}(1-w^2)(-1+10w^2-25w^4)\, dw =$ $|a_0|^2 \int_1^{-1}(25w^6 - 35w^4 + 11w^2 - 1)\, dw\ =\ |a_0|^2\ (-\frac{50}{7} + 14 - \frac{22}{3} + 2)\ =\ \frac{32}{21}|a_0|^2$ and $|a_0| = (21/32)^{1/2} = (42/64)^{1/2} = (42)^{1/2}/8$. Then $S_{3,1} = (42)^{1/2}8^{-1}(1-5\cos^2\theta)\sin\theta$ and $Y_3^1 = (42)^{1/2}8^{-1}(1-5\cos^2\theta)\sin\theta(2\pi)^{-1/2}e^{i\phi}$.

5.28
$$\hat{L}^2Y_2^0 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)b(3\cos^2\theta - 1),$$

where $b = \frac{1}{4}(5/\pi)^{1/2}$, and we used Table 5.1 and Eq. 5.99. Then

$(\partial/\partial\theta)(\cos^2\theta) = [2\cos\theta(-\sin\theta)] = -2\sin\theta\cos\theta;$

$(\partial^2/\partial\theta^2)(\cos^2\theta) = -2(\partial/\partial\theta)[\sin\theta(\cos\theta)] = -2[-\sin\theta(\sin\theta) + \cos\theta(\cos\theta)] =$

$-2[\cos^2\theta + \cos^2\theta - 1] = 2 - 4\cos^2\theta.$

$$\hat{L}^2Y_2^0 = -\hbar^2 b\left(6 - 12\cos^2\theta + \frac{\cos\theta}{\sin\theta}(-6\sin\theta\cos\theta) + 0\right) = -\hbar^2 b(6 - 18\cos^2\theta) =$$

$6\hbar^2 b(3\cos^2\theta - 1) = 2(3)\hbar^2 Y_2^0.$

5.29 $\hat{L}_z^3 Y_l^m = \hat{L}_z \hat{L}_z \hat{L}_z Y_l^m = \hat{L}_z \hat{L}_z (m\hbar) Y_l^m = m^3 \hbar^3 Y_l^m$.

5.30 From (5.43), $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$, so
$(\hat{L}_x^2 + \hat{L}_y^2) Y_l^m = (\hat{L}^2 - \hat{L}_z \hat{L}_z) Y_l^m = l(l+1)\hbar^2 Y_l^m - m^2\hbar^2 Y_l^m = [l(l+1)\hbar^2 - m^2\hbar^2] Y_l^m$.

5.31` **(a)** For $l = 2$, the possible eigenvalues of $\hat{L}_z$ are $-2\hbar,\ -\hbar,\ 0,\ \hbar,\ 2\hbar$, and since only eigenvalues can be found as the results of measurements, these are the possible outcomes of a measurement of $\hat{L}_z$.

(b) $12\hbar^2 = l(l+1)\hbar^2$ so $l = 3$. The possible outcomes are $-3\hbar,\ -2\hbar,\ -\hbar,\ 0,\ \hbar,\ 2\hbar,\ 3\hbar$.

5.32 Since the three directions of space are equivlent to one another and it is arbitrary as to whether we label a particular direction *x*, *y*, or *z*, the $\hat{L}_y$ eigenvalues are the same as the $\hat{L}_z$ eigenvalues, So the $\hat{L}_y$ eigenvalues for $l = 1$ are $-\hbar$, 0, and $\hbar$, and these are the possible outcomes of the measurement.

5.33 Since the state function is an eigenfunction of $\hat{L}^2$ with eigenvalue $2(2+1)\hbar^2$ and of $\hat{L}_z$ with eigenvalue $1\hbar$, measurement of L_z must give the result $\hbar$ = (6.626 × 10^{-34} J s)/2π = 1.055 × 10^{-34} J s and measurement of L^2 must give $6\hbar^2$ = 6(1.055 × 10^{-34} J s)^2 = 6.68 × 10^{-68} J^2 s^2.

5.34 $P_0^0(w) = (w^2 - 1)^0 = 1$, since the zeroth derivative of *f* is *f*. $P_1^0(w) = \dfrac{1}{2}\dfrac{d}{dw}(w^2 - 1) = w$.

$P_1^1 = \dfrac{1}{2}(1 - w^2)^{1/2}\dfrac{d^2}{dw^2}(w^2 - 1) = (1 - w^2)^{1/2}$. $P_2^0(w) = \dfrac{1}{8}\dfrac{d^2}{dw^2}(w^4 - 2w^2 + 1) = \frac{3}{2}w^2 - \frac{1}{2}$.

$P_2^1(w) = \dfrac{1}{8}(1 - w^2)^{1/2}\dfrac{d^3}{dw^3}(w^4 - 2w^2 + 1) = 3w(1 - w^2)^{1/2}$.

$P_2^2(w) = \dfrac{1}{8}(1 - w^2)\dfrac{d^4}{dw^4}(w^4 - 2w^2 + 1) = 3(1 - w^2)$.

5.35 From (5.107), (5.65), (5.66), and (1.28): $\hat{L}_- = \hat{L}_x - i\hat{L}_y =$

$$\hbar\left[(i\sin\phi - \cos\phi)\frac{\partial}{\partial\theta} + \cot\theta(i)(\cos\phi - i\sin\phi)\frac{\partial}{\partial\phi}\right] = \hbar\left(-e^{-i\phi}\frac{\partial}{\partial\theta} + i\cot\theta\, e^{-i\phi}\frac{\partial}{\partial\phi}\right).$$

From (5.99) and Table 5.1, $\hat{L}_- Y_1^1 = \hbar\left(-e^{-i\phi}\dfrac{\partial}{\partial\theta} + i\dfrac{\cos\theta}{\sin\theta}e^{-i\phi}\dfrac{\partial}{\partial\phi}\right)\frac{1}{2}(3/2\pi)^{1/2}e^{i\phi}\sin\theta =$

$\frac{1}{2}\hbar(3/2\pi)^{1/2}(-\cos\theta - \cos\theta) = -\hbar(3/2\pi)^{1/2}\cos\theta$, which Eq. (5.99) and Table 5.1 show is proportional to Y_1^0. Applying $\hat{L}_-$ again, we have

$\hbar\left(-e^{-i\phi}\dfrac{\partial}{\partial\theta} + i\cot\theta\, e^{-i\phi}\dfrac{\partial}{\partial\phi}\right)[-\hbar(3/2\pi)^{1/2}\cos\theta] =$

$-\hbar^2(3/2\pi)^{1/2}(e^{-i\phi}\sin\theta + 0) = -\hbar^2(3/2\pi)^{1/2}e^{-i\phi}\sin\theta$, which is proportional to Y_1^{-1}.

A third application of $\hat{L}_-$ gives $\hbar\left(-e^{-i\phi}\dfrac{\partial}{\partial\theta} + i\dfrac{\cos\theta}{\sin\theta}e^{-i\phi}\dfrac{\partial}{\partial\phi}\right)[-\hbar^2(3/2\pi)^{1/2}e^{-i\phi}\sin\theta] =$

$-\hbar^3(3/2\pi)^{1/2}(-e^{-2i\phi}\cos\theta + e^{-2i\phi}\cos\theta) = 0$.

5.36 Use of (3.11) and (3.12) gives $\hat{A}_+\hat{A}_- = (2m)^{-1}(\hat{p}_x + 2\pi i\nu m\hat{x})(\hat{p}_x - 2\pi i\nu m\hat{x}) =$ $(2m)^{-1}[\hat{p}_x^2 + 2\pi i\nu m(-\hat{p}_x\hat{x} + \hat{x}\hat{p}_x) + 4\pi^2\nu^2 m^2\hat{x}^2]$. But $(-\hat{p}_x\hat{x} + \hat{x}\hat{p}_x) = [\hat{x}, \hat{p}_x] = i\hbar$ [Eq. (5.6)], so $\hat{A}_+\hat{A}_- = \hat{p}_x^2/2m - \hbar\pi\nu + 2\pi^2\nu^2 m\hat{x}^2 = \hat{H} - \frac{1}{2}h\nu$. Similarly, $\hat{A}_-\hat{A}_+ = (2m)^{-1}(\hat{p}_x - 2\pi i\nu m\hat{x})(\hat{p}_x + 2\pi i\nu m\hat{x}) =$ $(2m)^{-1}[\hat{p}_x^2 + 2\pi i\nu m(\hat{p}_x\hat{x} - \hat{x}\hat{p}_x) + 4\pi^2\nu^2 m^2\hat{x}^2] = \hat{p}_x^2/2m + \hbar\pi\nu + 2\pi^2\nu^2 m\hat{x}^2 = \hat{H} + \frac{1}{2}h\nu$. Then $[\hat{A}_+, \hat{A}_-] = \hat{A}_+\hat{A}_- - \hat{A}_-\hat{A}_+ = \hat{H} - \frac{1}{2}h\nu - (\hat{H} + \frac{1}{2}h\nu) = -h\nu$. Next, $[\hat{H}, \hat{A}_+] = [\hat{H}, (2m)^{-1/2}(\hat{p}_x + 2\pi i\nu m\hat{x})] = (2m)^{-1/2}[\hat{H}, \hat{p}_x] + (2m)^{-1/2}2\pi i\nu m[\hat{H}, \hat{x}]$. Use of Eqs. (5.8) and (5.9) gives $[\hat{H}, \hat{A}_+] = (2m)^{-1/2}i\hbar(dV/dx) + (2m)^{-1/2}2\pi i\nu m(-i\hbar/m)\hat{p}_x$. From (4.27), $dV/dx = 4\pi^2\nu^2 mx$, so $[\hat{H}, \hat{A}_+] = h\nu(2m)^{-1/2}(\hat{p}_x + 2\pi i\nu mx) = h\nu\hat{A}_+$. Also, $[\hat{H}, \hat{A}_-] = (2m)^{-1/2}[\hat{H}, \hat{p}_x] - (2m)^{-1/2}2\pi i\nu m[\hat{H}, \hat{x}] = h\nu(2m)^{-1/2}(2\pi i\nu m\hat{x} - \hat{p}_x) = -h\nu\hat{A}_-$. Operating on $\hat{H}\psi = E\psi$ with $\hat{A}_+$ gives $\hat{A}_+\hat{H}\psi = E\hat{A}_+\psi$. But we showed $\hat{H}\hat{A}_+ - \hat{A}_+\hat{H} = h\nu\hat{A}_+$, so $(\hat{H}\hat{A}_+ - h\nu\hat{A}_+)\psi = E\hat{A}_+\psi$ and $\hat{H}(\hat{A}_+\psi) = (E + h\nu)(\hat{A}_+\psi)$. Hence $\hat{A}_+\psi$ is an eigenfunction of $\hat{H}$ with eigenvalue $E + h\nu$. Operating on $\hat{H}\psi = E\psi$ with $\hat{A}_-$ gives $\hat{A}_-\hat{H}\psi = E\hat{A}_-\psi$. But we showed $\hat{H}\hat{A}_- - \hat{A}_-\hat{H} = -h\nu\hat{A}_-$, so $(\hat{H}\hat{A}_- + h\nu\hat{A}_-)\psi = E\hat{A}_-\psi$ and $\hat{H}(\hat{A}_-\psi) = (E - h\nu)(\hat{A}_-\psi)$. Hence $\hat{A}_-\psi$ is an eigenfunction of $\hat{H}$ with eigenvalue $E - h\nu$. Let ψ_{min} be the minimum energy state. We showed that $\hat{A}_-\psi$ is an eigenfunction of $\hat{H}$ with eigenvalue $E - h\nu$. But since ψ_{min} has the lowest possible eigenvalue of $\hat{H}$, $\hat{A}_-\psi_{\text{min}}$ cannot be a valid wave function and so must be zero: $\hat{A}_-\psi_{\text{min}} = 0$. Operating on this equation with $\hat{A}_+$ and using the result $\hat{A}_+\hat{A}_- = \hat{H} - \frac{1}{2}h\nu$ derived above, we have $\hat{A}_+\hat{A}_-\psi_{\text{min}} = 0 = (\hat{H} - \frac{1}{2}h\nu)\psi_{\text{min}}$ and $\hat{H}\psi_{\text{min}} = \frac{1}{2}h\nu\psi_{\text{min}}$, so the lowest eigenvalue is $\frac{1}{2}h\nu$. Since we showed the eigenvalues to be spaced by $h\nu$, the allowed eigenvalues are $(n + \frac{1}{2})h\nu$, where n = 0, 1, 2,… .

5.37 **(a)** True. **(b)** False. **(c)** True. **(d)** True. **(e)** True. **(f)** False.

Chapter 6

The Hydrogen Atom

6.1 **(a)** T; **(b)** F.

6.2 **(a)** V is independent of θ and ϕ, so this is a central-force problem and Eq. (6.16) shows that $f = Y_l^m(\theta, \phi)$.

(b) For $r > b$, V is infinite and ψ must be zero. For $r \le b$ and $l = 0$, Eq. (6.17) is $-\hbar^2(2m)^{-1}(R'' + 2R'/r) = ER$. Let $g(r) \equiv rR(r)$. Then $R = gr^{-1}$ and the radial differential equation becomes
$-\hbar^2(2m)^{-1}(r^{-1}g'' - 2r^{-2}g' + 2gr^{-3} - 2gr^{-3} + 2r^{-2}g') = Egr^{-1}$ and $-(\hbar^2/2m)g''(r) = Eg$ so $g''(r) + 2mE\hbar^{-2}g(r) = 0$. This is the same as Eq. (2.10) with ψ_{II} replaced by g and x replaced by r, so Eq. (2.15) gives $g = rR = A\cos[\hbar^{-1}(2mE)^{1/2}r] + B\sin[\hbar^{-1}(2mE)^{1/2}r]$. Since Y_l^m is a constant for $l = 0$ and ψ is finite at $r = 0$, $R(r)$ must be finite at $r = 0$. Hence at $r = 0$, the equation for g becomes $g = 0 = A\cdot 1 + B\cdot 0$. Thus $A = 0$ and $g = rR = B\sin[\hbar^{-1}(2mE)^{1/2}r]$. Since $\psi = 0$ for $r > b$, continuity of ψ requires that $\psi = 0$ at $r = b$. Thus $R = 0$ at $r = b$. We have $0 = B\sin[\hbar^{-1}(2mE)^{1/2}b]$. B cannot be zero since this would make ψ equal to zero. Hence $\hbar^{-1}(2mE)^{1/2}b = n\pi$, where $n = 1, 2, 3, \ldots$. (n = 0 would make ψ zero and negative n values give essentially the same wave functions as positive n values.) Solving for E, we get $E = n^2h^2/8mb^2$. Substitution of this E expression in $rR = B\sin[\hbar^{-1}(2mE)^{1/2}r]$ gives $R(r) = (B/r)\sin[\hbar^{-1}(2mE)^{1/2}r] = (B/r)\sin(n\pi r/b)$. The $l = 0$ wave functions are found by multiplying this $R(r)$ by Y_0^0, which is a constant.

6.3 **(a)** and **(b)** We have $V = \frac{1}{2}k(x^2 + y^2 + z^2) = \frac{1}{2}kr^2$, which is a function of r only. Thus this is a central-force problem and Eq. (6.16) shows that $\psi = f(r)Y_l^m(\theta, \phi)$.

(c) Equation (6.17) with $R = f$ gives $-\dfrac{\hbar^2}{2m}\left(f'' + \dfrac{2}{r}f'\right) + \dfrac{l(l+1)\hbar^2}{2m}f + \frac{1}{2}kr^2 f = Ef$.

(d) Problem 4.20 showed that ψ is the product of three one-dimensional harmonic-oscillator wave functions. Because the three force constants are equal in Prob. 6.3, we have $\nu_x = \nu_y = \nu_z$ and $\alpha_x = \alpha_y = \alpha_z$. Use of (4.53) gives the ground-state ψ as $\psi = (\alpha/\pi)^{3/4}e^{-\alpha x^2/2}e^{-\alpha y^2/2}e^{-\alpha z^2/2} = (\alpha/\pi)^{3/4}e^{-\alpha r^2/2} = f(r)G(\theta, \phi)$, where G is a constant. With $f = e^{-\alpha r^2/2}$ and $l = 0$, the left side of the differential equation in (c) becomes $-\dfrac{\hbar^2}{2m}\left(-\alpha e^{-\alpha r^2/2}+\alpha^2 r^2 e^{-\alpha r^2/2}-\dfrac{2}{r}\alpha r e^{-\alpha r^2/2}\right)+\tfrac{1}{2}kr^2 e^{-\alpha r^2/2}=$

$$[-\hbar^2(2m)^{-1}(-3\alpha+\alpha^2 r^2)+\tfrac{1}{2}kr^2]f$$

Using Eqs. (4.31) and (4.23) for α and k, we have
$-\hbar^2(2m)^{-1}(-3\alpha+\alpha^2r^2)+\frac{1}{2}kr^2=-\hbar^2(2m)^{-1}(-6\pi\nu m/\hbar+4\pi^2\nu^2m^2r^2/\hbar^2)+2\pi^2\nu^2mr^2$
$=\frac{3}{2}h\nu$. The ground-state energy is $\frac{3}{2}h\nu$ (Prob. 4.20), so the equation in (c) is satisfied.

6.4 From (5.62), $\partial^2 f/\partial x^2=$

$$\left(\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\left(\sin\theta\cos\phi\frac{\partial f}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial f}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial f}{\partial\phi}\right)$$

$$=\sin^2\theta\cos^2\phi\frac{\partial^2 f}{\partial r^2}-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\frac{\partial f}{\partial\theta}+\frac{\sin\theta\cos\theta\cos^2\phi}{r}\frac{\partial^2 f}{\partial r\partial\theta}+\frac{\sin\theta\cos\phi\sin\phi}{r^2\sin\theta}\frac{\partial f}{\partial\phi}$$

$$-\frac{\sin\theta\cos\phi\sin\phi}{r\sin\theta}\frac{\partial^2 f}{\partial r\partial\phi}+\frac{\cos^2\theta\cos^2\phi}{r}\frac{\partial f}{\partial r}+\frac{\cos\theta\sin\theta\cos^2\phi}{r}\frac{\partial^2 f}{\partial\theta\partial r}-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\frac{\partial f}{\partial\theta}$$

$$+\frac{\cos^2\theta\cos^2\phi}{r^2}\frac{\partial^2 f}{\partial\theta^2}+\frac{\cos\theta\cos\phi\sin\phi(\sin\theta)^{-2}\cos\theta}{r^2}\frac{\partial f}{\partial\phi}-\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\frac{\partial^2 f}{\partial\theta\partial\phi}$$

$$+\frac{\sin^2\phi\sin\theta}{r\sin\theta}\frac{\partial f}{\partial r}-\frac{\sin\phi\sin\theta\cos\phi}{r\sin\theta}\frac{\partial^2 f}{\partial\phi\partial r}+\frac{\sin\phi\cos\theta\sin\phi}{r^2\sin\theta}\frac{\partial f}{\partial\theta}-\frac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta}\frac{\partial^2 f}{\partial\phi\partial\theta}$$

$$+\frac{\sin\phi\cos\phi}{r^2\sin^2\theta}\frac{\partial f}{\partial\phi}+\frac{\sin^2\phi}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

From (5.63), $\partial^2 f/\partial y^2=$

$$\left(\sin\theta\sin\phi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\left(\sin\theta\sin\phi\frac{\partial f}{\partial r}+\frac{\cos\theta\sin\phi}{r}\frac{\partial f}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\frac{\partial f}{\partial\phi}\right)$$

$$=\sin^2\theta\sin^2\phi\frac{\partial^2 f}{\partial r^2}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\frac{\partial f}{\partial\theta}+\frac{\sin\theta\cos\theta\sin^2\phi}{r}\frac{\partial^2 f}{\partial r\partial\theta}-\frac{\sin\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial f}{\partial\phi}$$

$$+\frac{\sin\theta\sin\phi\cos\phi}{r\sin\theta}\frac{\partial^2 f}{\partial r\partial\phi}+\frac{\cos^2\theta\sin^2\phi}{r}\frac{\partial f}{\partial r}+\frac{\cos\theta\sin\theta\sin^2\phi}{r}\frac{\partial^2 f}{\partial\theta\partial r}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\frac{\partial f}{\partial\theta}$$

$$+\frac{\cos^2\theta\sin^2\phi}{r^2}\frac{\partial^2 f}{\partial\theta^2}-\frac{\cos\theta\sin\phi\cos\phi(\sin\theta)^{-2}\cos\theta}{r^2}\frac{\partial f}{\partial\phi}+\frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial^2 f}{\partial\theta\partial\phi}$$

$$+\frac{\cos^2\phi\sin\theta}{r\sin\theta}\frac{\partial f}{\partial r}+\frac{\cos\phi\sin\theta\sin\phi}{r\sin\theta}\frac{\partial^2 f}{\partial\phi\partial r}+\frac{\cos\phi\cos\theta\cos\phi}{r^2\sin\theta}\frac{\partial f}{\partial\theta}+\frac{\cos\phi\cos\theta\sin\phi}{r^2\sin\theta}\frac{\partial^2 f}{\partial\phi\partial\theta}$$

$$-\frac{\cos\phi\sin\phi}{r^2\sin^2\theta}\frac{\partial f}{\partial\phi}+\frac{\cos^2\phi}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

From (5.64), $\partial^2 f/\partial z^2 = \left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\left(\cos\theta\frac{\partial f}{\partial r} - \frac{\sin\theta}{r}\frac{\partial f}{\partial\theta}\right) =$

$$\cos^2\theta\frac{\partial^2 f}{\partial r^2} + \frac{\cos\theta\sin\theta}{r^2}\frac{\partial f}{\partial\theta} - \frac{\cos\theta\sin\theta}{r}\frac{\partial^2 f}{\partial r\,\partial\theta} + \frac{\sin^2\theta}{r}\frac{\partial f}{\partial r} - \frac{\sin\theta\cos\theta}{r}\frac{\partial^2 f}{\partial\theta\,\partial r}$$

$$+\frac{\sin\theta\cos\theta}{r^2}\frac{\partial f}{\partial\theta} + \frac{\sin^2\theta}{r^2}\frac{\partial^2 f}{\partial\theta^2}$$

We find $\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{\partial^2 f}{\partial r^2} + \frac{\cos\theta}{r^2\sin\theta}\frac{\partial f}{\partial\theta} + \frac{2}{r}\frac{\partial f}{\partial r} + \frac{1}{r^2}\frac{\partial^2 f}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$, where identities such as $\sin^2\theta + \cos^2\theta = 1$, $\sin^2\phi + \cos^2\phi = 1$, $\partial^2 f/\partial r\,\partial\theta = \partial^2 f/\partial\theta\,\partial r$ were used.

6.5 **(a)** F. **(b)** T.

6.6 Equations (6.23) and (2.20) give

$$E = E_1 + E_2 = \frac{h^2}{8a^2}\left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2}\right) = \frac{(6.626\times10^{-34}\text{ J s})^2}{8(1.00\times10^{-10}\text{ m})^2(10^{-29}\text{ kg})}\left(\frac{n_1^2}{9.0} + \frac{n_2^2}{5.0}\right) =$$

$$5.49\times10^{-19}\text{ J}\left(\frac{n_1^2}{9.0} + \frac{n_2^2}{5.0}\right) = \frac{5.49\times10^{-19}\text{ J}}{5}\left(\frac{5.0n_1^2}{9.0} + n_2^2\right) = (1.10\times10^{-19}\text{ J})(0.556n_1^2 + n_2^2)$$

Trial and error gives the quantum numbers (n_1, n_2) and energies of the six lowest states as (1,1), (2,1), (1,2), (3,1), (2,2), (3,2) and 1.71×10^{-19} J, 3.54×10^{-19} J, 5.01×10^{-19} J, 6.60×10^{-19} J, 6.84×10^{-19} J, 9.90×10^{-19} J.

6.7 **(a)** True, since $\mu = m_1m_2/(m_1 + m_2) = m_2/(1 + m_2/m_1) < m_2$; similarly $\mu < m_1$.

(b) True.

6.8 **(a)** T; **(b)** F; **(c)** T; **(d)** T; **(e)** T.

6.9 **(a)** The lowest absorption frequency corresponds to the $J = 0$ to 1 transition. We have $E_{\text{upper}} - E_{\text{lower}} = 1(2)\hbar^2/2\mu d^2 - 0 = h\nu$ so $d = (h/4\pi^2\mu\nu)^{1/2}$. The reduced mass is $\mu = m_1m_2/(m_1 + m_2) = \{12(15.9949)/[27.9949(6.02214\times10^{23})]\}$ g = 1.13850×10^{-26} kg.

So $d = \left(\frac{6.62607\times10^{-34}\text{ J s}}{4\pi^2(1.13850\times10^{-26}\text{ kg})(115271\times10^6\text{ s}^{-1})}\right)^{1/2} = 1.13089\times10^{-10}\text{ m} = 1.13089\text{ Å}.$

(b) The next two frequencies are for the $J = 1$ to 2 and 2 to 3 transitions and as found in Eq. (6.54) and Fig. 6.4 are twice and three times the 0 to 1 frequency. So $\nu_{1\to2}$ = 2(115271 MHz) = 230542 MHz and $\nu_{2\to3} = 345813$ MHz.

(c) From part (a), $\nu = h/4\pi^2\mu d^2$. d is the bond length averaged over the zero-point vibrations, which differ for $^{12}C^{16}O$ and $^{13}C^{16}O$, so d will differ very slightly for these two species. We shall neglect this difference. We have for $^{13}C^{16}O$,
$\mu = \{13.0034(15.9949)/[28.9983(6.02214\times10^{23})]\}$ g = 1.19101 × 10^{-26} kg and

$$\nu = \frac{6.62607\times10^{-34}\ \text{J s}}{4\pi^2(1.19101\times10^{-26}\ \text{kg})(1.13089\times10^{-10}\ \text{m})^2} = 1.102\times10^{11}\ \text{Hz}$$

(d) The Boltzmann distribution law (4.63) gives $N_1/N_0 = (g_1/g_0)e^{-(E_1-E_0)/kT}$. The degeneracy of each rotational level is $2J + 1$, so $g_1 = 3$ and $g_0 = 1$. Also,
$E_1 - E_0 = h\nu_{0\to1} = (6.62607\times10^{-34}\ \text{J s})(115271\times10^6\ \text{s}^{-1})$ = 7.63794 × 10^{-23} J. Then
$N_1/N_0 = 3e^{(-7.63794\times10^{-23}\ \text{J})/[(1.38065\times10^{-23}\ \text{J/K})(298.15\ \text{K})]} = 2.944$.
We have $E_2 - E_0 = E_2 = J(J+1)\hbar^2/2I = 6\hbar^2/2I$ and $E_1 - E_0 = E_1 = 2\hbar^2/2I$, so
$E_2 - E_0 = 3(E_1 - E_0) =$ 3(7.63794 × 10^{-23} J) = 2.29138 × 10^{-22} J. Hence
$N_2/N_0 = 5e^{(-2.29138\times10^{-22}\ \text{J})/[(1.38065\times10^{-23}\ \text{J/K})(298.15\ \text{K})]} = 4.729$.

6.10 $h\nu_{5\to6} = E_6 - E_5 = 6(7)\hbar^2/2I - 5(6)\hbar^2/2I = 12\hbar^2/2I$ and
$h\nu_{2\to3} = E_3 - E_2 = 3(4)\hbar^2/2I - 2(3)\hbar^2/2I = 6\hbar^2/2I$. We have $\nu_{5\to6}/\nu_{2\to3} = 12/6 = 2$ and
$\nu_{5\to6}$ = 2(126.4 GHz) = 252.8 GHz.

6.11 $E_8 - E_7 = 8(9)\hbar^2/2I - 7(8)\hbar^2/2I = 16\hbar^2/2I = 2h^2/\pi^2\mu d^2 = h\nu$, so $d = (2h/\pi^2\mu\nu)^{1/2}$.

$$\mu = \frac{(34.96885)22.98977}{22.98977+34.96885}\,\frac{\text{g}}{6.022142\times10^{23}\ \text{mol}^{-1}} = 2.303281\times10^{-26}\ \text{kg}$$

$$d = \left[\frac{2(6.626069\times10^{-34}\ \text{J s})}{\pi^2(2.303281\times10^{-26}\ \text{kg})(104189.7\times10^6\ \text{s}^{-1})}\right]^{1/2} = 2.36541\times10^{-10}\ \text{m}$$

6.12 Let ν_1 and ν_2 be the lower and higher of the two frequencies, respectively. Let J' be the rotational quantum number of the lower level of the ν_1 transition. Then, since there are no lines between these two lines, Eq. (6.54) gives $\nu_1 = 2(J'+1)B$ and $\nu_2 = 2(J'+1+1)B$. So $\nu_2 - \nu_1 = 2B = 115.19$ GHz and $B = 57.60$ GHz.

6.13 **(a)** From (6.54) and the formula for the centrifugal-distortion energy correction, we get

$$\begin{aligned}\Delta E_{J\to J+1} &= 2(J+1)Bh - hD[(J+1)^2(J+2)^2 - J^2(J+1)^2]\\ &= 2(J+1)Bh - hD[(J+1)^2(J^2+4J+4) - J^2(J+1)^2]\\ &= 2(J+1)Bh - hD[(J+1)^2(4J+4)]\\ &= 2(J+1)Bh - 4hD(J+1)^3\end{aligned}$$

So $\nu_{0\to1} = 2B - 4D$ and $\nu_{4\to5} = 10B - 4(4+1)^3 D = 10B - 500D$. Then $\nu_{4\to5} - 5\nu_{0\to1} = -480D = [576267.92 - 5(115271.20)]\text{ MHz} = -88.08\text{ MHz}$ and $D = 0.183$ MHz.

(b) From (6.54) and the formula for B_v, the 0 to 1 rotational absorption frequency is $\nu_{0\to1} = 2B_\text{v} = 2[B_e - \alpha_e(\text{v} + \frac{1}{2})]$. For the $\text{v} = 0$ and $\text{v} = 1$ levels, we then have $\nu_{0\to1}(\text{v}=0) = 2(B_e - \frac{1}{2}\alpha_e)$ and $\nu_{0\to1}(\text{v}=1) = 2(B_e - \frac{3}{2}\alpha_e)$. So $\nu_{0\to1}(\text{v}=0) - \nu_{0\to1}(\text{v}=1) = 2\alpha_e = (115271.20 - 114221.74)$ MHz and $\alpha_e = 524.7$ MHz. (This answer is somewhat inaccurate because of additional anharmonicity correction terms that are being neglected.)

6.14 Equation (6.50) gives

$$I = (m_1\rho_1^2 + m_2\rho_2^2)\frac{m_1m_2}{m_1+m_2}\frac{m_1+m_2}{m_1m_2} = \mu\frac{m_1^2\rho_1^2 + m_1m_2\rho_1^2 + m_2m_1\rho_2^2 + m_2^2\rho_2^2}{m_1m_2}$$

. Use of (6.49) gives

$$I = \mu\frac{m_1\rho_1 m_2\rho_2 + m_1m_2\rho_1^2 + m_2m_1\rho_2^2 + m_2\rho_2m_1\rho_1}{m_1m_2} = \mu\frac{m_1m_2(\rho_1+\rho_2)^2}{m_1m_2} = \mu d^2.$$

6.15

$$\left|\frac{F_\text{el}}{F_\text{grav}}\right| = \frac{e^2}{4\pi\varepsilon_0 r^2}\frac{r^2}{Gm_em_p} =$$

$$\frac{(1.602\times10^{-19}\text{ C})^2}{4\pi(8.854\times10^{-12}\text{ C}^2/\text{N-m}^2)(6.674\times10^{-11}\text{ m}^3/\text{kg-s}^2)(9.109\times10^{-31}\text{ kg})(1.6726\times10^{-27}\text{ kg})}$$

$= 2.27 \times 10^{39}$. This is so large that the gravitational force can be ignored.

6.16 **(a)** The H-atom energies depend on *n* only, so all the various *l* and *m* possibilities for each *n* give different states that have the same energy. For each *l* value, there are $2l + 1$ allowed values of *m*, and *l* goes from 0 to $n - 1$. Hence the number of states for a given *n* is $\sum_{l=0}^{n-1}(2l+1)$.

(b) $\sum_{l=0}^{n-1}(2l+1) = \sum_{l=0}^{n-1}2l + \sum_{l=0}^{n-1}1$. We have $\sum_{l=0}^{n-1}2l = 2\sum_{l=1}^{n-1}l = 2[\frac{1}{2}(n-1)n] = n^2 - n$, where we used the sum in the text with *j* replaced by *l* and *k* replaced by $n - 1$. Also $\sum_{l=0}^{n-1}1 = 1(n) = n$, since this sum has *n* terms each equal to 1. Hence $\sum_{l=0}^{n-1}(2l+1) = n^2 - n + n = n^2$.

(c) Let *S* denote the desired sum. *S* is the sum of the first *k* positive integers, so $2S = [1+2+3+\cdots+k] + [k + (k-1) + (k-2) + \cdots + 1]$. The sum of any two corresponding terms of the two series in brackets is $k + 1$, and there are *k* terms in each series in brackets. Hence $2S = k(k+1)$ and $S = \frac{1}{2}k(k+1)$.

6.17 **(a)** From Eq. (6.108), the equation preceding (6.108), and Eq. (6.94), the H-atom energies are $E = -(2.17868\times10^{-18}\text{ J})/n^2$. So

$$h\nu = E_{\text{upper}} - E_{\text{lower}} = -(2.17868\times10^{-18}\text{ J})\left(\frac{1}{6^2}-\frac{1}{3^2}\right) = 1.81557\times10^{-19}\text{ J}$$

$$\nu = (1.81557\times10^{-19}\text{ J})/(6.62607\times10^{-34}\text{ J s}) = 2.74004\times10^{14}\text{ s}^{-1}$$

$$\lambda = c/\nu = (2.997925\times10^{8}\text{ m/s})/(2.74004\times10^{14}\text{ s}^{-1}) = 1.09412\times10^{-6}\text{ m} = 1094.12\text{ nm}$$

(b) He^+ is a hydrogenlike ion with $Z = 2$. From (6.94), E and ΔE are proportional to Z^2, so ν is proportional to Z^2 if the slight change in μ is neglected. Hence $\nu = 4(2.740\times10^{14}\text{ s}^{-1}) = 1.096\times10^{15}\text{ Hz}$ and $\lambda = (1094.12\text{ nm})/4 = 273.5\text{ nm}$.

6.18 From Eq. (6.108), the equation preceding (6.108), and Eq. (6.94), the H-atom energies are $E = -(2.17868\times10^{-18}\text{ J})/n^2$. So

$$\lambda = \frac{c}{\nu} = \frac{ch}{E_{\text{upper}} - E_{\text{lower}}} = \frac{(2.99792\times10^{8}\text{ m/s})(6.62607\times10^{-34}\text{ J s})}{(2.17868\times10^{-18}\text{ J})(n_l^{-2}-n_u^{-2})}$$

$$\frac{1}{n_l^2}-\frac{1}{n_u^2} = \frac{9.11764\times10^{-8}\text{ m}}{\lambda}$$

For the first line, $\dfrac{1}{n_l^2}-\dfrac{1}{n_u^2} = \dfrac{9.1176\times10^{-8}\text{ m}}{6564.7\times10^{-10}\text{ m}} = 0.138889$. The value $n_l = 1$ when combined with $n_u = 2$ or more gives values much larger than 0.139, so $n_l \neq 1$. With $n_l = 2,$ the value $n_u = 3$ gives $1/n_l^2 - 1/n_u^2 = 1/4 - 1/9 = 0.138889$, so these are the quantum numbers for the first line. For the remaining lines, we find $1/n_l^2 - 1/n_u^2 =$ 0.18750, 0.21000, and 0.22222. With $n_l = 2$, the n_u values 4, 5, and 6 fit the data for these three lines. With $n_l = 2$ and n_u = 7, 8 and ∞, we get $\lambda = 3971.2$, 3890.2, and 3647.1 Å.

6.19 A small fraction of hydrogen atoms in nature are the isotope deuterium, ^2H or D. From (6.94), the energy is proportional to the reduced mass μ, so the transition frequency is proportional to μ and λ is inversely proportional to μ. Thus

$\dfrac{\lambda_{\text{D}}}{\lambda_{\text{H}}} = \dfrac{\mu_{\text{H}}}{\mu_{\text{D}}} = \dfrac{m_e m_p}{m_e + m_p}\dfrac{m_e + m_d}{m_e m_d} = \dfrac{m_p}{m_d}\dfrac{m_e + m_d}{m_e + m_p}$, where m_d is the mass of a deuterium nucleus. From Appendix Table A.1, $m_p/m_e = 1836.15$. From Table A.3,

$$\frac{m(^2\text{H})}{m(^1\text{H})} = \frac{2.014102}{1.0078250} = 1.998464 = \frac{m_d + m_e}{m_p + m_e} = \frac{m_d}{m_p(1+1836.15^{-1})} + \frac{m_e}{1837.15 m_e}$$

$$= 0.9994557(m_d/m_p) + 0.0005443$$

which gives $m_d/m_p = 1.999008$. Hence $\dfrac{\lambda_D}{\lambda_H} = \dfrac{\mu_H}{\mu_D} = \dfrac{1}{1.999008}1.998464 = 0.999728$.

Multiplication of the wavelengths in Prob. 6.18 by 0.999728 gives 656.29, 486.14, 434.05, and 410.18 nm.

6.20 For $e^{2Cr} = 1 + 2Cr + \cdots + (2Cr)^j/j! + (2Cr)^{j+1}/(j+1)! + \cdots$, the ratio of successive powers of r for large j is

$$\frac{(2C)^{j+1}}{(j+1)!}\cdot\frac{j!}{(2C)^j} = \frac{2C}{j+1} \approx \frac{2C}{j}$$

The ratio of successive powers of r in (6.88) for large j is

$$\frac{b_{j+1}}{b_j} \approx \frac{2Cj}{j^2} = \frac{2C}{j}$$

6.21 For the H atom (and for the particle in a rectangular well), there is a maximum value V_{max} of the potential-energy function, and the energy levels above V_{max} are continuous. For the particle in a box and the harmonic oscillator, the potential-energy function goes to infinity at each end of the allowed region of the x axis, and all the energy levels are discrete.

6.22 Positronium is a hydrogenlike atom with reduced mass $\mu = m_e m_e/(m_e + m_e) = m_e/2$, which is about half the reduced mass (6.105) of the H atom. Since E in (6.94) is proportional to μ, the positronium ground-state energy is about half the energy in (6.108), namely, $-(13.6\text{ eV})/2 = -6.8\text{ eV}$.

6.23 We have, $\langle r\rangle = \int|\psi|^2 r\,d\tau = (Z^3/\pi a^3)\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-2Zr/a} r r^2 \sin\theta\,dr\,d\theta\,d\phi =$ $(Z^3/\pi a^3)\int_0^{2\pi} d\phi \int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty} e^{-2Zr/a} r^3\,dr = (Z^3/\pi a^3)(2\pi)(2)[3!/(2Z/a)^4] = 3a/2Z$, where (3.88), (5.77), (5.78), (6.104), and (A.8) were used. Alternatively, (6.101) (6.103), and (6.117) give $\langle r\rangle = \int|\psi|^2 r\,d\tau = \int_0^{\infty} r\,|R_{nl}(r)|^2\, r^2\,dr\int_0^{2\pi}\int_0^{\pi}|Y_l^m(\theta,\phi)|^2\sin\theta\,d\theta\,d\phi =$ $(4Z^3/a^3)\int_0^{\infty} r^3 e^{-2Zr/a}dr = (4Z^3/a^3)[3!/(2Z/a)^4] = 3a/2Z$.

6.24 We have, $\langle r\rangle = \int|\psi|^2 r\,d\tau = (Z^5/32\pi a^5)\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 e^{-Zr/a} r\cos^2\theta\, r^2\sin\theta\,dr\,d\theta\,d\phi =$ $(Z^5/32\pi a^5)\int_0^{2\pi} d\phi\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta\int_0^{\infty} e^{-Zr/a} r^5\,dr = (Z^5/32\pi a^5)(2\pi)(2/3)[5!/(Z/a)^6] =$ $5a/Z$, where (5.77), (5.78), (6.113), (A.8), and $\int\cos^2\theta\sin\theta\,d\theta = -(\cos^3\theta)/3$ were used.

6.25 $\langle r^2 \rangle = \int |\psi|^2 r^2\, d\tau = (Z^5/64\pi a^5)\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 e^{-Zr/a} r^2 \sin^2\theta\, e^{-i\phi} e^{i\phi} r^2 \sin\theta\, dr\, d\theta\, d\phi =$
$(Z^5/64\pi a^5)\int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} e^{-Zr/a} r^6\, dr = (Z^5/64\pi a^5)(2\pi)(4/3)[6!/(Z/a)^7] =$
$30a^2/Z^2$, where Eqs. (5.77), (5.78), (6.113), (A.8), and the integral-table result $\int \sin^3\theta\, d\theta = -\frac{1}{3}\cos\theta(\sin^2\theta + 2)$ were used.

6.26 $\langle r \rangle = \int |\psi|^2 r\, d\tau = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r\, |R_{nl}(r)|^2 |Y_l^m(\theta,\phi)|^2 r^2 \sin\theta\, dr\, d\theta\, d\phi =$
$\int_0^{\infty} r\, |R_{nl}(r)|^2 r^2\, dr \int_0^{2\pi}\int_0^{\pi} |Y_l^m(\theta,\phi)|^2 \sin\theta\, d\theta\, d\phi = \int_0^{\infty} r^3\, |R_{nl}(r)|^2\, dr$, where (6.117) was used.

6.27 From (6.100) and (6.99), $R_{2s} = r^0 e^{-Zr/2a}(b_0 + b_1 r)$ and
$b_1 = (Z/a)[-1/(1\cdot 2)]b_0 = -(Z/2a)b_0$. Hence $R_{2s} = b_0(1 - Zr/2a)e^{-Zr/2a}$. Normalization gives $1 = |b_0|^2 \int_0^{\infty} (1 - Zr/a + Z^2r^2/4a^2)e^{-Zr/a} r^2\, dr =$
$|b_0|^2 [2!(a/Z)^3 - (Z/a)3!(a/Z)^4 + (Z^2/4a^2)4!(a/Z)^5] = 2|b_0|^2 (a/Z)^3$, where Eq. (A.8) was used. Hence $|b_0| = (Z/a)^{3/2} 2^{-1/2}$ and $R_{2s} = (Z/a)^{3/2} 2^{-1/2}(1 - Zr/2a)e^{-Zr/2a}$.
From (6.100) and (6.99), $R_{2p} = re^{-Zr/2a} b_0$. Normalization gives
$1 = |b_0|^2 \int_0^{\infty} r^2 e^{-Zr/a} r^2\, dr = |b_0|^2\, 4!(a/Z)^5$, so $|b_0| = (24)^{-1/2}(Z/a)^{5/2}$ and
$R_{2p} = (24)^{-1/2}(Z/a)^{5/2} re^{-Zr/2a}$.

6.28 At the nucleus, $r = 0$ and the r^l factor in (6.100) and (6.101) shows that ψ is zero at the nucleus unless $l = 0$ (s states).

6.29 From (6.110) we have

letter	s	p	d	f	g	h	i	k	l	m	n	o	q	r	t
l	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

6.30 If we ignore the interelectronic-repulsion term (and neglect the difference between the reduced mass and the electron mass), the Hamiltonian operator (3.50) for internal motion in the He-atom becomes $-(\hbar^2/2m_e)\nabla_1^2 - (\hbar^2/2m_e)\nabla_2^2 - Ze^2/4\pi\varepsilon_0 r_1 - Ze^2/4\pi\varepsilon_0 r_2$, where Z equals 2 and r_1 and r_2 are the distances of electrons 1 and 2 from the nucleus. This $\hat{H}$ is the sum of $\hat{H}$'s ($\hat{H}_1$ and $\hat{H}_2$) for two noninteracting electrons. Hence the results of Sec. 6.2 tell us that $E = E_1 + E_2$, where $\hat{H}_1\psi_1 = E_1\psi_1$ and $\hat{H}_2\psi_2 = E_2\psi_2$. We recognize $\hat{H}_1$ and $\hat{H}_2$ as hydrogenlike Hamiltonians with $Z = 2$. Since the hydrogenlike energies (6.94) are proportional to Z^2, Eqs. (6.94) and (6.108) give
$E_1 = 2^2(-13.6\text{ eV}) = -54.4\text{ eV} = E_2$. Hence $E = -108.8$ eV. From Eq. (6.25),

$\psi = \psi_1(r_1, \theta_1\ \phi_1)\psi_2(r_2, \theta_2, \phi_2)$, where ψ_1 and ψ_2 are hydrogenlike wave functions with $Z = 2$. Of course, these results are very approximate, since the interelectronic repulsion was ignored. The percent error in E is $100\%[-108.8-(-79.0)]/(-79.0) = 38\%$.

6.31 The probability that the electron is between r and $r + dr$ is proportional to the radial distribution function, so we look for the maximum in $R_{1s}^2 r^2 = 4(Z^3/a^3)r^2 e^{-2Zr/a}$. At the maximum, the derivative is zero and $0 = (4Z^3/a^3)[2re^{-2Zr/a} - (2Zr^2/a)e^{-2Zr/a}]$, so $r(1 - Zr/a) = 0$. The root $r = 0$ is a minimum in Fig. 6.9, and the maximum is at $r = a/Z$.

6.32 The probability density is $|\psi_{1s}|^2 = (Z^3/\pi a^3)e^{-2Zr/a}$. The exponential function is a maximum at $r = 0$, the nucleus.

6.33 **(a)** Similar to the example after Eq. (6.117), the probability is $\int_{2a}^{\infty} R_{1s}^2 r^2\, dr = (4/a^3)\int_{2a}^{\infty} e^{-2r/a} r^2\, dr = (4/a^3)e^{-2r/a}(-\frac{1}{2}r^2 a - \frac{1}{2}ra^2 - \frac{1}{4}a^3)\,|_{2a}^{\infty} =$ $4e^{-4}(2+1+\frac{1}{4}) = 0.2381$.

(b) The classically forbidden region is where $E < V$. From (6.94) and (6.60), this condition is $-\mu e^4/2(4\pi\varepsilon_0)^2\hbar^2 < -e^2/4\pi\varepsilon_0 r$, which simplifies to $1/r < \mu e^2/8\pi\varepsilon_0\hbar^2$ or $r > 8\pi\varepsilon_0\hbar^2/\mu e^2 = 2a$, where a is defined by (6.63). The probability of finding $r > 2a$ was found in part (a) to be 0.2381.

6.34 From (6.104), $\psi = ce^{-r/a}$, where $c \equiv \pi^{-1/2}a^{-3/2}$. From (6.60), $V\psi = -(e^2/4\pi\varepsilon_0 r)\cdot ce^{-r/a} \neq$ const.$\cdot\psi$. From (6.6), $\hat{T}\psi = -(\hbar^2/2\mu)\nabla^2\psi = -(\hbar^2/2\mu)[\partial^2/\partial r^2 + (2/r)(\partial/\partial r)]ce^{-r/a} =$ $-(\hbar^2/2\mu)(1/a^2 - 2/ra)ce^{-r/a} \neq$ const.$\cdot\psi$. Use of $a \equiv 4\pi\varepsilon_0\hbar^2/\mu e^2$ gives $\hat{T}\psi = (-e^2/8\pi\varepsilon_0 a + e^2/4\pi\varepsilon_0 r)ce^{-r/a}$. So $(\hat{T}+\hat{V})\psi = \hat{T}\psi + \hat{V}\psi = (-e^2/8\pi\varepsilon_0 a)ce^{-r/a} = (-e^2/8\pi\varepsilon_0 a)\psi$.

6.35 $\langle H\rangle = \int \psi^* \hat{H}\psi\, d\tau = E\int \psi^*\psi\, d\tau = E$. Also $\langle H\rangle = \langle T+V\rangle = \langle T\rangle + \langle V\rangle$. Hence $E = \langle T\rangle + \langle V\rangle$.

6.36 **(a)** $\langle V\rangle = \int \psi^*(-e^2/4\pi\varepsilon_0 r)\psi\, d\tau = -(e^2/4\pi\varepsilon_0)\pi^{-1}a^{-3}\int_0^{\infty} e^{-2r/a} r\, dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi =$ $-(e^2/4\pi\varepsilon_0)\pi^{-1}a^{-3}(a/2)^2(2)(2\pi) = -e^2/4\pi\varepsilon_0 a$.

(b) $\langle T\rangle = E - \langle V\rangle = -e^2/8\pi\varepsilon_0 a + e^2/4\pi\varepsilon_0 a = e^2/8\pi\varepsilon_0 a$. Then $\langle T\rangle / \langle V\rangle = (e^2/8\pi\varepsilon_0 a)/(-e^2/4\pi\varepsilon_0 a) = -1/2$.

(c) $\langle T\rangle = \langle m_e \text{v}^2/2\rangle = (m_e/2)\langle \text{v}^2\rangle = e^2/8\pi\varepsilon_0 a$ so $\langle \text{v}^2\rangle^{1/2} = (e^2/4\pi\varepsilon_0 m_e a)^{1/2} =$

$$\left[\frac{(1.6022\times10^{-19}\ \text{C})^2}{4\pi(8.854\times10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})(9.109\times10^{-31}\ \text{kg})(0.529\times10^{-10}\ \text{m})}\right]^{1/2} = 2.19\times10^6\ \text{m/s}$$

$\langle \text{v}^2\rangle^{1/2}/c = (2.19\times10^6)/(2.998\times10^8) = 0.00730 = 1/137$.

6.37 **(a)**

$3d_{xy} = (3d_2 - 3d_{-2})/2^{1/2}i = (4/81)(30)^{-1/2}(Z/a)^{7/2}r^2 e^{-Zr/3a}\,\frac{1}{4}(15)^{1/2}\sin^2\theta(e^{2i\phi} - e^{-2i\phi})/(2\pi)^{1/2}$

We have $e^{2i\phi} - e^{-2i\phi} = \cos 2\phi + i\sin 2\phi - (\cos 2\phi - i\sin 2\phi) = 2i\sin 2\phi = 4i\sin\phi\cos\phi$, since $\sin 2x = 2\sin x\cos x$. So $3d_{xy}$ contains the factor $r\sin\theta\sin\phi\, r\sin\theta\cos\phi = xy$.

(b) As noted near the end of Sec. 6.6, , the real functions are formed by adding and subtracting the complex functions having the same $|m|$ values: $3d_{\text{real}} = N(3d_{|m|} \pm 3d_{-|m|})$, where N is a normalization constant. We have

$1 = |N|^2 \int [|3d_{|m|}|^2 \pm (3d_{|m|})^* 3d_{-|m|} \pm (3d_{-|m|})^* 3d_{|m|} + |3d_{-|m|}|^2]\,d\tau = |N|^2\ (1\pm 0\pm 0+1)$,

since the $3d$ AOs are orthonormal. So $|N| = 2^{-1/2}$. To ensure that $3d_{\text{real}} = N(3d_{|m|} \pm 3d_{-|m|})$ is real, we may need to include a factor of $1/i$ in N. From Eq. (5.99), the ϕ function in $3d_2 + 3d_{-2}$ is

$e^{i2\phi} + e^{-i2\phi} = \cos 2\phi + i\sin 2\phi + \cos 2\phi - i\sin 2\phi = 2\cos 2\phi$, which is real and so does not need the $1/i$ factor; also, Table 6.2 shows that this ϕ function occurs in $3d_{x^2-y^2}$. So $3d_{x^2-y^2} = 2^{-1/2}(3d_2 + 3d_{-2})$. Similarly the $3d_1 + 3d_{-1}$ function contains the ϕ function $2\cos\phi$, which Table 6.2 shows is in the $3d_{xz}$ function. So $3d_{xz} = 2^{-1/2}(3d_1 + 3d_{-1})$. The ϕ function in $3d_2 - 3d_{-2}$ is $e^{i2\phi} - e^{-i2\phi} = \cos 2\phi + i\sin 2\phi - (\cos 2\phi - i\sin 2\phi) = 2i\sin 2\phi$; $3d_2 - 3d_{-2}$ needs the $1/i$ factor and Table 6.2 tells us that $3d_{xy} = (2^{-1/2}/i)(3d_2 - 3d_{-2})$, as in part (a). Similarly the $3d_1 - 3d_{-1}$ function contains $2i\sin\phi$, which Table 6.2 shows is in the $3d_{yz}$ function. So $3d_{yz} = (2^{-1/2}/i)(3d_1 - 3d_{-1})$. The $3d_0$ function is independent of ϕ and Table 6.2 gives $3d_{z^2} = 3d_0$.

(c) From Table 6.2, $3d_{x^2-y^2}$ contains the factor

$r^2\sin^2\theta\cos 2\phi = r^2\sin^2\theta(\cos^2\phi - \sin^2\phi) = (r\sin\theta\cos\phi)^2 - (r\sin\theta\sin\phi)^2 = x^2 - y^2$.

6.38 Since $2p_z$ is the same as $2p_0$, the $2p_z$ function is an eigenfunction of $\hat{L}_z$ with eigenvalue zero. Since the x, y, and z directions of space are equivalent to one another in the central field of the H atom (it is arbitrary whether we call a particular direction x, y, or z), it follows by symmetry that the $2p_x$ function is an eigenfunction of $\hat{L}_x$ with eigenvalue zero and the $2p_y$ function is an eigenfunction of $\hat{L}_y$ with eigenvalue zero.

6.39 Since $\hat{A}$ is linear, $\hat{A}(c_1 f + c_2 g) = c_1\hat{A}f + c_2\hat{A}g = c_1 af + c_2 bg = a[c_1 f + (b/a)c_2 g]$. If and only if $a = b$, do we have $\hat{A}(c_1 f + c_2 g) = a(c_1 f + c_2 g)$ and the linear combination is an eigenfunction of $\hat{A}$.

6.40 **(a)** Since $2p_z$ is the same function as $2p_0$, it is an eigenfunction of $\hat{H}, \hat{L}^2$, and $\hat{L}_z$.

(b) $2p_x$ is an eigenfunction of $\hat{H}$ and of $\hat{L}^2$ but not of $\hat{L}_z$, as is evident from Eq. (6.118) and Prob. 6.39.

(c) $\hat{H}, \hat{L}^2$, and $\hat{L}_z$.

6.41 **(a)** The radial function is zero for particular values of r. The points where r has a particular value lie on the surface of a sphere centered at the nucleus.

(b) The real ϕ functions contain the factor $\sin|m|\phi$ or $\cos|m|\phi$. The functions $\sin\phi$ and $\cos\phi$ vanish for two values of ϕ in the range $0 \le \phi < 2\pi$. These two value differ by π, so they correspond to the same nodal plane, and there is one node in the ϕ factor for $|m| = 1$. The functions $\sin|m|\phi$ and $\cos|m|\phi$ vary $|m|$ times as rapidly as $\sin\phi$ and $\cos\phi$, so these functions contain $|m|$ nodal planes.

(c) These nodal surfaces have a fixed value of θ and so they are cones whose axis is the z axis. An exception is a node with $\theta = \pi/2$, which is the xy plane. [The problem in the text should say there are $l - |m|$ surfaces for which the θ factor vanishes. Note from (5.97) that $S(\theta)$ depends on $|m|$ and not on m.]

(d) There are $n - l - 1$ radial nodes, $l - |m|$ θ nodes, and $|m|$ ϕ nodes, for a total of $n - 1$ nodes.

6.42 The integral $\int (2p_x)^* 2p_y \, d\tau$ contains the factor $\int_0^{2\pi} \cos\phi \sin\phi \, d\phi = \frac{1}{2}\sin^2\phi \,|_0^{2\pi} = 0$. The integral $\int (2p_x)^* 2p_z \, d\tau$ contains the factor $\int_0^{2\pi} \cos\phi \, d\phi = \sin\phi \,|_0^{2\pi} = 0$. The integral $\int (2p_y)^* 2p_z \, d\tau$ contains the factor $\int_0^{2\pi} \sin\phi \, d\phi = -\cos\phi \,|_0^{2\pi} = 0$.

6.43 We want $0.95 = \int_V |\psi|^2 \, d\tau = (1/\pi a^3)\int_0^b e^{-2r/a} r^2 \, dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi$, where b is the orbital radius. Use of Eq. (A.7) gives $0.95 = (1/\pi a^3)[e^{-2r/a}(-ar^2/2 - 2ra^2/4 - 2a^3/8)]|_0^b \, 2(2\pi) = 1 - e^{-2b/a}[2(b/a)^2 + 2(b/a) + 1]$. We have $0.05 - e^{-2w}(2w^2 + 2w + 1) = 0$, where $w \equiv b/a$. Use of the Solver gives $w = 3.148$ and $b = 3.148a = 3.148(0.529 \text{ Å}) = 1.66_5$ Å.

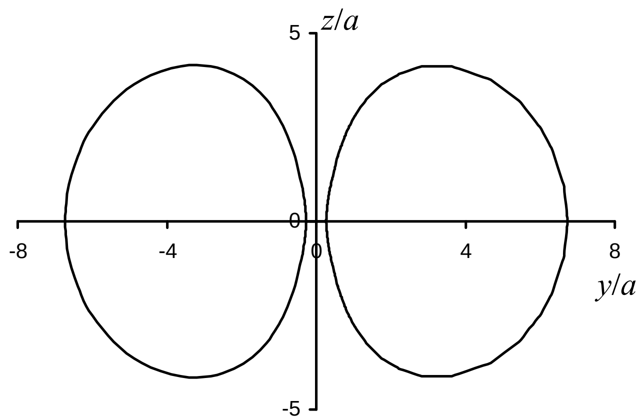
6.44 The maximum value of $|\sin\theta|$ is 1. To find the maximum of re^{-kr}, we have $0 = d(re^{-kr})/dr = e^{-kr} - kre^{-kr} = e^{-kr}(1 - kr)$, which gives $r = 1/k$. With $|\sin\theta| = 1$ and

$r = 1/k$, Eq. (6.123) gives $(\psi_{2p_y})_{\max} = k^{3/2}\pi^{-1/2}e^{-1}$. Hence (6.123) gives $|\psi|/|\psi_{\max}| = kere^{-kr}\,|\sin\theta| = 0.316$. Putting $k = 1/2a$ and e =2.71828, we have $0.2325 = (r/a)e^{-0.5r/a}\,|\sin\theta|$ and $|\sin\theta| = 0.2325e^{0.5(r/a)}/(r/a)$ (Eq. 1). We plot points on the orbital by taking values of r/a and calculating $|\sin\theta|$ from Eq. 1. Then we find θ, the angle with the z axis. y and z values can be found from $z = r\cos\theta$ and $y = r\sin\theta$. Some values are

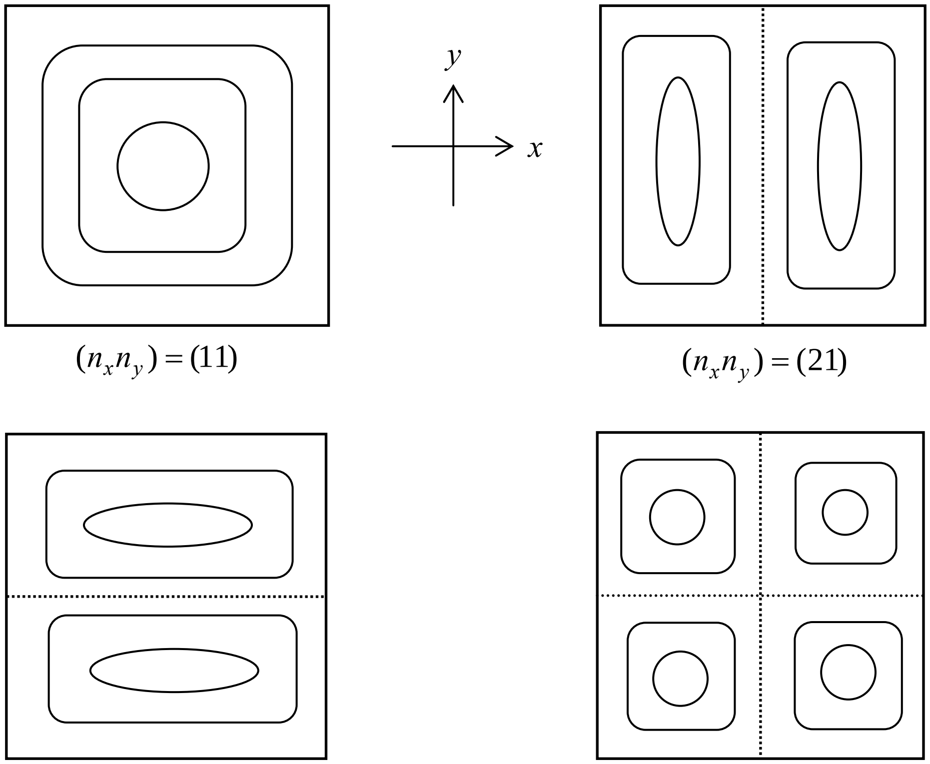
r/a	0.24	0.2655	0.28	0.30	0.36	0.45	0.6	0.8	1	1.5
$\sin\theta$	1.09	1.00	0.955	0.900	0.773	0.647	0.523	0.434	0.383	0.328
θ/rad		1.570	1.270	1.121	0.884	0.704	0.550	0.448	0.393	0.334
y		0.265	0.267	0.270	0.278	0.291	0.314	0.347	0.383	0.492
z		0	0.083	0.130	0.228	0.343	0.511	0.721	0.924	1.417

r/a	2.1	2.7	3.5	4.5	5.5	6	6.3	6.6	6.7312
$\sin\theta$	0.316	0.332	0.382	0.490	0.661	0.778	0.861	0.955	1.00
θ/rad	0.322	0.339	0.392	0.512	0.722	0.892	1.038	1.270	1.557
y	0.664	0.897	1.338	2.206	3.637	4.700	5.426	6.304	6.730
z	1.992	2.547	3.234	3.922	4.126	3.767	3.202	1.955	0

By taking the four combinations (y, z), $(y, -z)$, $(-y, z)$, $(-y, -z)$ of points in the table, we get the complete orbital cross-section, which looks like



6.45 The probability density is proportional to $\sin^2(n_x\pi x/a)\sin^2(n_y\pi y/a)$. For the 11 state, there are no interior nodes and the maximum in $|\psi|^2$ is at the center of the box. For the 12 state, there is nodal line (the dashed line) at $y = a/2$. The 21 state has a nodal line at $x = a/2$. The 22 state has nodal lines at $x = a/2$ and $y = a/2$. The rough sketches of the 12 and 21 states resemble p orbitals, and the 22 sketch resembles a d orbital.



$(n_x n_y) = (11)$ $(n_x n_y) = (21)$

$(n_x n_y) = (12)$ $(n_x n_y) = (22)$

6.46 From (6.135), each different value of the quantum number m gives a different energy, so the $2s$ and $2p_0$ states have the same energy, and there are three energy levels, the nondegenerate $2p_1$ level, the nondegenerate $2p_{-1}$ level, and a doubly degenerate level that consists of the two states $2s$ and $2p_0$.

6.47 **(a)** Let $E_r \equiv E/A$, $r_r \equiv r/B$, $A = \mu^a (e')^b \hbar^c$, $B = \mu^d (e')^f \hbar^g$. We have $[A] = \mathrm{ML^2T^{-2}} = [\mu]^a [e']^b [\hbar]^c = \mathrm{M}^a (\mathrm{L^{3/2}M^{1/2}T^{-1}})^b (\mathrm{ML^2T^{-1}})^c = \mathrm{M}^{a+b/2+c} \mathrm{L}^{3b/2+2c} \mathrm{T}^{-b-c}$, so $2a + b + 2c = 2,\ 3b + 4c = 4,\ -b - c = -2$. We find $b = 4$, $c = -2$, $a = 1$, so $A = \mu e'^4/\hbar^2$. Also, $[B] = \mathrm{L} = \mathrm{M}^d (\mathrm{L^{3/2}M^{1/2}T^{-1}})^f (\mathrm{ML^2T^{-1}})^g = \mathrm{M}^{d+f/2+g} \mathrm{L}^{3f/2+2g} \mathrm{T}^{-f-g}$, so $2d + f + 2g = 0,\ 3f + 4g = 2,\ f + g = 0$. We get $f = -2,\ g = 2,\ d = -1$, so $B = \hbar^2/\mu e'^2$.

(b) $R^2 r^2\, dr = F^2\, dr$ is a probability and so is dimensionless. So F has dimensions of $\mathrm{L}^{-1/2}$. Hence, as in (4.78), $F_r = F/B^{-1/2}$. Eq. (4.79) with ψ replaced by F and x replaced by r gives $d^2F/dr^2 = B^{-5/2}\, d^2F_r/dr_r^2 = B^{-1/2}B^{-2}\, d^2F_r/dr_r^2 = \hbar^{-4}\mu^2 e'^4 B^{-1/2}\, d^2F_r/dr_r^2$. Equation (6.137) (with m replaced by μ) becomes $-(\hbar^2/2\mu)\hbar^{-4}\mu^2 e'^4 B^{-1/2}\, d^2F_r/dr_r^2 + [-e'^2/\hbar^2\mu^{-1}e'^{-2}r_r + l(l+1)\hbar^2/2\mu\hbar^4\mu^{-2}e'^{-4}r_r^2]B^{-1/2}F_r =$ $\mu e'^4 \hbar^{-2} E_r B^{-1/2} F_r$ or $F_r'' - [l(l+1)/r_r^2 - 2/r_r]F_r = 2E_r F_r$, which is (6.140).

(c) $V_r = V/A = (-e'^2/r)/\mu e'^4\hbar^{-2} = -\hbar^2/\mu e'^2 r = -1/r_r$, where (6.139) was used.

6.48 **(a)** Cell B7 contains the formula =-D3*(D3+1)/A7^2-2/A7-2*B3, where D3 and B3 contain l and E_r, respectively.

(b) If we extend the integration interval to $r_r = 30$, the Solver gives this energy as –0.055416, which is considerably more accurate.

6.49 A and B are given by (4.73) and (4.74). The E_r and r_r equations are (4.75) with x replaced by r. As in (4.78) and Prob. 6.47b, $F_r = F/B^{-1/2}$. Eq. (4.79) with ψ replaced by F and x replaced by r gives $d^2F/dr^2 = B^{-5/2}\,d^2F_r/dr_r^2 = B^{-1/2}B^{-2}\,d^2F_r/dr_r^2 = B^{-1/2}m^{1/2}k^{1/2}\hbar^{-1}\,d^2F_r/dr_r^2$. Eq. (6.137) becomes $-(\hbar^2/2m)B^{-1/2}m^{1/2}k^{1/2}\hbar^{-1}\,d^2F_r/dr_r^2 + [\frac{1}{2}km^{-1/2}k^{-1/2}\hbar r_r^2 + \frac{1}{2}l(l+1)\hbar^2 m^{-1}/m^{-1/2}k^{-1/2}\hbar r_r^2]B^{-1/2}F_r = m^{-1/2}k^{1/2}\hbar E_r B^{-1/2}F_r$ or $F_r'' = [r_r^2 + l(l+1)/r_r^2 - 2E_r]F_r = G_r F_r$. Suppose we want eigenvalues up to $E_r = 10$. The classically forbidden region begins at the r_r value that satisfies $V_r = \frac{1}{2}r_r^2 = 10$, which is $r_r = 4.47$. We shall go to $r_r = 6$, starting at $r_r = 10^{-12}$ to avoid the infinity at the origin, and taking $s_r = 0.05$. With these choices, the Solver gives the lowest $l = 0$ dimensionless eigenvalues as 1.49999984, 3.4999985, 5.4999944, 7.499987 and gives the lowest $l = 1$ eigenvalues as 2.499986, 4.499964, 6.499933, 8.499902. The Prob. 4.20 result is $E = (\text{v}_x + \text{v}_y + \text{v}_z + \frac{3}{2})h\nu$ and $E_r = \text{v}_x + \text{v}_y + \text{v}_z + 1.5$. (The wave function is an even function if the sum $\text{v}_x + \text{v}_y + \text{v}_z$ is an even number and is odd if this sum is odd. Since Y_0^0 is an even function and Y_1^m are odd functions, the $l = 0$ eigenvalues have $\text{v}_x + \text{v}_y + \text{v}_z$ even and the $l = 1$ functions have $\text{v}_x + \text{v}_y + \text{v}_z$ odd.)

6.50 We use the spreadsheet prepared for Prob. 6.48. Column C contains the F_r values. We set up column D as $R_r = F_r/r_r$ and graph column D versus r_r. At $r_r = 10^{-15}$, F_r is extremely small but nonzero. However, we took F_r as 0 at $r_r = 10^{-15}$, which erroneously makes $R_r = F_r/r_r$ equal to zero at $r_r = 10^{-15}$. The graph of R_r indicates that it is somewhat greater than 0.4 at $r_r = 10^{-15}$.

6.51 The dimensionless variables are $E_r \equiv E/A$, $r_r \equiv r/B$, where A and B are given by the particle-in-a-box A and B (Prob. 4.30) with l replaced by b; thus, $E_r = E/(\hbar^2/mb^2)$ and $r_r = r/b$. As in (4.78) and Prob. 6.47b, $F_r = F/B^{-1/2}$. Equation (4.79) with ψ replaced by F and x replaced by r gives $d^2F/dr^2 = B^{-5/2}\,d^2F_r/dr_r^2 = B^{-1/2}B^{-2}\,d^2F_r/dr_r^2 = B^{-1/2}b^{-2}\,d^2F_r/dr_r^2$ and (6.137) becomes $-(\hbar^2/2m)B^{-1/2}b^{-2}\,d^2F_r/dr_r^2 + [l(l+1)\hbar^2/2mbr_r^2]B^{-1/2}F_r = (\hbar^2/mb^2)E_r B^{-1/2}F_r$ or

$F_r'' = [l(l+1)/r_r^2 - 2E_r]F_r = G_r F_r$. The variable r_r goes from 0 to 1. To avoid the infinity at the origin, we shall start at $r_r = 10^{-10}$. We shall take the interval as $s_r = 0.01$. For $l = 0$ the lowest three E_r values are 4.934803, 19.739208, 44.413205 and for $l = 1$ the lowest energies are 10.095357, 29.839696, 59.449675. The exact $l = 0$ E_r values are $E_r = E/(\hbar^2/mb^2) = (n^2h^2/8mb^2)/(\hbar^2/mb^2) = n^2\pi^2/2 =$ 4.934802, 19.739209, 44.413220.

6.52 **(a)** dx, 0 and l; **(b)** dx, $-\infty$ to ∞; **(c)** $dx\,dy\,dz$, $-\infty$ to ∞ for each variable; **(d)** $r^2 \sin\theta\, dr\, d\theta\, d\phi$, 0 to ∞ for r, 0 to π for θ, 0 to 2π for ϕ.

6.53 **(a)** The Boltzmann distribution law (4.63) gives $N_i/N_j = (g_i/g_j)e^{-(E_i-E_j)/kT}$. The degeneracy of the H-atom levels is given near the end of Sec. 6.5 as n^2. (When spin is included, this becomes $2n^2$, but the factor 2 cancels when taking a population ratio.) We have $N_2/N_1 = (2^2/1^2)\exp[-(2.1787\times10^{-18}\text{ J})(1/1-1/4)/(1.3807\times10^{-23}\text{ J/K})(298.15\text{ K})]$ = 1.63×10^{-172} at 25°C, where (6.94) and the equation before (6.108) were used.

(b) Replacement of 298.15 with 1000 gives 1.60×10^{-51}.

(c) Replacement of 298.15 with 10000 gives 0.0000290.

6.54 **(a)** The one-dimensional harmonic oscillator;
(b) the particle in a one-dimensional box; the rigid two-particle rotor;
(c) the H atom; the anharmonic oscillator with energies (4.60).

6.55 **(a)** The harmonic oscillator, the rigid two-particle rotor, the particle in a one-dimensional box, the hydrogen atom.

(b) The particle in a well; the anharmonic oscillator of Fig. 4.6.

(c) The rigid two-particle rotor.

6.56 **(a)** False. The rigid two-particle rotor has a zero eigenvalue. **(b)** True.

(c) False. e is the proton charge. **(d)** True. **(e)** False. **(f)** False.

(g) False. **(h)** True. **(i)** False.

Chapter 7

Theorems of Quantum Mechanics

7.1 **(a)** T; **(b)** T; **(c)** F.

7.2 $\langle cf_m|\hat{A}|f_n\rangle = \int (cf_m)^*\hat{A}f_n\,d\tau = c^*\int f_m^*\hat{A}f_n\,d\tau$ and
$\langle f_m|\hat{A}|cf_n\rangle = \int f_m^*\hat{A}(cf_n)\,d\tau = c\int f_m^*\hat{A}f_n\,d\tau$ if $\hat{A}$ is linear. Thus if $c = c^*$ (that is, if c is real) and if $\hat{A}$ is linear, the integrals are equal.

7.3 $\langle f\,|\,\hat{B}\,|\,g\rangle = \int f^*\hat{B}g\;d\tau = \int f^*(\hat{B}g)\;d\tau = \langle f\,|\,\hat{B}g\rangle.$
$\langle cf\,|\,\hat{B}\,|\,g\rangle = \int (cf)^*\hat{B}g\;d\tau = c^*\int f^*\hat{B}g\;d\tau = c^*\langle f\,|\,\hat{B}\,|\,g\rangle.$
$\langle f\,|\,\hat{B}\,|\,cg\rangle = \int f^*\hat{B}(cg)\;d\tau = c\int f^*\hat{B}g\;d\tau = c\langle f\,|\,\hat{B}\,|\,g\rangle,$ if $\hat{B}$ is linear.

7.4 This equation can be written as $\langle m\,|\,\hat{1}\,|\,n\rangle = \langle n\,|\,\hat{1}\,|\,m\rangle^*$, so the operator "multiplication by 1" is Hermitian.

7.5 From (7.12), $\langle f\,|\,\hat{B}\,|\,g\rangle = \langle g\,|\,\hat{B}\,|\,f\rangle^* = \langle g\,|\,\hat{B}f\rangle^* = \langle \hat{B}f\,|\,g\rangle,$ where (7.4) was used.

7.6 **(a)** We must prove that $\int f^*(c\hat{A})g\,d\tau = \int g(c\hat{A}f)^*d\tau$ (Eq. 1). The left side of Eq. 1 is $\int f^*(c\hat{A})g\,d\tau = c\int f^*\hat{A}g\,d\tau = c\int g(\hat{A}f)^*d\tau$, since $\hat{A}$ is Hermitian. The right side of Eq. 1 is $\int g(c\hat{A}f)^*d\tau = c^*\int g(\hat{A}f)^*d\tau = c\int g(\hat{A}f)^*d\tau$, where (1.32) and the fact that c is real were used. We have proved the two sides of Eq. 1 to be equal.
(b) We must show that $\int f^*(\hat{A}+\hat{B})g\,d\tau = \int g[(\hat{A}+\hat{B})f]^*d\tau$ (Eq. 2). The left side of Eq. 2 is $\int f^*(\hat{A}+\hat{B})g\,d\tau = \int f^*(\hat{A}g+\hat{B}g)\,d\tau = \int (f^*\hat{A}g + f^*\hat{B}g)\,d\tau = \int f^*\hat{A}g\,d\tau + \int f^*\hat{B}g\,d\tau$ (Eq. 3), where the definition of the sum of two operators was used. Because $\hat{A}$ and $\hat{B}$ are Hermitian, $\int f^*\hat{A}g\,d\tau = \int g(\hat{A}f)^*d\tau$ and $\int f^*\hat{B}g\,d\tau = \int g(\hat{B}f)^*d\tau$. Hence Eq. 3 becomes
$\int f^*(\hat{A}+\hat{B})g\,d\tau = \int g(\hat{A}f)^*d\tau + \int g(\hat{B}f)^*d\tau = \int [g(\hat{A}f)^* + g(\hat{B}f)^*]\,d\tau$
$= \int g[(\hat{A}f)^* + (\hat{B}f)^*]\,d\tau = \int g[(\hat{A}f+\hat{B}f)]^*d\tau = \int g[(\hat{A}+\hat{B})f]^*d\tau$, where (1.33) and the definition of the sum of operators were used. This completes the proof.

7.7 **(a)** We must show that $\int_{-\infty}^{\infty} f^*(d^2/dx^2)g\,dx = \int_{-\infty}^{\infty} g[(d^2/dx^2)f]^*dx$ (Eq. 1). Let $u \equiv f^*$ and $d\mathrm{v} \equiv (d^2g/dx^2)\,dx$. Then use of (7.16) gives the left side of Eq. 1 as $\int_{-\infty}^{\infty} f^*(d^2g/dx^2)\,dx = f^*(dg/dx)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}(dg/dx)(df^*/dx)\,dx = -\int_{-\infty}^{\infty}(dg/dx)(df^*/dx)\,dx$ (Eq. 2), since f^* must be zero at $\pm\infty$ for f to be quadratically integrable. Now let $u \equiv df^*/dx$ and $d\mathrm{v} = (dg/dx)\,dx$. Use of (7.16) gives the right side of Eq. 2 as $-\int_{-\infty}^{\infty}(dg/dx)(df^*/dx)\,dx = -(df^*/dx)g\,|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} g(d^2f^*/dx^2)\,dx = \int_{-\infty}^{\infty} g(d^2f^*/dx^2)\,dx$, which is the right side of Eq. 1, so we have proved that d^2/dx^2 is Hermitian. $\hat{T}_x$ equals a real constant times d^2/dx^2, so from Prob. 7.6a, $\hat{T}_x$ is Hermitian.

(b) $\langle T_x\rangle = -(\hbar^2/2m)\int \Psi^*(d^2\Psi/dx^2)\,dx$. Let $u \equiv \Psi^*$ and $d\mathrm{v} \equiv d^2\Psi/dx^2$. Then Eq. (7.16) gives $\langle T_x\rangle = -(\hbar^2/2m)[\Psi^*(d\Psi/dx)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}(d\Psi/dx)(d\Psi^*/dx)\,dx] =$ $(\hbar^2/2m)\int_{-\infty}^{\infty}(d\Psi/dx)(d\Psi/dx)^*dx = (\hbar^2/2m)\int_{-\infty}^{\infty}|d\Psi/dx|^2\,dx$, since Ψ is zero at $\pm\infty$.

(c) From (3.45) $\hat{T} = \hat{T}_x + \hat{T}_y + \hat{T}_z$, and (3.90) gives $\langle T\rangle = \langle T_x\rangle + \langle T_y\rangle + \langle T_z\rangle$.

(d) Since the integrand in $(\hbar^2/2m)\int_{-\infty}^{\infty}|d\Psi/dx|^2\,dx$ is never negative, it follows from part (a) that $\langle T_x\rangle \ge 0$. Similarly $\langle T_y\rangle \ge 0$ and $\langle T_z\rangle \ge 0$, and it follows from part c that $\langle T\rangle \ge 0$.

7.8 From Prob. 7.6a, if $\hat{A}$ is Hermitian, then $c\hat{A}$ is Hermitian if c is a real number. Also, it is clear from the proof in Prob. 7.6a that $c\hat{A}$ is not Hermitian if $c \ne c^*$, that is, if c is imaginary. Since d^2/dx^2 is Hermitian (Prob. 7.7a), it follows that $4\,d^2/dx^2$ is Hermitian and $i\,d^2/dx^2$ is not Hermitian. Since $\hat{p}_x = (\hbar/i)(d/dx) = -\hbar i(d/dx)$ is Hermitian, it follows that $i(d/dx)$ is Hermitian and $d/dx = (i/\hbar)\hat{p}_x$ is not Hermitian.

7.9 **(a)** This operator is not linear and cannot represent a physical quantity.

(b) d/dx is not Hermitian (Prob. 7.8) and so cannot represent a physical quantity.

(c) d^2/dx^2 is linear and Hermitian and can represent a physical quantity.

(d) $i(d/dx)$ is linear and Hermitian and can represent a physical quantity.

7.10 $\int_0^{2\pi} f^*\hat{L}_z g\,d\phi = \int_0^{2\pi} f^*(\hbar/i)(d\,g/d\phi)\,d\phi$. Let $u = f^*$ and $d\mathrm{v} = (\hbar/i)dg/d\phi$. Then integration by parts gives $\int_0^{2\pi} f^*(\hbar/i)(d\,g/d\phi)\,d\phi = (\hbar/i)f^*g\,|_0^{2\pi} - \int_0^{2\pi}(\hbar/i)g\,(df^*/d\phi)\,d\phi =$ $\int_0^{2\pi} g[(\hbar/i)(df/d\phi)]^*d\phi = \int_0^{2\pi} g(\hat{L}_z f)^*d\phi$, since a well-behaved function is single-valued and so has the same value at $\phi = 0$ as at $\phi = 2\pi$. [For simplicity, the proof took f and g as functions of ϕ only. If f and g are taken as functions of r, θ, and ϕ, the integral becomes

$\int_0^\pi \int_0^\infty \left[\int_0^{2\pi} f^*(\hbar/i)(\partial g/\partial\phi)\,d\phi\right] r^2 \sin\theta\,dr\,d\theta$ and the same manipulations of the ϕ integral show $\hat{L}_z$ to be Hermitian.]

7.11 $\langle A^2\rangle = \int \Psi^*\hat{A}^2\Psi\,d\tau = \int \Psi^*\hat{A}(\hat{A}\Psi)\,d\tau = \int (\hat{A}\Psi)(\hat{A}\Psi)^*\,d\tau = \int |\hat{A}\Psi|^2\,d\tau$. In this proof, the Hermitian property $\int f^*\hat{A}g\,d\tau = \int g(\hat{A}f)^*\,d\tau$ with $f = \Psi$ and $g = \hat{A}\Psi$ was used.

7.12 **(a)** We must show that $\int f^*\hat{A}\hat{B}g\,d\tau = \int g(\hat{A}\hat{B}f)^*\,d\tau$ (Eq. 1). Use of the Hermitian property of $\hat{A}$ gives the left side of Eq. 1 as $\int f^*\hat{A}(\hat{B}g)\,d\tau = \int(\hat{B}g)(\hat{A}f)^*\,d\tau = \int(\hat{A}f)^*\hat{B}g\,d\tau = \int g(\hat{B}\hat{A}f)^*\,d\tau$ (Eq. 2), where the Hermitian property of $\hat{B}$ was used to get the last equality. If $\hat{B}\hat{A} = \hat{A}\hat{B}$, then the rightmost side of Eq. 2 equals the right side of Eq. 1, and the result is proved. If $\hat{B}\hat{A} \neq \hat{A}\hat{B}$, the rightmost side of Eq. 2 does not equal the right side of Eq. 1 and $\hat{A}\hat{B}$ is not Hermitian.

(b) Interchange of $\hat{A}$ and $\hat{B}$ in Eq. 2 of part (a) gives $\int f^*\hat{B}(\hat{A}g)\,d\tau = \int g(\hat{A}\hat{B}f)^*\,d\tau$ (Eq. 3). Adding Eqs. 2 and 3, we get $\int f^*(\hat{A}\hat{B} + \hat{B}\hat{A})g\,d\tau = \int g[(\hat{A}\hat{B} + \hat{B}\hat{A})f]^*\,d\tau$, which completes the proof.

(c) Both $\hat{x}$ and $\hat{p}_x$ are Hermitian, but these two operators do not commute, so by the result of part (a), $\hat{x}\hat{p}_x$ is not Hermitian.

(d) The results of part (b) and Prob. 7.6(a) show that $\frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})$ is Hermitian.

7.13 **(a)** In Eq. (7.16), let $u \equiv f^*$ and $\mathrm{v} = g$. Then (7.16) becomes
$\langle f \mid d/dx \mid g\rangle = \int_{-\infty}^{\infty} f^*(d/dx)g\;dx = f^*g\,|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} g(d/dx)f^*\,dx = -\langle g \mid d/dx \mid f\rangle^*$.

(b) Since $\hat{A}$ is Hermitian, $\int f^*\hat{A}(\hat{B}g)\,d\tau = \int(\hat{B}g)(\hat{A}f)^*\,d\tau = \int(\hat{A}f)^*\hat{B}g\,d\tau = \int g(\hat{B}\hat{A}f)^*\,d\tau$, where the Hermitian property of $\hat{B}$ was used. Interchange of $\hat{A}$ and $\hat{B}$ gives $\int f^*\hat{B}(\hat{A}g)\,d\tau = \int g(\hat{A}\hat{B}f)^*\,d\tau$. Subtracting the second equation from the first, we get $\int f^*(\hat{A}\hat{B} - \hat{B}\hat{A})g)\,d\tau = \int g[(\hat{B}\hat{A} - \hat{A}\hat{B})f]^*\,d\tau = -\int g[(\hat{A}\hat{B} - \hat{B}\hat{A})f]^*\,d\tau$, so the commutator is anti-Hermitian.

7.14 **(a)** From Eq. (6.14), $\hat{L}_z(3p_{-1}) = -\hbar(3p_{-1})$, so $\langle 2p_1 \,|\, \hat{L}_z \,|\, 3p_{-1}\rangle = -\hbar\langle 2p_1 \,|\, 3p_{-1}\rangle = 0$, since $2p_1$ and $3p_{-1}$ are eigenfunctions of the Hermitian operator $\hat{L}_z$ with different eigenvalues and so are orthogonal.

(b) $\hat{L}_z(3p_0) = 0(3p_0) = 0$, so this integral is zero because its integrand is zero.

7.15 **(a)** We have $\hat{H}f_n = (n + \frac{1}{2})h\nu f_n$, so $\langle f_m \,|\, \hat{H} \,|\, f_n\rangle = (n + \frac{1}{2})h\nu\langle f_m \,|\, f_n\rangle = (n + \frac{1}{2})h\nu\delta_{mn}$.

(b) $\hat{H}f_n = (n^2h^2/8ml^2)f_n$, so $\langle f_m \mid \hat{H} \mid f_n\rangle = (n^2h^2/8ml^2)\langle f_m \mid f_n\rangle = (n^2h^2/8ml^2)\delta_{mn}$.

7.16 $\langle \psi_2|\hat{H}|f(x)\rangle = \langle f(x)|\hat{H}|\psi_2\rangle^* = \langle f(x)|\hat{H}\psi_2\rangle^* = \langle f(x)|E_2\psi_2\rangle^* = E_2\langle\psi_2|f(x)\rangle =$ $\frac{5}{2}h\nu\langle\psi_2|f(x)\rangle$, since $\hat{H}$ is Hermitian and E_2 is real.

7.17 **(a)** $\langle 2p_1 \mid 2p_x\rangle = \langle 2p_1 \mid 2^{-1/2}(2p_1 + 2p_{-1})\rangle = 2^{-1/2}\langle 2p_1 \mid 2p_1\rangle + 2^{-1/2}\langle 2p_1 \mid 2p_{-1}\rangle =$ $2^{-1/2} + 0 = 2^{-1/2}$, since the ψ_{nlm} hydrogenlike functions are orthonormal.

(b) Let the orthogonal functions be $g_1 \equiv 2p_1$ and $g_2 \equiv 2p_x + c2p_1$. We require that $\langle 2p_1 \mid 2p_x + c2p_1\rangle = 0$, so $0 = \langle 2p_1 \mid 2p_x\rangle + c\langle 2p_1 \mid 2p_1\rangle = 2^{-1/2} + c$, where the result of part (a) was used. Hence $c = -2^{-1/2}$ and $g_2 = 2p_x - 2^{-1/2}2p_1$. The normalized function is Ng_2 and $1 = \langle Ng_2|Ng_2\rangle = |N|^2\langle 2p_x - 2^{-1/2}2p_1 \mid 2p_x - 2^{-1/2}2p_1\rangle =$
$|N|^2[\langle 2p_x \mid 2p_x\rangle - 2^{-1/2}\langle 2p_x \mid 2p_1\rangle - 2^{-1/2}\langle 2p_1 \mid 2p_x\rangle + 2^{-1}\langle 2p_1 \mid 2p_1\rangle] =$
$|N|^2(1 - 2^{-1/2}2^{-1/2} - 2^{-1/2}2^{-1/2} + 2^{-1}) = \frac{1}{2}|N|^2$ and $|N| = 2^{1/2}$. So the orthonormal functions are $2p_1$ and $2^{1/2}2p_x - 2p_1$ [which from (6.118) equals $2p_{-1}$]. These are eigenfunctions of the H-atom $\hat{H}$ and of $\hat{L}^2$ (and also of $\hat{L}_z$). [An alternative is to take $g_1 = 2p_x$ and then one finds $g_2 = 2^{1/2}2p_1 - 2p_x$ (which equals $i2p_y$).]

7.18 **(a)** We have $a_n = (2/l)^{1/2}\left[l\int_0^l x\sin(n\pi x/l)\,dx - \int_0^l x^2\sin(n\pi x/l)\,dx\right]$. Use of Eq. (A.1) and $\int x^2 \sin bx\,dx = (2x/b^2)\sin bx + (2/b^3 - x^2/b)\cos bx$ gives

$$a_n = (2l)^{1/2}[(l/n\pi)^2\sin(n\pi x/l) - (xl/n\pi)\cos(n\pi x/l)]\big|_0^l$$
$$- (2/l)^{1/2}[(2xl^2/n^2\pi^2)\sin(n\pi x/l) + (2l^3/n^3\pi^3 - x^2l/n\pi)\cos(n\pi x/l)]\big|_0^l.$$

Use of $\sin n\pi = 0$ and $\cos n\pi = (-1)^n$ gives

$$a_n = -(2^{1/2}l^{5/2}/n\pi)(-1)^n - \{(2^{3/2}l^{5/2}/n^3\pi^3)[(-1)^n - 1] - (2^{1/2}l^{5/2}/n\pi)(-1)^n\} =$$
$$(2^{3/2}l^{5/2}/n^3\pi^3)[1 - (-1)^n].$$

(b) Setting $x = \frac{1}{2}l$ in the final equation of the example and multiplying by $4\pi^3/l^2$, we get

$$\pi^3 = 16\sum_{n=1}^{\infty}[1 - (-1)^n]n^{-3}\sin(n\pi/2) =$$

$32 + 0 - 32/3^3 + 0 + 32/5^3 + 0 - 32/7^3 + 0 + 32/9^3 + \cdots \approx 31.0214$. The accurate value is $\pi^3 = 31.0063$.

(c) For $x = l/4$, the expansion is

$$\tfrac{3}{16}l^2 = (4l^2/\pi^3)[2\sin(\pi/4) + (2/3^3)\sin(3\pi/4) + (2/5^3)\sin(5\pi/4) + (2/7^3)\sin(7\pi/4) + (2/9^3)\sin(9\pi/4) + \cdots].$$

The left side is $0.18750l^2$. With 1, 3, and 5 nonzero terms included, the right side equals $0.18244l^2$, $0.18774l^2$, and $0.18746l^2$, respectively. The percent errors are -2.7%, 0.13%, and -0.02%.

7.19 **(a)** In $f = \sum_n \langle g_n \mid f \rangle g_n$ [Eq. (7.41)], the complete set is $g_n = (2/l)^{1/2}\sin(n\pi x/l)$. The expansion coefficients are

$\langle g_n \mid f \rangle = (2/l)^{1/2}\int_0^{l/2}\sin(n\pi x/l)(-1)\,dx + (2/l)^{1/2}\int_{l/2}^{l}\sin(n\pi x/l)(1)\,dx =$

$(2/l)^{1/2}(l/n\pi)\cos(n\pi x/l)\big|_0^{l/2} - (2/l)^{1/2}(l/n\pi)\cos(n\pi x/l)\big|_{l/2}^{l} =$

$(2/l)^{1/2}(l/n\pi)[\cos(n\pi/2)-1] - (2/l)^{1/2}(l/n\pi)[\cos(n\pi) - \cos(n\pi/2)] =$

$[(2l)^{1/2}/n\pi][2\cos(n\pi/2) - 1 - (-1)^n]$. Hence

$f = \sum_{n=1}^{\infty}(2/n\pi)[2\cos(n\pi/2) - 1 - (-1)^n]\sin(n\pi x/l)$.

(b) At $x = l/4$, the expansion in (a) becomes

$-1 = (2/\pi)[0 - 4/2 + 0 + 0 + 0 + 4/6 + 0 + 0 + 0 - 4/10 + 0 + 0 + 0 + 4/14 + \cdots] =$

$(4/\pi)(-1 + 1/3 - 1/5 + 1/7 - 1/9 + \cdots)$. With 1, 3, and 5 nonzero terms, the right side is -1.273, -1.103, and -1.063, respectively. The errors are 27%, 10%, and 6%.

7.20 **(a)** F; **(b)** F; **(c)** T, since $\hat{L}_z$ commutes with $\hat{H}$ and $2p_x$ and $3p_x$ have different eigenvalues of $\hat{H}$, Theorem 6 tells us the integral is zero.

7.21 If m is even, then $\hat{\Pi}^m = \hat{\Pi}^{2n} = (\hat{\Pi}^2)^n = \hat{1}^n = \hat{1}$, where n is an integer and Eq. (7.54) was used. If m is odd, then $\hat{\Pi}^m = \hat{\Pi}^{2n+1} = (\hat{\Pi}^2)^n\hat{\Pi} = \hat{1}^n\hat{\Pi} = \hat{\Pi}$.

7.22 **(a)** An s hydrogenlike function depends on r only and $r = (x^2 + y^2 + z^2)^{1/2}$. Hence ψ_{2s} is an even function.

(b) From (6.119), ψ_{2p_x} equals x times a function of r, and so is an odd function.

(c) This function is a linear combination of two functions with the same energy eigenvalue, and so is an eigenfunction of $\hat{H}$. This function is a linear combination of two functions with different parity eigenvalues and so is not an eigenfunction of $\hat{\Pi}$.

7.23 Since ψ_j is an even or odd function according to whether the vibrational quantum number j is even or odd, respectively, we have $\hat{\Pi}\psi_j = (-1)^j\psi_j$ and

$$\Pi_{ij} = (-1)^j\int_{-\infty}^{\infty}\psi_i{}^*\psi_j\,dx = (-1)^j\,\delta_{ij}.$$

7.24 **(a)** From Prob. 7.22, the $2s$ function is even and $2p_x$ is odd. Hence the integrand in $\langle 2s \mid x \mid 2p_x\rangle$ is an even function and parity does not require this integral to be zero.

(b) The integrand is an odd function and the integral must be zero.

(c) The integrand is the product of three odd functions and so is an odd function. The integral must therefore be zero.

7.25 We have $\hat{R}f_i = r_i f_i$, where r_i and f_i are the eigenvalues and eigenfunctions of $\hat{R}$. We operate on this equation with $\hat{R}$ and use the linearity of $\hat{R}$ and the eigenvalue equation to get $R^2 f_i = r_i \hat{R} f_i = r_i r_i f_i = r_i^2 f_i$. Operating with $\hat{R}$ again, we get $\hat{R}^3 f_i = r_i^3 f_i$. Operating with $\hat{R}$ a total of $n-1$ times, we get $\hat{R}^n f_i = r_i^n f_i$. But $\hat{R}^n = 1$, so $f_i = r_i^n f_i$ and $r_i^n = 1$. Hence the eigenvalues are the *n*th roots of unity, given by (1.36).

7.26 **(a)**
$\hat{\Pi}[f(x, y, z) + g(x, y, z)] = f(-x, -y, -z) + g(-x, -y, -z) = \hat{\Pi} f(x, y, z) + \hat{\Pi} g(x, y, z)$.
Also, $\hat{\Pi}[cf(x, y, z)] = cf(-x, -y, -z) = c\hat{\Pi} f(x, y, z)$. Hence $\hat{\Pi}$ is linear.

(b) We must show that $\int_{-\infty}^{\infty}[f(x)]^*\hat{\Pi} g(x)\,dx = \int_{-\infty}^{\infty} g(x)[\hat{\Pi} f(x)]^*\,dx$. We have $\int_{-\infty}^{\infty}[f(x)]^*\hat{\Pi} g(x)\,dx = \int_{-\infty}^{\infty}[f(x)]^* g(-x)\,dx$ (Eq. 1). Let $z \equiv -x$. Then $dz = -dx$ and the right side of Eq. 1 becomes $-\int_{\infty}^{-\infty}[f(-z)]^* g(z)\,dz = \int_{-\infty}^{\infty} g(z)[f(-z)]^*\,dz =$ $\int_{-\infty}^{\infty} g(z)[\hat{\Pi} f(z)]^*\,dz = \int_{-\infty}^{\infty} g(x)[\hat{\Pi} f(x)]^*\,dx$, which completes the proof.

7.27 As shown in Sec. 7.5, if two eigenfunctions *f* and *g* of $\hat{\Pi}$ have different eigenvalues, then one function must be odd and the other even. Hence the integrand in $\int f^* g\,d\tau$ is an odd function and the integral is zero.

7.28 The harmonic-oscillator wave functions are even or odd according to whether the quantum number v is even or odd, respectively. If v_1 and v_2 are both even numbers or both odd numbers, then the integrand in $\langle v_2 | x | v_1 \rangle$ is an odd function and the integral must be zero. The integral might be zero in other cases also.

7.29 **(a)** Since $r = (x^2 + y^2 + z^2)^{1/2}$, replacement of *x*, *y*, *z* by $-x, -y, -z$ leaves *r* unchanged. The points (*x*, *y*, *z*) and $(-x, -y, -z)$ lie on opposite ends of a line that goes through the origin, as shown in the first and last figures in Fig. 12.6 in the text. The angle θ made by the radius vector with the positive half of the *z* axis is the same in the second figure as in the first, and when the radius vector is reflected in the *xy* plane to generate the third figure from the second, the angle with the positive *z* axis becomes $\pi - \theta$. In going from the first figure to the second, the angle made by the projection of the radius vector in the *xy* plane with the positive half of the *x* axis increases from ϕ to $\phi + \pi$, and remains unchanged on going from the second to the third figure.

(b) From part (a), $\hat{\Pi}e^{im\phi} = e^{im(\phi+\pi)} = e^{im\phi}e^{im\pi} = e^{im\phi}(\cos m\pi + i\sin m\pi) = (-1)^m e^{im\phi}$, since $\cos m\pi = (-1)^m$ and $\sin m\pi = 0$.

(c) From (a), θ goes to $\pi-\theta$. Use of trigonometric identities gives $\cos(\pi-\theta) = \cos\pi\cos\theta + \sin\pi\sin\theta = -\cos\theta$ and $\sin(\pi-\theta) = \sin\pi\cos\theta - \cos\pi\sin\theta = \sin\theta$. So the parity operator does not affect the $\sin^{|m|}\theta$ factor in (5.97). The transformation of θ to $\pi-\theta$ changes $\cos^j\theta$ to $\cos^j(\pi-\theta) = (-1)^j\cos^j\theta$. In (5.97), the j values are all odd or are all even, depending on whether $l-|m|$ is odd or even, respectively. Hence if $l-|m|$ is even, there is no effect on $S_{l,m}(\theta)$, and if $l-|m|$ is odd, $S_{l,m}(\theta)$ is multiplied by -1. Hence $\hat{\Pi}S_{l,m}(\theta) = (-1)^{l-|m|}S_{l,m}(\theta)$. If $m > 0$, then $|m| = m$. If $m < 0$, then $|m| = -m$ and $(-1)^{l-|m|} = (-1)^{l+m} = (-1)^{l+m}/(-1)^{2m} = (-1)^{l-m}$. Hence $\hat{\Pi}S_{l,m}(\theta) = (-1)^{l-m}S_{l,m}(\theta)$.

(d) $Y_l^m = S_{l,m}(\theta)T_m(\phi)$. From (b), $\hat{\Pi}$ multiplies T_m by $(-1)^m$ and from (c) it multiplies $S_{l,m}$ by $(-1)^{l-m}$. Hence $\hat{\Pi}$ multiplies Y_l^m by $(-1)^l$, and Y_l^m is even if l is even and is odd if l is odd.

7.30 The integral can be written as

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} f(q_1,\ldots,q_k,q_{k+1},\ldots,q_m)\,dq_1\cdots dq_k\right]dq_{k+1}\cdots dq_m$$

For the multiple integral in brackets, q_{k+1} through q_m are constants. By virtue of the first equation in the problem, the contributions from $f(-q_1,\ldots,-q_k,q_{k+1},\ldots,q_m)$ and $f(q_1,\ldots,q_k,q_{k+1},\ldots,q_m)$ cancel so the integral in brackets equals zero and the complete integral is zero.

7.31 **(a)** From (6.122), the $2p_z$ function is the same as the $2p_0$ function, which is an eigenfunction of $\hat{L}_z$ with eigenvalue zero, so the value 0 will be obtained with 100% certainty when L_z is measured.

(b) From (6.120), $2p_y = i2^{-1/2}(2p_{-1}) - i2^{-1/2}(2p_1)$. Theorem 8 of Sec. 7.6 tells us that the probability of getting $-\hbar$ is $|i2^{-1/2}|^2 = (i2^{-1/2})^*(i2^{-1/2}) = (-i2^{-1/2})(i2^{-1/2}) = \frac{1}{2}$ and the probability of getting $\hbar$ is $|-i2^{-1/2}|^2 = (-i2^{-1/2})^*(-i2^{-1/2}) = (i2^{-1/2})(-i2^{-1/2}) = \frac{1}{2}$.

(c) $2p_1$ is an eigenfunction of $\hat{L}_z$ with eigenvalue $\hbar$, so $\hbar$ will always be found.

In (a), $\langle L_z\rangle = 0$ and in (c) $\langle L_z\rangle = \hbar$.

In (b), Eq. (3.81) gives $\langle L_z\rangle = 0.5(-\hbar) + 0(0) + 0.5\hbar = 0$.

7.32 Theorem 8 of Sec. 7.6 tells us that the probability of getting $\hbar$ is $|6^{-1/2}|^2 + |-3^{-1/2}|^2 = \frac{1}{6} + \frac{1}{3} = \frac{1}{2}$ and the probability of getting 0 is $|-2^{-1/2}i|^2 = \frac{1}{2}$. Use of Eq. (3.81) gives $\langle L_z \rangle = \frac{1}{2}\hbar + \frac{1}{2}(0) = \frac{1}{2}\hbar.$

7.33 The first two functions in the linear combination each have $\hat{L}^2$ eigenvalue $1(2)\hbar^2 = 2\hbar^2$ and the third function has $\hat{L}^2$ eigenvalue $2(3)\hbar^2 = 6\hbar^2$. Hence Theorem 8 of Sec. 7.6 says that the probability of getting $2\hbar^2$ is $|6^{-1/2}|^2 + |-2^{-1/2}i|^2 = \frac{1}{6} + \frac{1}{2} = \frac{2}{3}$ and the probability of getting $6\hbar^2$ is $|-3^{-1/2}|^2 = \frac{1}{3}$. Equation (3.81) gives $\langle L^2 \rangle = \frac{2}{3}(2\hbar^2) + \frac{1}{3}(6\hbar^2) = \frac{10}{3}\hbar^2$.

7.34 The first two functions in the linear combination each have energy eigenvalue $-e^2/(4\pi\varepsilon_0)8a$ and the third function has energy eigenvalue $-e^2/(4\pi\varepsilon_0)18a$. The probability of getting $-e^2/(4\pi\varepsilon_0)8a$ is $|6^{-1/2}|^2 + |-2^{-1/2}i|^2 = \frac{1}{6} + \frac{1}{2} = \frac{2}{3}$ and the probability of getting $-e^2/(4\pi\varepsilon_0)18a$ is $|-3^{-1/2}|^2 = \frac{1}{3}$. From (3.81), $\langle E \rangle = \frac{2}{3}[-e^2/(4\pi\varepsilon_0)8a] + \frac{1}{3}[-e^2/(4\pi\varepsilon_0)18a] = -\frac{11}{108}(e^2/4\pi\varepsilon_0).$

7.35 The L^2 value of $2\hbar^2$ means that just after the measurement the particle has angular-momentum quantum number $l = 1$. Since the labeling of directions in space is arbitrary, the possible outcomes of a measurement of L_x are the same as the possible outcomes of a measurement of L_z, namely, $-\hbar$, 0, and $\hbar$.

7.36 The first function in the linear combination is an eigenfunction of the particle-in-a-box $\hat{H}$ with eigenvalue $h^2/8ml^2$ and the second function is an eigenfunction of $\hat{H}$ with eigenvalue $2^2h^2/8ml^2$. Hence the probability of obtaining $h^2/8ml^2$ is $|\frac{1}{2}e^{-ih^2t/8ml^2}|^2 = (\frac{1}{2}e^{-ih^2t/8ml^2})^*(\frac{1}{2}e^{-ih^2t/8ml^2}) = (\frac{1}{2}e^{ih^2t/8ml^2})(\frac{1}{2}e^{-ih^2t/8ml^2}) = \frac{1}{4}$ and the probability of obtaining $2^2h^2/8ml^2$ is $|\frac{1}{2}\sqrt{3}e^{i\pi}e^{-ih^2t/2ml^2}|^2 = (\frac{1}{2}\sqrt{3}e^{i\pi}e^{-ih^2t/2ml^2})^*(\frac{1}{2}\sqrt{3}e^{i\pi}e^{-ih^2t/2ml^2}) = \frac{3}{4}$

7.37 The possible outcomes are the eigenvalues $n^2h^2/8ml^2$ of the energy (Hamiltonian) operator. The probabilities are given by Eq. (7.73) as $|\int_0^l (2/l)^{1/2}\sin(n\pi x/l)(105/l^7)^{1/2}x^2(l-x)\,dx|^2 = (210/l^8)\,|\int_0^l \sin(n\pi x/l)(x^2l - x^3)\,dx|^2$.
Use of a table of integrals or the website integrals.wolfram.com gives
$\int x^2 \sin bx\,dx = (2x/b^2)\sin bx + (2/b^3 - x^2/b)\cos bx$ and
$\int x^3 \sin bx\,dx = (3x^2/b^2 - 6/b^4)\sin bx + (6x/b^3 - x^3/b)\cos bx$.
Since $\sin n\pi = 0$ and $\sin 0 = 0$, the sine terms contribute nothing and the probability is
$(210/l^8)\,|[(2l^4/n^3\pi^3 - x^2l^2/n\pi)\cos(n\pi x/l) - (6xl^3/n^3\pi^3 - x^3l/n\pi)\cos(n\pi x/l)]\big|_0^l|^2 =$

$(210/l^8)\,|\,(2l^4/n^3\pi^3 - l^4/n\pi)(-1)^n - (6l^4/n^3\pi^3 - l^4/n\pi)(-1)^n - 2l^4/n^3\pi^3\,|^2 =$
$(210/l^8)\,|\,(-4l^4/n^3\pi^3)(-1)^n - 2l^4/n^3\pi^3\,|^2 = 210[16/n^6\pi^6 + (-1)^n 16/n^6\pi^6 + 4/n^6\pi^6] =$
$(840/n^6\pi^6)[5 + 4(-1)^n]$. (For n = 1, 2, and 3, the probabilities are 0.87374, 0.1229, and 0.0012, respectively.)

7.38 This energy is the ground-state energy and Eq. (7.73) gives the probability of getting this energy as $|\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}(1/\pi a^3)^{1/2}e^{-r/a}(27/\pi a^3)^{1/2}e^{-3r/a}r^2\sin\theta\,dr\,d\theta\,d\phi\,|^2 =$
$(27/\pi^2 a^6)\,|\,4\pi\int_0^{\infty}e^{-4r/a}r^2\,dr\,|^2 = (432/a^6)\,|2(a/4)^3|^2 = 27/64 = 0.421875.$

7.39 **(a)** $\Psi = c_1 e^{-iEt/\hbar}e^{i(2mE)^{1/2}x/\hbar} + c_2 e^{-iEt/\hbar}e^{-i(2mE)^{1/2}x/\hbar} \equiv c_1 f_1 + c_2 f_2$.

(b) $\hat{p}_x f_1 = (\hbar/i)\partial f_1/\partial x = (\hbar/i)[i(2mE)^{1/2}/\hbar]f_1 = (2mE)^{1/2}f_1$ and $\hat{p}_x f_2 = -(2mE)^{1/2}f_2$.

(c) The possible outcomes are the eigenvalues $(2mE)^{1/2}$ and $-(2mE)^{1/2}$, whose eigenfunctions occur in the linear combination in (a). The probabilities are proportional to $|c_1|^2$ and $|c_2|^2$. (They are not equal to $|c_1|^2$ and $|c_2|^2$ because a free-particle wave function is not normalizable.) Let the proportionality constant be k. The probabilities add to 1, so $k|c_1|^2 + k|c_2|^2 = 1$ and $k = 1/(|c_1|^2 + |c_2|^2)$. The probability of getting $(2mE)^{1/2}$ is thus $|c_1|^2/(|c_1|^2 + |c_2|^2)$ and the probability of getting $-(2mE)^{1/2}$ is $|c_2|^2/(|c_1|^2 + |c_2|^2)$.

7.40 The sum of the probabilities in (7.74) must equal 1. Also, $1-(-1)^n$ equals 0 if n is even and equals 2 if n is odd. Hence $\sum_{n=1,3,5\ldots}^{\infty} 2^2(240/n^6\pi^6) = 1$. Let $m \equiv (n-1)/2$. Then m goes from 0 to ∞ in steps of 1, and $n = 2m+1$. Hence $\sum_{m=1}^{\infty}[960/(2m+1)^6\pi^6] = 1$ and $\sum_{m=1}^{\infty}1/(2m+1)^6 = \pi^6/960$.

7.41 **(a)** From (7.76), (2.23), and (3.36) with A replaced by N and k by p, the desired probability is $|\int_0^l Ne^{-ipx/\hbar}(2/l)^{1/2}\sin(n\pi x/l)\,dx\,|^2\,dp = (2/l)\,|N|^2\,|\int_0^l e^{-ibx}\sin(sx)\,dx|^2\,dp$, where $b \equiv p/\hbar$ and $s \equiv n\pi/l$. A table of integrals (or the website integrals.wolfram.com) gives $\int e^{ax}\sin(sx)\,dx = (a^2+s^2)^{-1}e^{ax}(a\sin sx - s\cos sx)$. The probability is thus
$(2/l)\,|N|^2\,(s^2-b^2)^{-2}\,|\,e^{-ibx}(-ib\sin sx - s\cos sx)\,|_0^l|^2\,dp = A\,|\,e^{-ibl}[-s(-1)^n] + s\,|^2\,dp$,
where $A \equiv (2/l)\,|N|^2\,(s^2-b^2)^{-2}$ and we used $\sin sl = \sin n\pi = 0$ and $\cos n\pi = (-1)^n$.
The probability is
$A\{e^{-ibl}[-s(-1)^n]+s\}^*\{e^{-ibl}[-s(-1)^n]+s\}\,dp = A\{e^{ibl}[-s(-1)^n]+s\}\{e^{-ibl}[-s(-1)^n]+s\}\,dp =$

$A[s^2 - s^2(-1)^n(e^{ibl} + e^{-ibl}) + s^2]\,dp = 2As^2[1-(-1)^n \cos bl]\,dp =$
$(4/l)\,|N|^2\,[s^2/(s^2-b^2)^2][1-(-1)^n \cos bl]\,dp$, where (1.28) and (2.14) were used.

(b) At $p = \pm nh/2l$, we have $b \equiv p/\hbar = \pm n\pi/l = \pm s$, so $b^2 = s^2$ and the denominator in (a) is zero; also, $1-(-1)^n \cos bl = 1-(-1)^n \cos(\pm n\pi) = 1-(-1)^n(-1)^n = 1-1 = 0$, so the numerator is also zero. Using l'Hospital's rule, we differentiate the numerator and the denominator with respect to *b*. Thus $\lim_{b\to s}\{[1-(-1)^n \cos bl]/(s^2-b^2)^2\} =$ $\lim_{b\to s}[l(-1)^n \sin bl/2(s^2-b^2)(-2b)]$. Since $bl = \pm n\pi$, we again have 0/0. Differentiating again, we get $\lim_{b\to s}[l^2(-1)^n \cos bl/(12b^2-4s^2)] = l^2(-1)^{2n}/8s^2 = l^2/8s^2$ and the probability at $p = \pm nh/2l$ is $\frac{1}{2}l\,|N|^2\,dp$.

7.42 **(a)** The displayed equation after Eq. (7.91) gives $\int_{-\infty}^{\infty} \delta(x)\,dx = 1$.

(b) Eq. (7.83) gives $\delta(x) = 0$ for $-\infty \le x \le -1$, so $\int_{-\infty}^{-1} \delta(x)\,dx = 0$.

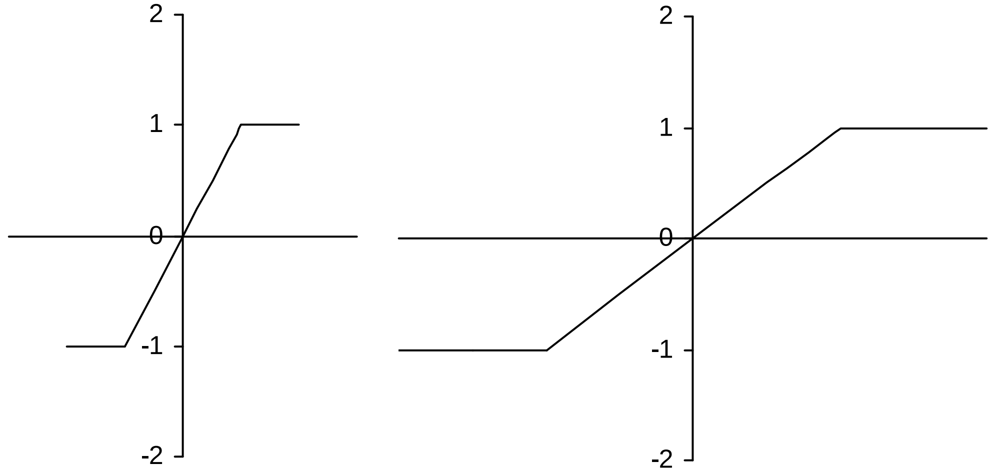
(c) $1 = \int_{-\infty}^{\infty} \delta(x)\,dx = \int_{-\infty}^{-1} \delta(x)\,dx + \int_{-1}^{1} \delta(x)\,dx + \int_{1}^{\infty} \delta(x)\,dx = \int_{-1}^{1} \delta(x)\,dx$, where the result of (b) and $\int_{1}^{\infty} \delta(x)\,dx = 0$ were used.

(d) Since $\delta(x-3)$ is zero except at $x = 3$, the integrand is zero for all points in the range from $x = 1$ to 2 and the integral is therefore zero.

7.43 Let $z \equiv x - a$. Then $\int_{-\infty}^{\infty} [\delta(x-a)]^2\,dx = \int_{-\infty}^{\infty} \delta(z)\delta(z)\,dz$. Use of (7.91) with *x* replaced by *z,* with $a = 0$, and with $f = \delta$ gives $\int_{-\infty}^{\infty} \delta(z)\delta(z)\,dz = \delta(0) = \infty$.

7.44 We use the procedure used to derive Eq. (7.91), except that we set $a = 0$ and take the lower limit of the integral as 0 instead of $-\infty$.The first term on the right side of the equation that precedes (7.90) becomes $f(x)H(x)|_0^{\infty} = f(\infty) - \frac{1}{2}f(0)$, where (7.81) was used. The right side of the equation preceding (7.91) becomes $f(\infty) - \frac{1}{2}f(0) - f(x)|_0^{\infty} =$ $f(\infty) - \frac{1}{2}f(0) - f(\infty) + f(0) = \frac{1}{2}f(0)$ and (7.91) becomes $\int_0^{\infty} f(x)\delta(x)\,dx = \frac{1}{2}f(0)$. This result is intuitively clear from Fig. 7.5.

7.45 From (7.82), the value of the δ function equals the slope of the *H* versus *x* graph. The values of the Fig. 7.5 approximate δ functions at and near the origin increase in going from function 1 to 2 to 3 and the width of the nonzero region decreases in going from 1 to 2 to 3. Hence the corresponding approximate *H*(*x*) graphs show an increasing slope and a decreasing width of the nonzero-slope region as we go to more-accurate approximations. Thus the figures are



7.46 Substitution of $\Psi(q,t) = \sum_i c_i(t)\psi_i(q)$ (Eq. 1) in (7.97) gives
$-(\hbar/i)\sum_i [dc_i(t)/dt]\psi_i(q) = \hat{H}\sum_i c_i(t)\psi_i(q) = \sum_i c_i(t)\hat{H}\psi_i(q) = \sum_i c_i(t)E_i\psi_i(q)$.
Multiplication by $\psi_m^*(q)$ followed by integration over all space gives
$-(\hbar/i)\sum_i [dc_i(t)/dt]\int \psi_m^*(q)\psi_i(q)\,d\tau = \sum_i c_i(t)E_i \int \psi_m^*(q)\psi_i(q)\,d\tau$. Use of orthonormality gives $-(\hbar/i)\sum_i [dc_i(t)/dt]\delta_{mi} = \sum_i c_i(t)E_i\delta_{mi}$, which becomes $-(\hbar/i)\,dc_m/dt = c_m E_m$. So $c_m^{-1}\,dc_m = -(i/\hbar)E_m\,dt$. Integration gives $\ln[c_m(t)/c_m(t_0)] = -(iE_m/\hbar)(t-t_0)$ and $c_m(t) = c_m(t_0)e^{-iE_m(t-t_0)/\hbar}$ (Eq. 2).

To find $c_m(t_0)$, we multiply Eq. 1 at $t = t_0$ by ψ_m^* and integrate over all space to get $\int \psi_m^*\Psi(q,t_0)\,d\tau = \sum_i c_i(t_0)\int \psi_m^*(q)\psi_i(q)\,d\tau = \sum_i c_i(t_0)\delta_{mi} = c_m(t_0)$.
Equation 2 becomes $c_m(t) = \langle \psi_m | \Psi(q,t_0)\rangle e^{-iE_m(t-t_0)/\hbar}$ (Eq. 3). Substitution of Eq. 3 into Eq. 1 gives $\Psi(q,t) = \sum_m \langle \psi_m | \Psi(q,t_0)\rangle e^{-iE_m(t-t_0)/\hbar}\psi_m(q)$, which is (7.101).

7.47 **(a)** $T = 8ml^2/3h = 8(9.11\times10^{-31}\text{ kg})(2.00\times10^{-10}\text{ m})^2/3(6.626\times10^{-34}\text{ J s}) = 1.47\times10^{-16}\text{ s}$.

(b) $\Psi^*\Psi = (2^{-1/2}e^{iE_1t/\hbar}\psi_1 + 2^{-1/2}e^{iE_2t/\hbar}\psi_2)(2^{-1/2}e^{-iE_1t/\hbar}\psi_1 + 2^{-1/2}e^{-iE_2t/\hbar}\psi_2) =$
$\frac{1}{2}\psi_1^2 + \frac{1}{2}e^{-i(E_2-E_1)t/\hbar}\psi_1\psi_2 + \frac{1}{2}e^{i(E_2-E_1)t/\hbar}\psi_2\psi_1 + \frac{1}{2}\psi_2^2 =$
$\frac{1}{2}\psi_1^2 + \frac{1}{2}\psi_2^2 + \cos[(E_2-E_1)t/\hbar]\psi_1\psi_2$, where (1.28) and (2.14) were used.

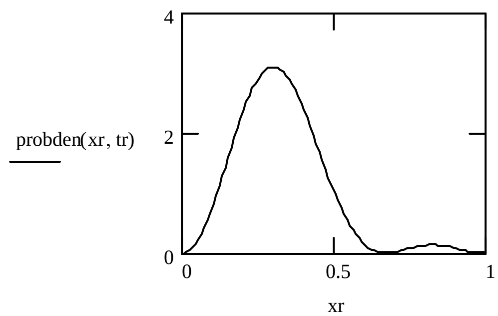
(c) We plot $l\Psi^2 = \sin^2(\pi x_r) + \sin^2(2\pi x_r) + 2\sin(\pi x_r)\sin(2\pi x_r)\cos(2\pi j/8)$ vs. x_r for each j value. The results are shown on the next page. The $j = 8$ plot is the same as $j = 0$.

(d) A Mathcad worksheet (that can also be used for Prob. 7.48b) is shown below. In the Animate dialog box, let FRAME go from 0 to 100 at 10 frames per second.

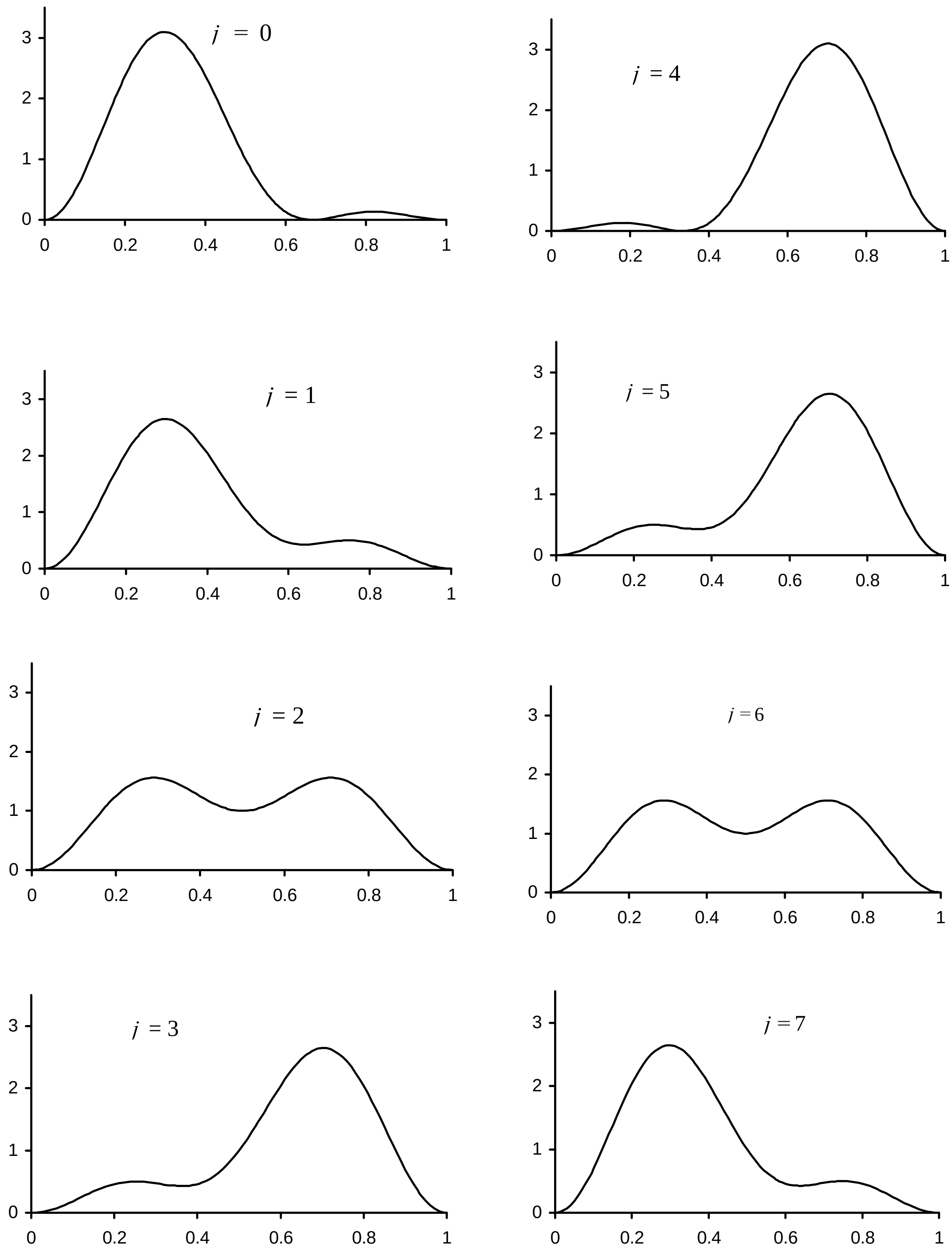
Animation-Particle in box- n=1 plus n = n

$$tr := \frac{FRAME}{100} \qquad xr := 0, 0.01 .. 1 \qquad n := 2$$

$$probden(xr, tr) := \sin(\pi \cdot xr)^2 + \sin(\pi \cdot n \cdot xr)^2 + 2 \cdot \sin(\pi \cdot xr) \cdot \sin(n \cdot \pi \cdot xr) \cdot \cos\left[2 \cdot \pi \cdot tr \cdot \left(n^2 - 1\right)\right]$$



Figures for Prob. 7.47(c):



7.48 **(a)** Replacement of the 2 subscript in ψ_2 and E_2 by n in the derivation in Prob. 7.47 gives $\Psi^*\Psi = \frac{1}{2}\psi_1^2 + \frac{1}{2}\psi_n^2 + \cos[(E_n - E_1)t/\hbar]\psi_1\psi_n$ (Eq. 7.102′). The equations immediately after (7.102) become $(E_n - E_1)T/\hbar = 2\pi$ and

$T = 2\pi\hbar/(E_n - E_1) = 8ml^2/(n^2 - 1)h$. Using the expressions for ψ_1, ψ_n, and T, we get $l\,|\Psi|^2 = \sin^2(\pi x_r) + \sin^2(n\pi x_r) + 2\sin(\pi x_r)\sin(n\pi x_r)\cos(2\pi t/T)$ (Eq. 7.102′).

(b) We have $\Psi = c_1(t)\psi_1(x) + c_n(t)\psi_n(x)$ and

$|\Psi|^2 = |c_1(t)|^2\,[\psi_1(x)]^2 + (c_1^* c_n + c_n^* c_1)\psi_1(x)\psi_n(x) + |c_n(t)|^2\,[\psi_n(x)]^2$. With the origin at the center of the box, ψ_1 is an even function; ψ_n is even for $n = 3, 5, \ldots$ and is odd for $n = 2, 4, \ldots$. Therefore $|\Psi|^2$ is even for $n = 3, 5, \ldots$ and for these values of n, $|\Psi|^2$ is symmetrical about the box midpoint at all times.

7.49 **(a)** $\mathbf{AB} = \begin{pmatrix} 2 & 1 \\ 0 & -3 \end{pmatrix}\begin{pmatrix} 1 & -1 \\ 4 & 4 \end{pmatrix} = \begin{pmatrix} 2\cdot 1 + 1\cdot 4 & 2\cdot(-1) + 1\cdot 4 \\ 0\cdot 1 + (-3)\cdot 4 & 0\cdot(-1) + (-3)\cdot 4 \end{pmatrix} = \begin{pmatrix} 6 & 2 \\ -12 & -12 \end{pmatrix}$

(b) $\mathbf{BA} = \begin{pmatrix} 1 & -1 \\ 4 & 4 \end{pmatrix}\begin{pmatrix} 2 & 1 \\ 0 & -3 \end{pmatrix} = \begin{pmatrix} 1\cdot 2 + (-1)\cdot 0 & 1\cdot 1 + (-1)\cdot(-3) \\ 4\cdot 2 + 4\cdot 0 & 4\cdot 1 + 4\cdot(-3) \end{pmatrix} = \begin{pmatrix} 2 & 4 \\ 8 & -8 \end{pmatrix}$

(c) $\mathbf{A} + \mathbf{B} = \begin{pmatrix} 2 & 1 \\ 0 & -3 \end{pmatrix} + \begin{pmatrix} 1 & -1 \\ 4 & 4 \end{pmatrix} = \begin{pmatrix} 2+1 & 1+(-1) \\ 0+4 & -3+4 \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 4 & 1 \end{pmatrix}$

(d) $3\mathbf{A} = 3\begin{pmatrix} 2 & 1 \\ 0 & -3 \end{pmatrix} = \begin{pmatrix} 3\cdot 2 & 3\cdot 1 \\ 3\cdot 0 & 3\cdot(-3) \end{pmatrix} = \begin{pmatrix} 6 & 3 \\ 0 & -9 \end{pmatrix}$

(e) $\mathbf{A} - 4\mathbf{B} = \begin{pmatrix} 2 & 1 \\ 0 & -3 \end{pmatrix} - 4\begin{pmatrix} 1 & -1 \\ 4 & 4 \end{pmatrix} = \begin{pmatrix} 2-4 & 1+4 \\ 0-16 & -3-16 \end{pmatrix} = \begin{pmatrix} -2 & 5 \\ -16 & -19 \end{pmatrix}$

7.50 **C** is a 3 by 1 matrix and **D** is 1 by 3, so **CD** is a 3 by 3 matrix and **DC** is a 1 by 1 matrix.

$$\mathbf{CD} = \begin{pmatrix} 5 \\ 0 \\ -1 \end{pmatrix}\begin{pmatrix} i & 2 & 1 \end{pmatrix} = \begin{pmatrix} 5i & 5\cdot 2 & 5\cdot 1 \\ 0\cdot i & 0\cdot 2 & 0\cdot 1 \\ -i & (-1)\cdot 2 & (-1)\cdot 1 \end{pmatrix} = \begin{pmatrix} 5i & 10 & 5 \\ 0 & 0 & 0 \\ -i & -2 & -1 \end{pmatrix}$$

$$\mathbf{DC} = \begin{pmatrix} i & 2 & 1 \end{pmatrix}\begin{pmatrix} 5 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} i\cdot 5 + 2\cdot 0 + 1\cdot(-1) \end{pmatrix} = \begin{pmatrix} -1 + 5i \end{pmatrix}$$

7.51 Let $\{f_i\}$ denote the orthonormal basis set. The matrix representative of the unit operator in this basis has matrix elements $\langle f_j\,|\hat{1}|\,f_k\rangle = \langle f_j\,|\,f_k\rangle = \delta_{jk}$. Hence the matrix representative is a unit matrix of dimension equal to the number of basis functions in $\{f_i\}$.

7.52 Let $\{f_i\}$ denote the basis set. We have
$D_{ij} = \langle f_i \mid \hat{D} \mid f_j \rangle = \langle f_i \mid k\hat{C} \mid f_j \rangle = k\langle f_i \mid \hat{C} \mid f_j \rangle = kC_{ij}$.

7.53 Since the set $\{f_i\}$ is complete, we can expand the function $\hat{A}f_j$ in terms of this set. We have $\hat{A}f_j = \sum_k c_k f_k$ (Eq. 1). To find the expansion coefficients, we multiply this equation by f_m^* and integrate over all space to get
$\langle f_m \mid \hat{A} \mid f_j \rangle = \sum_k c_k \langle f_m \mid f_k \rangle = \sum_k c_k \delta_{mk} = c_m$. Hence $c_m = \langle f_m \mid \hat{A} \mid f_j \rangle = a_m \delta_{mj}$, where the given expression for $\langle f_m \mid \hat{A} \mid f_j \rangle$ was used. Hence Eq. 1 becomes
$\hat{A}f_j = \sum_k a_k \delta_{kj} f_k = a_j f_j$, which shows f_j is an eigenfunction of $\hat{A}$ with eigenvalue a_j.

7.54 **(a)** Expanding u in terms of the complete orthonormal set, we have $u = \sum_i b_i f_i$.
Multiplication by f_k^*, integration over all space, and use of orthonormality gives
$b_k = \langle f_k \mid u \rangle$ [Eq. (7.40)], so $u = \sum_i \langle f_i \mid u \rangle f_i$. Application of $\hat{A}$ gives
$\hat{A}u = \hat{A}\sum_i \langle f_i \mid u \rangle f_i = \sum_i \langle f_i \mid u \rangle \hat{A}f_i$ (Eq. 1), since $\hat{A}$ is linear. Expanding $\hat{A}f_i$ using the complete set, we have $\hat{A}f_i = \sum_j c_j f_j$ (Eq. 2). Multiplication by f_m^* and integration over all space gives $c_m = \langle f_m \mid \hat{A} \mid f_i \rangle$ (as in Prob. 7.53). Hence Eq. 2 becomes
$\hat{A}f_i = \sum_j \langle f_j \mid \hat{A} \mid f_i \rangle f_j$ (Eq. 3). Substitution of Eq. 3 into Eq. 1 gives
$\hat{A}u = \sum_i \left(\langle f_i \mid u \rangle \sum_j \langle f_j \mid \hat{A} \mid f_i \rangle f_j \right) = \sum_j \left(\sum_i \langle f_j \mid \hat{A} \mid f_i \rangle \langle f_i \mid u \rangle \right) f_j$.

(b) Multiplication of $u = \sum_i u_i f_i$ by f_j^*, integration, and use of orthonormality gives $u_j = \langle f_j \mid u \rangle$ or $u_i = \langle f_i \mid u \rangle$ [Eq. (7.41)]. Hence the result of (a) is $\hat{A}u = \sum_j \left(\sum_i A_{ji} u_i \right) f_j$.
Comparison with $\hat{A}u = w = \sum_j w_j f_j$ gives $w_j = \sum_i A_{ji} u_i$ (Eq. 3). Since **A** is an n by n matrix (where n is the number of basis functions and may be infinite) and **u** is an n by 1 column matrix (whose elements are u_i), **Au** is an n by 1 column matrix whose element $(\mathbf{Au})_j$ is calculated from row j of **A** and column 1 (the only column) of **u**. Hence Eq. 3 shows that each element of **Au** equals the corresponding element of **w**. Thus $\mathbf{Au} = \mathbf{w}$.

7.55 The matrix elements are $\langle Y_2^{m_j} \mid \hat{L}_z \mid Y_2^{m_k} \rangle = m_k \hbar \langle Y_2^{m_j} \mid Y_2^{m_k} \rangle = m_k \hbar \delta_{m_j m_k}$ (Eq. 1), where orthogonality follows from Theorem 2 in Sec. 7.2. The quantum numbers m_j and m_k each range from -2 to 2. Equation 1 gives

$$\begin{pmatrix} -2\hbar & 0 & 0 & 0 & 0 \\ 0 & -\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 2\hbar \end{pmatrix}$$

7.56 **(a)** From (5.11), $(\Delta L_z)^2 = \langle L_z^2\rangle - \langle L_z\rangle^2 = \langle 2p_z \,|\, \hat{L}_z^2 \,|\, 2p_z\rangle - \langle 2p_z \,|\, \hat{L}_z \,|\, 2p_z\rangle^2$. Since $2p_z = 2p_0$, $\hat{L}_z 2p_z = 0(2p_z) = 0$ and $\hat{L}_z^2 2p_z = \hat{L}_z(\hat{L}_z 2p_z) = \hat{L}_z(0) = 0$, so $(\Delta L_z)^2 = 0 - 0 = 0$, and $\Delta L_z = 0$, which is obvious since $2p_z$ is an eigenfunction of $\hat{L}_z$ and only zero will be obtained when L_z is measured.

(b) $(\Delta L_z)^2 = \langle L_z^2\rangle - \langle L_z\rangle^2 = \langle 2p_x \,|\, \hat{L}_z^2 \,|\, 2p_x\rangle - \langle 2p_x \,|\, \hat{L}_z \,|\, 2p_x\rangle^2$ (Eq. 1). From (6.118), $\hat{L}_z(2p_x) = 2^{-1/2}\hat{L}_z(2p_1 + 2p_{-1}) = 2^{-1/2}(\hat{L}_z 2p_1 + \hat{L}_z 2p_{-1}) = 2^{-1/2}(\hbar 2p_1 - \hbar 2p_{-1})$ and $\hat{L}_z^2(2p_x) = \hat{L}_z[\hat{L}_z(2p_x)] = \hat{L}_z[2^{-1/2}(\hbar 2p_1 - \hbar 2p_{-1})] = 2^{-1/2}(\hbar\hat{L}_z 2p_1 - \hbar\hat{L}_z 2p_{-1}) =$
$2^{-1/2}(\hbar^2 2p_1 + \hbar^2 2p_{-1})$. We have
$\langle 2p_x \,|\, \hat{L}_z^2 \,|\, 2p_x\rangle = \langle 2^{-1/2}(2p_1 + 2p_{-1}) \,|\, 2^{-1/2}(\hbar^2 2p_1 + \hbar^2 2p_{-1})\rangle =$
$\frac{1}{2}\hbar^2[\langle 2p_1 \,|\, 2p_1\rangle + \langle 2p_1 \,|\, 2p_{-1}\rangle + \langle 2p_{-1} \,|\, 2p_1\rangle + \langle 2p_{-1} \,|\, 2p_{-1}\rangle] = \frac{1}{2}\hbar^2(1+0+0+1) = \hbar^2$.
Also, $\langle 2p_x \,|\, \hat{L}_z \,|\, 2p_x\rangle^2 = \langle 2^{-1/2}(2p_1 + 2p_{-1}) \,|\, 2^{-1/2}(\hbar 2p_1 - \hbar 2p_{-1})\rangle^2 =$
$(\frac{1}{2}\hbar)^2[\langle 2p_1 \,|\, 2p_1\rangle - \langle 2p_1 \,|\, 2p_{-1}\rangle + \langle 2p_{-1} \,|\, 2p_1\rangle - \langle 2p_{-1} \,|\, 2p_{-1}\rangle]^2 = \frac{1}{4}\hbar^2(1-0+0-1)^2 = 0$.
Hence $(\Delta L_z)^2 = \langle L_z^2\rangle - \langle L_z\rangle^2 = \langle 2p_x \,|\, \hat{L}_z^2 \,|\, 2p_x\rangle - \langle 2p_x \,|\, \hat{L}_z \,|\, 2p_x\rangle^2 = \hbar^2$ and $\Delta L_z = \hbar$.

7.57 **(a)** $\Psi = \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2$, where E_1, E_2, ψ_1, ψ_2 are particle-in-a-box stationary-state energies and wave functions with $n=1$ and $n=2$. Then
$\langle \Psi \,|\, \Psi\rangle = \langle \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2 \,|\, \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2\rangle =$
$\frac{1}{4}e^{iE_1t/\hbar}e^{-iE_1t/\hbar}\langle\psi_1 \,|\, \psi_1\rangle + \frac{1}{4}\sqrt{3}e^{i\pi}e^{iE_1t/\hbar}e^{-iE_2t/\hbar}\langle\psi_1 \,|\, \psi_2\rangle + \frac{1}{4}\sqrt{3}e^{-i\pi}e^{iE_2t/\hbar}e^{-iE_1t/\hbar}\langle\psi_2 \,|\, \psi_1\rangle +$
$\frac{3}{4}e^{-i\pi}e^{iE_2t/\hbar}e^{i\pi}e^{-iE_2t/\hbar}\langle\psi_2 \,|\, \psi_2\rangle = \frac{1}{4} + 0 + 0 + \frac{3}{4} = 1$.

(b) $\langle E\rangle = \langle \Psi \,|\, \hat{H} \,|\, \Psi\rangle = \langle \Psi \,|\, \hat{H} \,|\, \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2\rangle =$
$\langle \Psi \,|\, \frac{1}{2}e^{-iE_1t/\hbar}\hat{H}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\hat{H}\psi_2\rangle = \langle \Psi \,|\, \frac{1}{2}e^{-iE_1t/\hbar}E_1\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}E_2\psi_2\rangle =$
$\langle \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2 \,|\, \frac{1}{2}e^{-iE_1t/\hbar}E_1\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}E_2\psi_2\rangle =$
$\frac{1}{4}e^{iE_1t/\hbar}e^{-iE_1t/\hbar}E_1\langle\psi_1 \,|\, \psi_1\rangle + \frac{1}{4}\sqrt{3}e^{i\pi}e^{iE_1t/\hbar}e^{-iE_2t/\hbar}E_2\langle\psi_1 \,|\, \psi_2\rangle + \frac{1}{4}\sqrt{3}e^{-i\pi}e^{iE_2t/\hbar}e^{-iE_1t/\hbar}E_1\langle\psi_2 \,|\, \psi_1\rangle +$
$\frac{3}{4}e^{-i\pi}e^{iE_2t/\hbar}e^{i\pi}e^{-iE_2t/\hbar}E_2\langle\psi_2 \,|\, \psi_2\rangle = \frac{1}{4}E_1 + 0 + 0 + \frac{3}{4}E_2 = \frac{1}{4}E_1 + \frac{3}{4}E_2$, which makes sense in view of the answer to Prob. 7.36. We get $\langle E\rangle = 13h^2/32ml^2$.

(c)
$\langle x\rangle = \langle \Psi \,|\, \hat{x} \,|\, \Psi\rangle = \langle \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2 \,|\, x \,|\, \frac{1}{2}e^{-iE_1t/\hbar}\psi_1 + \frac{1}{2}\sqrt{3}e^{i\pi}e^{-iE_2t/\hbar}\psi_2\rangle =$

$\frac{1}{4}e^{iE_1t/\hbar}e^{-iE_1t/\hbar}\langle\psi_1 | x | \psi_1\rangle + \frac{1}{4}\sqrt{3}e^{i(\pi+E_1t/\hbar-E_2t/\hbar)}\langle\psi_1 | x | \psi_2\rangle + \frac{1}{4}\sqrt{3}e^{-i(\pi+E_1t/\hbar-E_2t/\hbar)}\langle\psi_2 | x | \psi_1\rangle +$ $\frac{3}{4}e^{-i\pi}e^{iE_2t/\hbar}e^{i\pi}e^{-iE_2t/\hbar}\langle\psi_2 | x | \psi_2\rangle$. From Fig. 2.4 (see also Prob. 3.48), $\langle\psi_1 | x | \psi_1\rangle = \frac{1}{2}l = \langle\psi_2 | x | \psi_2\rangle$. Also $\langle\psi_1 | x | \psi_2\rangle = \langle\psi_2 | x | \psi_1\rangle$. Hence, $\langle x\rangle = \frac{1}{8}l + \frac{1}{2}\sqrt{3}\cos[\pi + (E_1 - E_2)t/\hbar]\langle\psi_1 | x | \psi_2\rangle + \frac{3}{8}l$ (Eq. 1), where a result of Prob. 1.29 was used. We have $\langle\psi_1 | x | \psi_2\rangle = (2/l)\int_0^l x\sin(\pi x/l)\sin(2\pi x/l)\,dx$. A table of integrals or use of the website integrals.wolfram.com gives

$\int x\sin(ax)\sin(bx)\,dx = \dfrac{\cos[(a-b)x]}{2(a-b)^2} + \dfrac{x\sin[(a-b)x]}{2(a-b)} - \dfrac{\cos[(a+b)x]}{2(a+b)^2} - \dfrac{x\sin[(a+b)x]}{2(a+b)}$. So

$\dfrac{2}{l}\int_0^l x\sin(2\pi x/l)\sin(\pi x/l)\,dx = \dfrac{2}{l}\left[\dfrac{\cos(\pi x/l)}{2(\pi/l)^2} + \dfrac{x\sin(\pi x/l)}{2(\pi/l)} - \dfrac{\cos(3\pi x/l)}{2(3\pi/l)^2} - \dfrac{x\sin(3\pi x/l)}{2(3\pi/l)}\right]\Bigg|_0^l =$

$(l/\pi^2)[-1+0+\frac{1}{9}-0-(1+0-\frac{1}{9}-0)] = -16l/9\pi^2 = \langle\psi_1 | x | \psi_2\rangle$. Equation 1 becomes $\langle x\rangle = \frac{1}{2}l - (8\sqrt{3}/9\pi^2)l\cos(\pi - 6\pi ht/8ml^2)$. The cosine function ranges from -1 to 1, so the minimum and maximum $\langle x\rangle$ values are $\frac{1}{2}l - (8\sqrt{3}/9\pi^2)l = 0.344l$ and $\frac{1}{2}l + (8\sqrt{3}/9\pi^2)l = 0.656l$.

7.58 From (7.97) and its complex conjugate, $\partial\Psi/\partial t = -(i/\hbar)\hat{H}\Psi$ and $\partial\Psi^*/\partial t = (i/\hbar)(\hat{H}\Psi)^*$. So $\int(\partial\Psi^*/\partial t)\hat{A}\Psi\,d\tau = (i/\hbar)\int(\hat{H}\Psi)^*\hat{A}\Psi\,d\tau = (i/\hbar)\int(\hat{A}\Psi)(\hat{H}\Psi)^*d\tau =$ $(i/\hbar)[\int(\hat{A}\Psi)^*(\hat{H}\Psi)\,d\tau]^* = (i/\hbar)[\int\Psi(\hat{H}\hat{A}\Psi)^*d\tau]^* = (i/\hbar)\int\Psi^*\hat{H}\hat{A}\Psi\,d\tau$, where the Hermitian property of $\hat{H}$ was used. Also $\int\Psi^*\hat{A}(\partial\Psi/\partial t)\,d\tau = -(i/\hbar)\int\Psi^*\hat{A}\hat{H}\Psi\,d\tau$.
The equation for $d\langle A\rangle/dt$ becomes

$d\langle A\rangle/dt = \int\Psi^*(\partial\hat{A}/\partial t)\Psi\,d\tau + (i/\hbar)\int\Psi^*(\hat{H}\hat{A} - \hat{A}\hat{H})\Psi\,d\tau =$
$\langle\partial\hat{A}/\partial t\rangle + (i/\hbar)\int\Psi^*[\hat{H}, \hat{A}]\Psi\,d\tau$

7.59 We set $\hat{A} = \hat{x}$ in (7.113). Time *t* does not occur in the operator $\hat{x}$, so $\partial\hat{x}/\partial t = 0$. From (5.8), $[\hat{H}, \hat{x}] = -(i\hbar/m)\hat{p}_x$ and (7.113) becomes $d\langle x\rangle/dt = (1/m)\int\Psi^*\hat{p}_x\Psi\,d\tau = \langle p_x\rangle/m = (1/m)\int\Psi^*(\hbar/i)(\partial\Psi/\partial x)\,d\tau$. Differentiation of this equation with respect to *t* gives $d^2\langle x\rangle/dt^2 = m^{-1}d\langle p_x\rangle/dt$. Setting $A = p_x$ in (7.113), we have

$d\langle p_x\rangle/dt = (i/\hbar)\int\Psi^*[\hat{H}, \hat{p}_x]\Psi\,d\tau = (i/\hbar)\int\Psi^* i\hbar(\partial V/\partial x)\Psi\,d\tau = \int\Psi^* F_x\Psi\,d\tau = \langle F_x\rangle$.

7.60 **(a)** $0 \le \langle u | u\rangle = \langle f - cg | f - cg\rangle = \langle f | f\rangle - c\langle f | g\rangle - c^*\langle g | f\rangle + c^*c\langle g | g\rangle =$
$\langle f | f\rangle - \langle g | f\rangle\langle f | g\rangle/\langle g | g\rangle - \langle f | g\rangle\langle g | f\rangle/\langle g | g\rangle + \langle g | f\rangle\langle f | g\rangle\langle g | g\rangle/\langle g | g\rangle^2$

$0 \le \langle f \mid f\rangle - \langle g \mid f\rangle\langle f \mid g\rangle/\langle g \mid g\rangle$. Multiplication by the positive quantity $\langle g \mid g\rangle$ gives $0 \le \langle f \mid f\rangle\langle g \mid g\rangle - \langle g \mid f\rangle\langle f \mid g\rangle$.

(b) $\langle f|f\rangle = \langle(\hat{A}-\langle A\rangle)\Psi \mid (\hat{A}-\langle A\rangle)\Psi\rangle = \langle(\hat{A}-\langle A\rangle)\Psi \mid \hat{A}-\langle A\rangle \mid \Psi\rangle$ (Eq. 1). Since the sum of two Hermitian operators is Hermitian, $\hat{A}-\langle A\rangle$ is Hermitian, and Eq. 1 becomes $\langle f \mid f\rangle = \langle \Psi \mid \hat{A}-\langle A\rangle \mid (\hat{A}-\langle A\rangle)\Psi\rangle^* = \langle \Psi \mid (\hat{A}-\langle A\rangle)^2 \mid \Psi\rangle^* = [(\Delta A)^2]^*$, where (5.10) was used. The complex conjugate of this equation is $\langle f \mid f\rangle^* = (\Delta A)^2$. Equation (7.4) with $m = n$ gives $\langle f \mid f\rangle^* = \langle f \mid f\rangle$, so $\langle f \mid f\rangle = (\Delta A)^2$. The same arguments used for $\langle f \mid f\rangle$ give $\langle g \mid g\rangle = \langle g \mid g\rangle^* = (\Delta B)^2$.

(c) $(z-z^*)/2i = [(x+iy)-(x-iy)]/2i = y$. Substitution of $\langle f \mid f\rangle = (\Delta A)^2$ and $\langle g \mid g\rangle = (\Delta B)^2$ into the Schwarz inequality and use of the inequality proved in (c) in the text give $(\Delta A)^2(\Delta B)^2 \ge |\langle f \mid g\rangle|^2 \ge -\frac{1}{4}(\langle f \mid g\rangle - \langle g \mid f\rangle)^2$.

(d) Let $\bar{A} \equiv \langle A\rangle$ and $\bar{B} \equiv \langle B\rangle$. Then, since $\hat{A}-\bar{A}$ is Hermitian, we have

$\langle f \mid g\rangle = \langle g \mid f\rangle^* = \langle(\hat{B}-\bar{B})\Psi \mid (\hat{A}-\bar{A})\Psi\rangle^* = \langle(\hat{B}-\bar{B})\Psi \mid (\hat{A}-\bar{A}) \mid \Psi\rangle^* =$

$\langle \Psi \mid (\hat{A}-\bar{A}) \mid (\hat{B}-\bar{B})\Psi\rangle^{**} = \langle \Psi \mid (\hat{A}-\bar{A}) \mid (\hat{B}-\bar{B})\Psi\rangle =$

$\langle \Psi \mid \hat{A}\hat{B} \mid \Psi\rangle - \bar{B}\langle \Psi \mid \hat{A} \mid \Psi\rangle - \bar{A}\langle \Psi \mid \hat{B} \mid \Psi\rangle + \bar{A}\bar{B}\langle \Psi \mid \Psi\rangle = \langle \Psi \mid \hat{A}\hat{B} \mid \Psi\rangle - \bar{A}\bar{B}$.

Interchanging f and g and $\hat{A}$ and $\hat{B}$ in $\langle f \mid g\rangle = \langle \Psi \mid \hat{A}\hat{B} \mid \Psi\rangle - \bar{A}\bar{B}$, we get $\langle g \mid f\rangle = \langle \Psi \mid \hat{B}\hat{A} \mid \Psi\rangle - \bar{A}\bar{B}$. Substitution of the last two equations into the last equation in (c) gives $(\Delta A)^2(\Delta B)^2 \ge -\frac{1}{4}\left(\langle \Psi \mid \hat{A}\hat{B} \mid \Psi\rangle - \langle \Psi \mid \hat{B}\hat{A} \mid \Psi\rangle\right)^2 = -\frac{1}{4}\left(\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle\right)^2$.

(e) From Prob. 7.13(b), the commutator is anti-Hermitian, so $\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle = -\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle^*$, and the last equation in (d) becomes

$(\Delta A)^2(\Delta B)^2 \ge -\frac{1}{4}\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle(-1)\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle^* = \frac{1}{4}\left|\langle \Psi \mid [\hat{A}, \hat{B}] \mid \Psi\rangle\right|^2$.

7.61 In the following C++ program, xr is x/l and fr is f/l.

```
#include <iostream>
#include <cmath>
using namespace std;
int main() {
  double pi, xr, fr, sum;
  int m, n;
  pi = 3.1415926535897;
  for (m=5; m<=20; m=m+5) {
    cout << "Number of terms =  " << m << endl;
      for (xr=0; xr<=1; xr=xr+0.1) {
        sum = 0;
          for (n=1; n<=m; n=n+1) {
```

```
            sum=sum+pow(-1,n+1)*sin((2*n-1)*pi*xr)/pow(2*n-1,2);
          }
        fr=(4/(pi*pi))*sum;
        cout << "xr =  " << xr << " fr =  " << fr << endl;
      }
    }
  return 0;
}
```

7.62 The derivation of Eq. (5.131) depends on the result of Prob. 7.11, which shows that $\langle\psi \mid \hat{A}^2 \mid \psi\rangle = \langle\hat{A}\psi \mid \hat{A}\psi\rangle \geq 0$ if $\hat{A}$ is a Hermitian operator. The Hermitian property $\langle\psi \mid \hat{A}^2 \mid \psi\rangle = \langle\hat{A}\psi \mid \hat{A}\psi\rangle$ is valid only if ψ is a well-behaved function. [See the sentences following Eqs. (7.6), (7.11), and (7.17).]

7.63 See Section 7.1.

7.64 **(a)** F. [See, for example, Eq. (7.101).]

(b) T. **(c)** F.

(d) F. (This is only true if the eigenfunctions all have the same eigenvalue.)

(e) F. **(f)** T. **(g)** F. **(h)** F.

(i) F. (They must have different eigenvalues for us to be sure this is true.)

(j) F. **(k)** T. **(l)** F. **(m)** F. **(n)** T. **(o)** T.

(p) F. It is valid for all well-behaved functions.

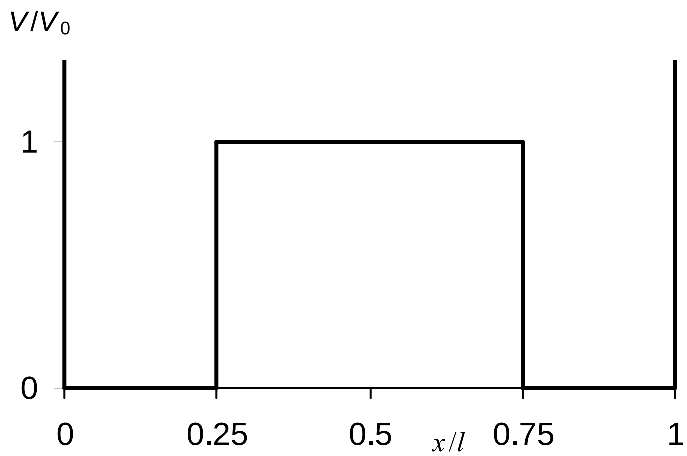
(q) T. **(r)** F. (Only true for stationary states.)

Chapter 8

The Variation Method

8.1 ≤ -203.2 eV.

8.2 **(a)**



We have $\langle \phi | \hat{H} | \phi \rangle = \langle \phi | \hat{T} | \phi \rangle + \langle \phi | \hat{V} | \phi \rangle$. For the particle in a box (PIB), $V = 0$ inside the box, so the PIB Hamiltonian equals $\hat{T}$; $\hat{H}_{\text{PIB}} = \hat{T}$. Also the variation function ϕ_1 in (a) equals the normalized ground-state (gs) PIB wave function: $\phi_1 = \psi_{\text{PIB,gs}}$. So $\langle \phi_1 | \hat{T} | \phi_1 \rangle = \langle \psi_{\text{PIB,gs}} | \hat{H}_{\text{PIB}} | \psi_{\text{PIB,gs}} \rangle = E_{\text{PIB,gs}} \langle \psi_{\text{PIB,gs}} | \psi_{\text{PIB,gs}} \rangle = E_{\text{PIB,gs}} = h^2/8ml^2 =$ $4\pi^2\hbar^2/8ml^2 = 4.93480\hbar^2/ml^2$. Using Appendix Eq. (A.2), we have $\langle \phi_1 | V | \phi_1 \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin^2(\pi x/l)\, dx = (V_0/l)[x - (l/2\pi)\sin 2\pi x/l)]|_{l/4}^{3l/4} =$ $V_0[\frac{3}{4} - \frac{1}{4} - (2\pi)^{-1}\sin(3\pi/2) + (2\pi)^{-1}\sin(\pi/2)] = V_0(\frac{1}{2} + \pi^{-1}) = 0.818310V_0 =$ $0.818310\hbar^2/ml^2$, since V is zero in the first and last quarter of the box. Then $\langle \phi_1 | \hat{H} | \phi_1 \rangle = (4.93480 + 0.81831)\hbar^2/ml^2 = 5.75311\hbar^2/ml^2$. The error is 0.048%.

(b) The variation function ϕ_1 in (b) is the same as that in Eq. (8.11) and $\hat{H}_{\text{PIB}} = \hat{T}$. So $\langle \phi_2 | \hat{H}_{\text{PIB}} | \phi_2 \rangle = \hbar^2 l^3/6m = 0.166667\hbar^2 l^3/m = \langle \phi_2 | \hat{T} | \phi_2 \rangle$. Then $\langle \phi_2 | V | \phi_2 \rangle = \int_{l/4}^{3l/4} V_0 x^2 (l-x)^2\, dx = V_0[l^2x^3/3 - 2lx^4/4 + x^5/5]|_{l/4}^{3l/4} =$ $V_0 l^5 (\frac{0.75^3}{3} - \frac{0.75^4}{2} + \frac{0.75^5}{5} - \frac{1}{3\cdot 4^3} + \frac{1}{2\cdot 4^4} - \frac{1}{5\cdot 4^5}) = 0.026432V_0 l^5 = 0.026432(\hbar^2/m)l^3$. So

$\langle \phi_2 \mid \hat{H} \mid \phi_2 \rangle = (0.166667 + 0.026432)\hbar^2 l^3/m = 0.193099\hbar^2 l^3/m$. Also, Eq. (8.13) gives $\int \phi_2 {}^* \phi_2 \, d\tau = l^5/30$. So $\langle \phi_2 \mid \hat{H} \mid \phi_2 \rangle / \langle \phi_2 \mid \phi_2 \rangle = 5.79297\hbar^2/ml^2$. The error is 0.74%.

8.3 $d^2 e^{-cx^2}/dx^2 = d(-2cxe^{-cx^2})/dx^2 = -2ce^{-cx^2} + 4c^2x^2e^{-cx^2}$ and

$$\int \phi^* \hat{H} \phi \, d\tau = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} e^{-cx^2}(-2ce^{-cx^2} + 4c^2x^2e^{-cx^2})\,dx + 2\pi^2\nu^2 m\int_{-\infty}^{\infty} x^2 e^{-2cx^2}\,dx =$$

$$-\frac{2\hbar^2}{m}\int_0^{\infty}(-ce^{-2cx^2} + 2c^2x^2e^{-2cx^2})\,dx + 4\pi^2\nu^2 m\int_0^{\infty} x^2e^{-2cx^2}\,dx =$$

$$\frac{\hbar^2 c\pi^{1/2}}{m(2c)^{1/2}} - \frac{4c^2\hbar^2\pi^{1/2}}{4m(2c)^{3/2}} + \frac{4\pi^2\nu^2 m\pi^{1/2}}{4(2c)^{3/2}} = \frac{\hbar^2 c^{1/2}\pi^{1/2}}{2^{1/2}m} - \frac{c^{1/2}\hbar^2\pi^{1/2}}{2^{3/2}m} + \frac{\pi^{5/2}\nu^2 m}{8^{1/2}c^{3/2}} =$$

$$\frac{c^{1/2}\hbar^2\pi^{1/2}}{8^{1/2}m} + \frac{\pi^{5/2}\nu^2 m}{8^{1/2}c^{3/2}}.$$

8.4 *Hint*: Read carefully the statement of the variation theorem at the beginning of Sec. 8.1.

8.5 From the last paragraph of Sec. 6.2, we know ψ has the form $f(x)g(y)h(z)$, so we take $\phi = x(a-x)y(b-y)z(c-z)$, which satisfies the boundary conditions of being zero on the walls of the box. Since *f*, g, and *h* have the form of Eq. (8.11), we use integrals evaluated in the first example in Sec. 8.1. We have

$$\int \phi^* \phi \, d\tau = \int_0^c\int_0^b\int_0^a | f(x)g(y)h(z)|^2 \,dx\,dy\,dz = \int_0^a | f(x)|^2\,dx\int_0^b | g(y)|^2\,dy\int_0^c |(z)|^2\,dz =$$

$(a^5/30)(b^5/30)(c^5/30)$. Also,

$\hat{H}\phi = (\hat{H}_x + \hat{H}_y + \hat{H}_z)[f(x)g(y)h(z)] = gh\hat{H}_x f + fh\hat{H}_y g + fg\hat{H}_z h$ and

$$\int \phi^* \hat{H}\phi \, d\tau = \int_0^a f(x)^*\hat{H}_x f(x)\,dx\int_0^b | g(y)|^2\,dy\int_0^c | h(z)|^2\,dz +$$

$$\int_0^a |f(x)|^2\,dx\int_0^c |h(z)|^2\,dz\int_0^b g(y)^*\hat{H}_y g(y)\,dy +$$

$$\int_0^a |f(x)|^2\,dx\int_0^b |g(y)|^2\,dy\int_0^c h(z)^*\hat{H}_z h(z)\,dz$$

$= (\hbar^2a^3/6m)(b^5/30)(c^5/30) + (a^5/30)(c^5/30)(\hbar^2b^3/6m) + (a^5/30)(b^5/30)(\hbar^2c^3/6m)$. Then

$\int \phi^* \hat{H}\phi \, d\tau \Big/ \int \phi^*\phi \, d\tau = (\hbar^2a^3/6m)/(a^5/30) + (\hbar^2b^3/6m)/(b^5/30) + (\hbar^2c^3/6m)/(c^5/30) =$

$\frac{5h^2}{4\pi^2 m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right) = 0.12665\frac{h^2}{m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)$, compared with the true value

$\frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)$. The error is 1.3%.

8.6 **(a)** $\int \phi^*\phi\, d\tau = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^b (b-r)^2 r^2\, dr = 4\pi(b^5/3 - 2b^5/4 + b^5/5) = 2\pi b^5/15$.

Since $V = 0$ inside the box and ϕ is independent of the angles, Eq. (6.8) gives $\hat{H}\phi = -(\hbar^2/2m)(d^2/dr^2 + 2r^{-1}d/dr)(b-r) = \hbar^2/mr$. So $\int \phi^*\hat{H}\phi\, d\tau = (\hbar^2/m)\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^b (b-r)r^{-1}r^2\, dr = (4\pi\hbar^2/m)b^3(\frac{1}{2}-\frac{1}{3}) =$ $h^2b^3/6\pi m$ and $\int \phi^*\hat{H}\phi\, d\tau \Big/ \int \phi^*\phi\, d\tau = 5h^2/4\pi^2 mb^2 = 0.126651h^2/mb^2$, compared with the true value $0.125h^2/mb^2$.

(b) Your function must vanish at $r = b$ and should have no nodes for $r < b$.

8.7 To minimize *W*, we set $\partial W/\partial c = 0 = \hbar^2/2m - 45a/64c^4$, so $c = 45^{1/4}m^{1/4}a^{1/4}/32^{1/4}\hbar^{1/2}$. Then $W = (45^{1/4}m^{1/4}a^{1/4}/32^{1/4}\hbar^{1/2})(\hbar^2/2m) + (15a/64)32^{3/4}\hbar^{3/2}/45^{3/4}m^{3/4}a^{3/4} =$ $0.7259795a^{1/4}\hbar^{3/2}/m^{3/4}$.

8.8 **(a)** Since *V* is infinite for $x < 0$, ψ must be zero for $x < 0$. Since ψ must be continuous, it must be zero at $x = 0$.

(b) $\langle\phi\,|\,\phi\rangle = \int_0^\infty x^2 e^{-2cx}\, dx = \dfrac{2!}{(2c)^3} = \dfrac{1}{4c^3}$, where Eq. (A.8) was used.

$$\langle\phi|\hat{V}|\phi\rangle = \int_0^\infty bx^3 e^{-2cx}\, dx = b\frac{3!}{(2c)^4} = \frac{3b}{8c^4}.$$

$$\langle\phi|\hat{T}|\phi\rangle = -\frac{\hbar^2}{2m}\int_0^\infty xe^{-cx}\frac{d^2(xe^{-cx})}{dx^2}dx = -\frac{\hbar^2}{2m}\int_0^\infty (c^2x^2e^{-2cx} - 2cxe^{-2cx})\, dx = \frac{\hbar^2}{8mc}$$

$$\langle\phi|\hat{H}|\phi\rangle = \frac{3b}{8c^4} + \frac{\hbar^2}{8mc} \qquad W = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi\,|\,\phi\rangle} = \frac{3b}{2c} + \frac{\hbar^2 c^2}{2m}$$

$\dfrac{\partial W}{\partial c} = 0 = -\dfrac{3b}{2c^2} + \dfrac{\hbar^2 c}{m}$ and $c = \left(\dfrac{3bm}{2\hbar^2}\right)^{1/3}$. Substitution of this equation for *c* into *W* gives

$$W = \frac{b^{2/3}\hbar^{1/3}}{m^{1/3}}\left(\frac{3^{2/3}}{2^{2/3}} + \frac{3^{2/3}}{2^{5/3}}\right) = \frac{b^{2/3}\hbar^{1/3}}{m^{1/3}}(1.3103707 + 0.6551853) = 1.965556\frac{b^{2/3}\hbar^{1/3}}{m^{1/3}}.$$

The fact that $\langle V\rangle$ is twice $\langle T\rangle$ for this variation function is an example of the virial theorem (Sec. 14.4).

8.9 Each function can be multiplied by a normalization constant and then substituted into the form (8.1) of the variation theorem. The normalized functions (denoted by a prime) are $\phi_2' = N_2(f + cg)$ and $\phi_1' = N_1(af + bg) = N_1 a[f + (b/a)g]$. Defining $N_1 a = N_2$ and $b/a = c$, we see that these two functions are really the same function.

8.10 $\int \phi^* \phi \, d\tau = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-2cr} r^2 \sin\theta \, dr \, d\theta \, d\phi = 2(2\pi) \int_0^{\infty} e^{-2cr} r^2 \, dr = 4\pi[2/(2c)^3] = \pi/c^3$,

where Eq. A.8 was used. From (6.60) and (6.6),

$$\hat{H}\phi = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)e^{-cr} + 0 - \frac{Ze^2}{4\pi\varepsilon_0 r}e^{-cr} = -\frac{\hbar^2}{2\mu}(c^2 e^{-cr} - 2cr^{-1}e^{-cr}) - \frac{Ze^2}{4\pi\varepsilon_0 r}e^{-cr},$$

since the variation function ϕ is independent of the angles. So

$$\int \phi^* \hat{H}\phi \, d\tau = \int_0^{\infty}\left[-\frac{\hbar^2}{2\mu}(c^2 r^2 e^{-2cr} - 2cre^{-2cr}) - \frac{Ze^2}{4\pi\varepsilon_0} re^{-2cr}\right] dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi =$$

$$2(2\pi)\left[-\frac{\hbar^2}{2\mu}(2c^2/8c^3 - 2c/4c^2) - \frac{Ze^2}{(4\pi\varepsilon_0)4c^2}\right] = \frac{\pi\hbar^2}{2\mu c} - \frac{Ze^2\pi}{4\pi\varepsilon_0 c^2}$$, where we used (A.8). So

$W \equiv \int \phi^* \hat{H}\phi \, d\tau / \int \phi^* \phi \, d\tau = \hbar^2 c^2/2\mu - Ze^2 c/4\pi\varepsilon_0$ (Eq. 1). To minimize W, we take $\partial W/\partial c = 0 = \hbar^2 c/\mu - Ze^2/4\pi\varepsilon_0$. So $c = Ze^2\mu/4\pi\varepsilon_0\hbar^2$. Then Eq. 1 becomes $W = Z^2 e^4 \mu/2(4\pi\varepsilon_0)^2\hbar^2 - Z^2 e^4\mu/(4\pi\varepsilon_0)^2\hbar^2 = -Z^2 e^4\mu/2(4\pi\varepsilon_0)^2\hbar^2$. From (6.94), this is the exact ground-state hydrogenlike energy, so there is no error. This is because the variation function has the same form as the true ground-state wave function.

8.11 A reasonable guess might be the function $\phi = e^{-bx^2}$, which has the form of the ground-state harmonic-oscillator wave function. Then $\langle\phi|\hat{H}|\phi\rangle = \langle\phi|\hat{T}|\phi\rangle + \langle\phi|\hat{V}|\phi\rangle$. From the second example in Sec. 8.1 and Prob. 8.3, $\langle\phi|\hat{T}|\phi\rangle = (\pi/8)^{1/2}(\hbar^2/m)b^{1/2}$. Also,

$$\langle\phi|\hat{V}|\phi\rangle = c\int_{-\infty}^{\infty} x^4 e^{-2bx^2} dx = 2c\int_0^{\infty} x^4 e^{-2bx^2} dx = (3c/4)[\pi^{1/2}/(2b)^{5/2}] = 3c(\pi/2)^{1/2}/16b^{5/2}.$$

Also $\int \phi^* \phi \, d\tau = 2\int_0^{\infty} e^{-2bx^2} dx = \pi^{1/2}/(2b)^{1/2}$. So

$W = \langle\phi|\hat{H}|\phi\rangle/\langle\phi|\phi\rangle = \hbar^2 b/2m + 3c/16b^2$. To minimize W, we set $\partial W/\partial b = 0 = \hbar^2/2m - 6c/16b^3$. Then $b = (3/4)^{1/3}(cm)^{1/3}/\hbar^{2/3}$ and $W = (c^{1/3}\hbar^{4/3}/m^{2/3})(3/4)^{1/3}(\frac{1}{2} + \frac{1}{4}) = 0.68142(c^{1/3}\hbar^{4/3}/m^{2/3})$ compared with the Numerov value $0.66799c^{1/3}\hbar^{4/3}/m^{2/3}$.

8.12 **(a)** $\int \phi^* \phi \, d\tau = \int_0^l x^{2k}(l-x)^{2k} \, dk = l^{4k+1}\dfrac{[\Gamma(2k+1)]^2}{\Gamma(4k+2)}$. We have

$\hat{H}\phi = -(\hbar^2/2m)(d^2/dx^2)[x^k(l-x)^k] = -(\hbar^2/2m)(d/dx)[kx^{k-1}(l-x)^k - kx^k(l-x)^{k-1}] =$
$-(\hbar^2/2m)[k(k-1)x^{k-2}(l-x)^k - k^2 x^{k-1}(l-x)^{k-1} - k^2 x^{k-1}(l-x)^{k-1} + k(k-1)x^k(l-x)^{k-2}]$.

Then $\int \phi^* \hat{H}\phi \, d\tau =$

$$-\frac{\hbar^2}{2m}\int_0^l [k(k-1)x^{2k-2}(l-x)^{2k} - 2k^2 x^{2k-1}(l-x)^{2k-1} + k(k-1)x^{2k}(l-x)^{2k-2}] \, dk =$$

$$-\frac{\hbar^2}{2m}\left[\frac{k(k-1)l^{4k-1}\Gamma(2k-1)\Gamma(2k+1)}{\Gamma(4k)}-\frac{2k^2l^{4k-1}\Gamma(2k)\Gamma(2k)}{\Gamma(4k)}+\frac{k(k-1)l^{4k-1}\Gamma(2k+1)\Gamma(2k-1)}{\Gamma(4k)}\right]$$

When we evaluate $W \equiv \langle\phi\,|\,\hat{H}\,|\,\phi\rangle/\langle\phi\,|\,\phi\rangle$, we have the factor $\Gamma(4k+2)/\Gamma(4k)=(4k+1)\Gamma(4k+1)/\Gamma(4k)=(4k+1)(4k)\Gamma(4k)/\Gamma(4k)=4k(4k+1)$, where $\Gamma(z+1)=z\Gamma(z)$ was used twice. Then

$$W=-\frac{\hbar^2}{2m}\frac{4k(4k+1)}{l^2}\left[\frac{k(k-1)\Gamma(2k-1)}{\Gamma(2k+1)}-\frac{2k^2\Gamma(2k)\Gamma(2k)}{\Gamma(2k+1)\Gamma(2k+1)}+\frac{k(k-1)\Gamma(2k-1)}{\Gamma(2k+1)}\right]$$

$$W=-\frac{\hbar^2}{2m}\frac{4k(4k+1)}{l^2}\left[\frac{k(k-1)}{2k(2k-1)}-\frac{2k^2}{(2k)(2k)}+\frac{k(k-1)}{2k(2k-1)}\right]$$

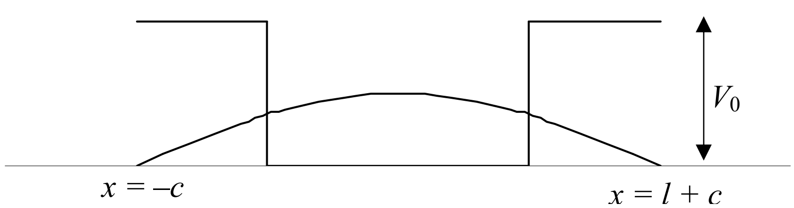
$$W=-\frac{\hbar^2k(4k+1)}{ml^2}\left[\frac{k-1}{2k-1}-1+\frac{k-1}{2k-1}\right]=\frac{h^2(4k^2+k)}{4\pi^2ml^2(2k-1)}$$, where $\Gamma(z+1)=z\Gamma(z)$ was used.

(b) To minimize W, we set

$$\frac{\partial W}{\partial k}=0=\frac{\hbar^2}{ml^2}\left(\frac{8k+1}{2k-1}-\frac{(4k^2+k)2}{(2k-1)^2}\right)=\frac{\hbar^2}{ml^2}\frac{(8k+1)(2k-1)-8k^2-2k}{(2k-1)^2}=\frac{\hbar^2}{ml^2}\frac{8k^2-8k-1}{(2k-1)^2}$$

so $8k^2-8k-1=0$ and $k=(8+96^{1/2})/16=1.11237244$. Then $W=0.125372(h^2/ml^2)$, compared with the exact ground-state energy $0.125(h^2/ml^2)$. The error is 0.30%.

8.13 (a)



$$\int|\phi|^2\,d\tau=\int_{-c}^{l+c}\sin^2\left[\frac{\pi(x+c)}{l+2c}\right]dx=\int_0^{l+2c}\sin^2\left[\frac{\pi z}{l+2c}\right]dz=\left[\frac{z}{2}-\frac{l+2c}{4\pi}\sin\frac{2\pi z}{l+2c}\right]\Bigg|_0^{l+2c}$$ and

$$\int|\phi|^2\,d\tau=\frac{l+2c}{2}$$ **(Eq. I)**, where we used the substitution $z\equiv x+c$ and Eq. (A.2). We have $\int\phi^*\hat{H}\phi\,d\tau=\int\phi^*\hat{T}\phi\,d\tau+\int\phi^*V\phi\,d\tau$. Now

$$\hat{T}\phi=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin\frac{\pi(x+c)}{l+2c}=\frac{h^2}{8\pi^2m}\left(\frac{\pi}{l+2c}\right)^2\sin\frac{\pi(x+c)}{l+2c}=\frac{h^2}{8m(l+2c)^2}\sin\frac{\pi(x+c)}{l+2c}$$

so $\int \phi^* \hat{T} \phi \, d\tau = \dfrac{h^2}{8m(l+2c)^2} \int_{-c}^{l+c} \sin^2\left[\dfrac{\pi(x+c)}{l+2c}\right] dx = \dfrac{h^2}{8m(l+2c)^2} \int |\phi|^2 \, d\tau =$

$\dfrac{h^2}{8m(l+2c)^2} \dfrac{l+2c}{2} = \dfrac{h^2}{16m(l+2c)}$, where Eq. I was used. Also

$\int \phi^* V \phi \, d\tau = V_0 \int_{-c}^{0} \phi^2 dx + V_0 \int_{l}^{l+c} \phi^2 dx = V_0 \int_{-c}^{l+c} \phi^2 dx - V_0 \int_{0}^{l} \phi^2 dx = V_0 \dfrac{l+2c}{2} - V_0 \int_0^l \phi^2 dx$,

where Eq. I was used. We have

$\int_0^l |\phi|^2 \, dx = \int_0^l \sin^2\left[\dfrac{\pi(x+c)}{l+2c}\right] dx = \int_c^{l+c} \sin^2\left[\dfrac{\pi z}{l+2c}\right] dz = \left[\dfrac{z}{2} - \dfrac{l+2c}{4\pi} \sin \dfrac{2\pi z}{l+2c}\right]\Bigg|_c^{l+c} =$

$\dfrac{l}{2} - \dfrac{l+2c}{4\pi}\left[\sin \dfrac{2\pi(l+c)}{l+2c} - \sin \dfrac{2\pi c}{l+2c}\right]$. Use of the identity

$\sin A - \sin B = 2\cos[\frac{1}{2}(A+B)]\sin[\frac{1}{2}(A-B)]$ gives

$\int_0^l |\phi|^2 \, dx = \dfrac{l}{2} - \dfrac{l+2c}{4\pi}\left[2\cos \dfrac{2\pi(l+2c)}{2(l+2c)} \sin \dfrac{2\pi l}{2(l+2c)}\right] = \dfrac{l}{2} + \dfrac{l+2c}{2\pi}\left[\sin \dfrac{\pi l}{l+2c}\right]$. So

$\int \phi^* V \phi \, d\tau = V_0 c - V_0 \dfrac{l+2c}{2\pi}\left[\sin \dfrac{\pi l}{l+2c}\right]$. Then $W \equiv \dfrac{\int \phi^* \hat{H} \phi \, d\tau}{\int |\phi|^2 \, d\tau} = \dfrac{\int \phi^* (\hat{T} + \hat{V}) \phi \, d\tau}{\int |\phi|^2 \, d\tau} =$

$\dfrac{2}{l+2c} \dfrac{h^2}{16m(l+2c)} + \dfrac{2}{l+2c}\left[V_0 c - V_0 \dfrac{l+2c}{2\pi}\left(\sin \dfrac{\pi l}{l+2c}\right)\right] =$

$\dfrac{h^2}{8m(l+2c)^2} + \dfrac{2V_0 c}{l+2c} - \dfrac{V_0}{\pi} \sin \dfrac{\pi l}{l+2c} = W$ **(Eq. II)**. To minimize *W*, we set

$\partial W / \partial c = 0 = -\dfrac{h^2}{2m(l+2c)^3} + \dfrac{2V_0}{l+2c} - \dfrac{4V_0 c}{(l+2c)^2} + \dfrac{2V_0 l}{(l+2c)^2} \cos \dfrac{\pi l}{l+2c}$. Multiplication by

$\frac{1}{2}(l+2c)^3 V_0^{-1}$ gives $0 = -\dfrac{h^2}{4mV_0} + (l+2c)^2 - 2c(l+2c) + l(l+2c)\cos \dfrac{\pi l}{l+2c} =$

$-\dfrac{h^2}{4mV_0} + (l+2c)l + l(l+2c)\cos \dfrac{\pi l}{l+2c}$. Division by *l* gives

$0 = -\dfrac{h^2}{4mlV_0} + l + 2c + (l+2c)\cos \dfrac{\pi l}{l+2c}$ **(Eq. III)**. Since V_0 has not been specified, we cannot go further.

(b) Substitution of V_0 into Eq. III gives $0 = -\dfrac{\pi^2}{20} l + l + 2c + (l+2c)\cos \dfrac{\pi l}{l+2c}$. We have two lengths, *c* and *l*. To relate *c* to *l*, we define *k* as $k \equiv c/l$. Substitution of $c = kl$ into the last equation gives after division by *l*, $0 = -\dfrac{\pi^2}{20} + 1 + 2k + (1+2k)\cos \dfrac{\pi}{1+2k}$. To solve this equation for *k*, we use the Solver in a spreadsheet or a graphing calculator with equation-solving capability. One finds that the only positive solution is *k* = 0.1920400. Substitution

of $c = kl = 0.1920400l$ and $V_0 = 5h^2/\pi^2 ml^2$ into Eq. II gives
$W = \dfrac{h^2}{8ml^2(1+2k)^2} + \dfrac{10h^2k}{\pi^2 ml^2(1+2k)} - \dfrac{5h^2}{\pi^3 ml^2}\sin\dfrac{\pi}{1+2k} = 0.0824\dfrac{h^2}{ml^2}$. The true result is $(2.814/4\pi^2)(h^2/ml^2) = 0.07128\,(h^2/ml^2)$. The percent error is 16%.

8.14 Since the ground state is nondegenerate, we have $c \equiv E_2 - E_1 > 0$ and $E_1 + c = E_2$. Let $b \equiv \frac{1}{2}c$. Then $b > 0$ and $E_1 + b < E_2 \le E_3 \le E_4 \cdots$ (Eq. 1). Use of Eq. 1 in Eq. (8.4) gives $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = |a_1|^2 E_1 + \sum_{k=2}^{\infty}|a_k|^2 E_k > |a_1|^2 E_1 + \sum_{k=2}^{\infty}|a_k|^2 (E_1 + b) =$
$E_1\sum_{k=1}^{\infty}|\,a_k\,|^2 + b\sum_{k=2}^{\infty}|\,a_k\,|^2$. We have $\sum_{k=1}^{\infty}|\,a_k\,|^2 = 1$ [Eq. (8.6)] and $b\sum_{k=2}^{\infty}|\,a_k\,|^2 > 0$, since $b > 0$ and at least one a_k is nonzero (since ϕ is not the ground-state wave function). Hence $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle > E_1$.

8.15 *Hint*: Consider the case where one of the parameters has a certain simple value.

8.16 **(a)** Let *f* obey the boundary conditions of being zero at $x = 0$ and at $x = l$. Let $u \equiv f$ and $d\mathsf{v} \equiv f''\,dx$. Then $du = f'\,dx$ and $\mathsf{v} = f'$. The integration-by-parts formula (7.16) gives $\int_0^l ff''\,dx = ff'\,|_0^l - \int_0^l (f')^2\,dx = -\int_0^l (f')^2\,dx = -\int_0^{l/2}(f')^2\,dx - \int_{l/2}^l (f')^2\,dx$. With $\phi = f$, where *f* is defined by (7.35), we have
$\langle\phi\,|\,\phi\rangle = \int_0^{l/2} x^2\,dx + \int_{l/2}^l (l-x)^2\,dx = \dfrac{1}{3}\dfrac{l^3}{8} + l^2(\tfrac{1}{2}l) - 2l(\tfrac{1}{2})(l^2 - \tfrac{1}{4}l^2) + \tfrac{1}{3}(l^3 - \tfrac{1}{8}l^3) = \dfrac{l^3}{12}$.
$\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = -(\hbar^2/2m)\int_0^l f^* f''\,dx = (\hbar^2/2m)\int_0^l (f')^2\,dx =$
$(\hbar^2/2m)\int_0^{l/2}(f')^2\,dx + (\hbar^2/2m)\int_{l/2}^l (f')^2\,dx = (\hbar^2/2m)\int_0^{l/2} 1^2\,dx + (\hbar^2/2m)\int_{l/2}^l (-1)^2\,dx =$
$\hbar^2 l/2m$. So $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle / \langle\phi\,|\,\phi\rangle = 6\hbar^2/ml^2 = 3h^2/2\pi^2 ml^2 = 0.152h^2/ml^2$, compared with the true ground-state energy $0.125h^2/ml^2$ (a 21.6% error). Alternatively, (7.85) and (7.86) give $f' = 1 - 2H(x - \tfrac{1}{2}l)$, so $f'' = -2(d/dx)H(x - \tfrac{1}{2}l) = -2\delta(x - \tfrac{1}{2}l)$. Then
$\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = -(\hbar^2/2m)\int_0^l f^* f''\,dx = (\hbar^2/m)\int_0^l f\,\delta(x - \tfrac{1}{2}l)\,dx = (\hbar^2/m) f(\tfrac{1}{2}l) = \hbar^2 l/2m$.

(b) $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = -(\hbar^2/2m)\int_{-\infty}^{\infty} f^* f''\,dx = (\hbar^2/2m)\int_{-\infty}^{\infty}(f')^2\,dx =$
$(\hbar^2/2m)\int_{-\infty}^{0}(f')^2\,dx + (\hbar^2/2m)\int_0^l (f')^2\,dx + (\hbar^2/2m)\int_l^{\infty}(f')^2\,dx = 0 + (\hbar^2/2m)\int_0^l (f')^2\,dx + 0$
$= (\hbar^2/2m)\int_0^l (l-2x)^2\,dx = (\hbar^2/2m)[l^2(l) - 4l(\tfrac{1}{2}l^2) + 4(\tfrac{1}{3}l^3)] = \hbar^2 l^3/6m$.

8.17 **(a)** $\langle\phi\,|\,\phi\rangle = \int_0^\infty e^{-2cr^2/a_0^2} r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi(1/2^2)\pi^{1/2}(a_0^2/2c)^{3/2} =$

$\pi^{3/2}a_0^3/2^{3/2}c^{3/2}$, where (A.10) was used. The variation function ϕ is a function of r only, so Eq. (6.8) gives:

$\hat{T}\phi = -(\hbar^2/2m)(d^2/dr^2 + 2r^{-1}d/dr)(e^{-cr^2/a_0^2}) =$

$-(\hbar^2/2m)e^{-cr^2/a_0^2}(4c^2r^2/a_0^4 - 2c/a_0^2 - 4c/a_0^2)$.

$\langle\phi\,|\,\hat{T}\,|\,\phi\rangle = -(\hbar^2/m)\int_0^\infty e^{-2cr^2/a_0^2}(2c^2r^4/a_0^4 - 3cr^2/a_0^2)\,dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi =$

$-4\pi(\hbar^2/m)[(2c^2/a_0^4)(3/8)\pi^{1/2}(a_0^2/2c)^{5/2} - (3c/a_0^2)(1/4)\pi^{1/2}(a_0^2/2c)^{3/2}] =$

$3a_0\hbar^2\pi^{3/2}/2^{5/2}mc^{1/2}$, where (A.10) was used. From (6.43),

$\langle\phi\,|\,V\,|\,\phi\rangle = -Z(e^2/4\pi\varepsilon_0)\int_0^\infty e^{-2cr^2/a_0^2} r\,dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = -4\pi Z(e^2/4\pi\varepsilon_0)(\tfrac{1}{2})\int_0^\infty e^{-2cw/a_0^2}dw =$

$-2\pi Z(e^2/4\pi\varepsilon_0)(-a_0^2/2c)e^{-2cw/a_0^2}\,|_0^\infty = -\pi Ze^2a_0^2/4\pi\varepsilon_0 c$.

So $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = \langle\phi\,|\,\hat{T}\,|\,\phi\rangle + \langle\phi\,|\,V\,|\,\phi\rangle = 3a_0\hbar^2\pi^{3/2}/2^{5/2}mc^{1/2} - \pi Ze^2a_0^2/4\pi\varepsilon_0 c$.

$W \equiv \langle\phi\,|\,\hat{H}\,|\,\phi\rangle / \langle\phi\,|\,\phi\rangle = 3\hbar^2 c/a_0^2 2m - 2^{3/2}Ze^2c^{1/2}/4\pi\varepsilon_0 a_0\pi^{1/2}$

Then $\partial W/\partial c = 0 = 3\hbar^2/2a_0^2 m - 2^{1/2}Ze^2/4\pi\varepsilon_0 a_0\pi^{1/2}c^{1/2}$ and

$c = [2^3Z^2e^4m^2/9\pi\hbar^4(4\pi\varepsilon_0)^2]a_0^2 = [2^3Z^2e^4m^2/9\pi\hbar^4(4\pi\varepsilon_0)^2][\hbar^4(4\pi\varepsilon_0)^2/m^2e^4] = 8Z^2/9\pi$

Substitution in W gives $W =$

$4\hbar^2Z^2/3\pi a_0^2 m - 8Z^2e^2/12\pi\varepsilon_0 a_0\pi = 4Z^2e^2/12\pi^2\varepsilon_0 a_0 - 8Z^2e^2/12\pi^2\varepsilon_0 a_0 = -4Z^2e^2/12\pi^2\varepsilon_0 a_0$

$= -0.42441Z^2e^2/4\pi\varepsilon_0 a_0$, compared with the exact value $-0.5Z^2e^2/4\pi\varepsilon_0 a_0$ for an infinitely heavy nucleus. The error is 15.1%.

(b) Time can be saved by suitably modifying the equations in (a). We have

$\langle\phi\,|\,\phi\rangle = \int_0^\infty e^{-2cr^2/a_0^2} r^2 dr \int_0^{2\pi}\int_0^\pi |Y_2^0|^2 \sin\theta\, d\theta\, d\phi = (1/2^2)\pi^{1/2}(a_0^2/2c)^{3/2}\cdot 1 =$

$\pi^{1/2}a_0^3/2^{7/2}c^{3/2}$, since Y_2^0 is normalized. Equations (6.8) and (6.13) give

$\hat{T}\phi = -(\hbar^2/2m)(\partial^2/\partial r^2 + 2r^{-1}\partial/\partial r - \hbar^{-2}r^{-2}\hat{L}^2)(e^{-cr^2/a_0^2}Y_2^0) =$

$-(\hbar^2/2m)[4c^2r^2/a_0^4 - 6c/a_0^2 - \hbar^{-2}r^{-2}2(3)\hbar^2]e^{-cr^2/a_0^2}Y_2^0$.

$\langle\phi\,|\,\hat{T}\,|\,\phi\rangle = -(\hbar^2/m)\int_0^\infty e^{-2cr^2/a_0^2}(2c^2r^4/a_0^4 - 3cr^2/a_0^2 - 3)\,dr \int_0^{2\pi}\int_0^\pi |Y_2^0|^2 \sin\theta\, d\theta\, d\phi =$

$-(\hbar^2/m)[(2c^2/a_0^4)(3/8)\pi^{1/2}(a_0^2/2c)^{5/2} - (3c/a_0^2)(1/4)\pi^{1/2}(a_0^2/2c)^{3/2} - 3(2^{-1})\pi^{1/2}a_0/(2c)^{1/2}]$

$= 27a_0\hbar^2\pi^{1/2}/2^{9/2}mc^{1/2}$.

$\langle\phi\,|\,V\,|\,\phi\rangle = -Z(e^2/4\pi\varepsilon_0)\int_0^\infty e^{-2cr^2/a_0^2} r\,dr \int_0^{2\pi}\int_0^\pi |Y_2^0|^2 \sin\theta\, d\theta\, d\phi =$

$-Z(e^2/4\pi\varepsilon_0)(\tfrac{1}{2})\int_0^\infty e^{-2cw/a_0^2}dw = -Z(e^2/4\pi\varepsilon_0)(\tfrac{1}{2})(-a_0^2/2c)e^{-2cw/a_0^2}\,|_0^\infty = -Ze^2a_0^2/4(4\pi\varepsilon_0)c$.

Then $\langle\phi\,|\,\hat{H}\,|\,\phi\rangle = \langle\phi\,|\,\hat{T}\,|\,\phi\rangle + \langle\phi\,|\,V\,|\,\phi\rangle = 27a_0\hbar^2\pi^{1/2}/2^{9/2}mc^{1/2} - Ze^2a_0^2/4(4\pi\varepsilon_0)c$.

$W \equiv \langle\phi\,|\,\hat{H}\,|\,\phi\rangle / \langle\phi\,|\,\phi\rangle = 27\hbar^2 c/2a_0^2 m - 2^{3/2}Ze^2c^{1/2}/4\pi\varepsilon_0 a_0\pi^{1/2}$. Then

$\partial W/\partial c = 0 = 27\hbar^2/2a_0^2 m - 2^{1/2}Ze^2/4\pi\varepsilon_0 a_0 \pi^{1/2}c^{1/2}$ and

$c = [2^3 Z^2 e^4 m^2/729\pi\hbar^4(4\pi\varepsilon_0)^2]a_0^2 = [2^3 Z^2 e^4 m^2/729\pi\hbar^4(4\pi\varepsilon_0)^2][(4\pi\varepsilon_0)^2\hbar^4/m^2e^4] = 8Z^2/729\pi$

$$W = \frac{27\hbar^2}{2a_0 m}\frac{me^2}{4\pi\varepsilon_0\hbar^2}\frac{8Z^2}{729\pi} - \frac{2^{3/2}Ze^2}{4\pi\varepsilon_0 a_0\pi^{1/2}}\frac{8^{1/2}Z}{27\pi^{1/2}} = \frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\frac{4-8}{27\pi} = -0.0471570\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}$$

The calculation gives an upper bound to the energy of the lowest level with $l = 2$, which is the $n = 3$ level. The true energy is $-(1/3^2)(Z^2e^2/8\pi\varepsilon_0 a_0) = -0.0555555(Z^2e^2/4\pi\varepsilon_0 a_0)$.

8.18 With the origin at the center of the box, the figure in Prob. 8.2 shows that V is an even function. As noted in Secs. 8.2 and 7.5, the ground-state wave function in this one-dimensional problem will be an even function and the first excited state will be an odd function. The $n = 2$ particle-in-a-box (PIB) wave function is an odd function (see Fig. 2.3) and so must be orthogonal to the true ground-state ψ, which is even. Hence using this function as the variation function will give an upper bound to the energy of the first excited state. Modifying the equations in the Prob. 8.2 solution, we have

$\langle\phi\,|\,\hat{T}\,|\,\phi\rangle = \langle\psi_{\text{PIB},2}\,|\,\hat{H}_{\text{PIB}}\,|\,\psi_{\text{PIB},2}\rangle = E_{\text{PIB},2}\langle\psi_{\text{PIB},2}\,|\,\psi_{\text{PIB},2}\rangle = E_{\text{PIB},2} = 2^2h^2/8ml^2 =$

$4\pi^2\hbar^2/2ml^2 = 19.73921\hbar^2/ml^2$.

$\langle\phi\,|\,V\,|\,\phi\rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin^2(2\pi x/l)\,dx = (V_0/l)[x - (l/4\pi)\sin 4\pi x/l)]|_{l/4}^{3l/4} =$

$V_0[\frac{3}{4} - \frac{1}{4} - (4\pi)^{-1}\sin(3\pi) + (4\pi)^{-1}\sin\pi] = 0.5V_0 = 0.5\hbar^2/ml^2$. Then

$\langle\phi_1\,|\,\hat{H}\,|\,\phi_1\rangle = (19.73921 + 0.50000)\hbar^2/ml^2 = 20.23921\hbar^2/ml^2$. The error is 0.016%.

8.19 **(a)** We use column 3, which has a zero, to expand the determinant:

$$\begin{vmatrix} 3 & 1 & i \\ -2 & 4 & 0 \\ 5 & 7 & \frac{1}{2} \end{vmatrix} = i\begin{vmatrix} -2 & 4 \\ 5 & 7 \end{vmatrix} - 0 + \frac{1}{2}\begin{vmatrix} 3 & 1 \\ -2 & 4 \end{vmatrix} = i(-14-20) + \frac{1}{2}(12+2) = 7 - 34i$$

(b) We begin by adding column 4 to columns 2 and 3 and adding -2.5 times column 4 to column 1. Then the fourth-row elements are used to expand the determinant:

$$\begin{vmatrix} 2 & 5 & 1 & 3 \\ 8 & 0 & 4 & -1 \\ 6 & 6 & 6 & 1 \\ 5 & -2 & -2 & 2 \end{vmatrix} = \begin{vmatrix} -5.5 & 8 & 4 & 3 \\ 10.5 & -1 & 3 & -1 \\ 3.5 & 7 & 7 & 1 \\ 0 & 0 & 0 & 2 \end{vmatrix} = 2\begin{vmatrix} -5.5 & 8 & 4 \\ 10.5 & -1 & 3 \\ 3.5 & 7 & 7 \end{vmatrix} = 2\begin{vmatrix} -5.5 & 4 & 4 \\ 10.5 & -4 & 3 \\ 3.5 & 0 & 7 \end{vmatrix} =$$

$$2\begin{vmatrix} -5.5 & 4 & 4 \\ 5 & 0 & 7 \\ 3.5 & 0 & 7 \end{vmatrix} = 2(-4)\begin{vmatrix} 5 & 7 \\ 3.5 & 7 \end{vmatrix} = 2(-4)[5(7) - 3.5(7)] = -84.$$

In the first third-order determinant, the third column was subtracted from the second and then the first row was added to the second row.

8.20 **(a)**

$$\begin{vmatrix} a & b & c & d & \cdots \\ 0 & f & g & h & \cdots \\ 0 & 0 & j & k & \cdots \\ 0 & 0 & 0 & m & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix} = a\begin{vmatrix} f & g & h & \cdots \\ 0 & j & k & \cdots \\ 0 & 0 & m & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} + 0 + 0 + 0 + \cdots = af\begin{vmatrix} j & k & \cdots \\ 0 & m & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = afj\begin{vmatrix} m & \cdots \\ \vdots & \ddots \end{vmatrix} =$$

etc., where each determinant was expanded using the elements of the first column.

(b) The expansion (8.22) of a second-order determinant has 2 terms. When we expand a third-order determinant, as in (8.23), we use 3 elements from the same row (or column), each element being multiplied by its cofactor, which is ± 1 times a determinant of order $3-1=2$, which has 2 terms; hence there are 3(2) = 6 terms in the expansion of a third-order determinant. When a fourth-order determinant is expanded, we use 4 elements from the same row (or column), each element being multiplied by its cofactor, which is ± 1 times a determinant of order 3, which has 3(2) terms. Hence there are 4(3)(2) terms in the expansion of a fourth-order determinant. Continuing in this manner, we see that an nth-order determinant has $n!$ terms.

8.21 Expanding using the elements of the top row, we get

$$\begin{vmatrix} a & b & 0 & \cdots & 0 \\ c & d & 0 & \cdots & 0 \\ 0 & 0 & e & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & \cdot & \cdots & \cdot \end{vmatrix} = a\begin{vmatrix} d & 0 & \cdots & 0 \\ 0 & e & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ 0 & \cdot & \cdots & \cdot \end{vmatrix} - b\begin{vmatrix} c & 0 & \cdots & 0 \\ 0 & e & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ 0 & \cdot & \cdots & \cdot \end{vmatrix}$$

Expanding the two determinants on the right of this equation using the top-row elements, we get

$$ad\begin{vmatrix} e & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} - bc\begin{vmatrix} e & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} = \begin{vmatrix} a & b \\ c & d \end{vmatrix}\begin{vmatrix} e & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

A similar expansion of the second determinant on the right of this last equation completes the proof.

8.22 **(a)** 123–even, 132–odd, 213–odd, 231–even, 321–odd, 312–even.

(b) The first term on the right of (8.24) corresponds to the even permutation 123 and has a plus sign. The second term $(-a_{11}a_{23}a_{32})$ has the odd permutation 132. The third term has the odd permutation 213. The fourth term $(a_{12}a_{23}a_{31})$ has the even permutation 231. The fifth term has the even permutation 312. The sixth term $(-a_{13}a_{22}a_{31})$ has the odd permutation 321.

(c) $\sum(\pm 1)a_{1i}a_{2j}\cdots a_{np}$, where $ij...p$ is one of the permutations of the integers $12\ldots n$, the sum is over the n! different permutations of these integers, and the sign of each term is positive or negative according to whether the permutation is even or odd, respectively.

8.23

$$\begin{matrix} 2 & -1 & 4 & 2 & 16 \\ 3 & 0 & -1 & 4 & -5 \\ 2 & 1 & 1 & -2 & 8 \\ -4 & 6 & 2 & 1 & 3 \end{matrix} \rightarrow \begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 3 & 0 & -1 & 4 & -5 \\ 2 & 1 & 1 & -2 & 8 \\ -4 & 6 & 2 & 1 & 3 \end{matrix} \rightarrow \begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 0 & \frac{3}{2} & -7 & 1 & -29 \\ 0 & 2 & -3 & -4 & -8 \\ 0 & 4 & 10 & 5 & 35 \end{matrix} \rightarrow$$

$$\begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 0 & 1 & -\frac{14}{3} & \frac{2}{3} & -\frac{58}{3} \\ 0 & 2 & -3 & -4 & -8 \\ 0 & 4 & 10 & 5 & 35 \end{matrix} \rightarrow \begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 0 & 1 & -\frac{14}{3} & \frac{2}{3} & -\frac{58}{3} \\ 0 & 0 & \frac{19}{3} & -\frac{16}{3} & \frac{92}{3} \\ 0 & 0 & \frac{86}{3} & \frac{7}{3} & \frac{337}{3} \end{matrix} \rightarrow \begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 0 & 1 & -\frac{14}{3} & \frac{2}{3} & -\frac{58}{3} \\ 0 & 0 & 1 & -\frac{16}{19} & \frac{92}{19} \\ 0 & 0 & \frac{86}{3} & \frac{7}{3} & \frac{337}{3} \end{matrix} \rightarrow$$

$$\begin{matrix} 1 & -\frac{1}{2} & 2 & 1 & 8 \\ 0 & 1 & -\frac{14}{3} & \frac{2}{3} & -\frac{58}{3} \\ 0 & 0 & 1 & -\frac{16}{19} & \frac{92}{19} \\ 0 & 0 & 0 & \frac{1509}{57} & -\frac{1509}{57} \end{matrix}$$

The bottom row is $(1509/57)x_4 = -1509/57$, so $x_4 = -1$.

The third row is $x_3 - (16/19)x_4 = 92/19 = x_3 + 16/19$ and $x_3 = 4$.

The second row is $x_2 - (14/3)x_3 + (2/3)x_4 = -58/3 = x_2 - 56/3 - 2/3$ and $x_2 = 0$.

The first row is $x_1 - \frac{1}{2}x_2 + 2x_3 + x_4 = 8 = x_1 + 0 + 8 - 1$ and $x_1 = 1$.

8.24 Division by a very small coefficient produces very large coefficients, which when added or subtracted from coefficients that are not large can lead to large errors in the solution, due to the fact that the computer or calculator uses a limited number of significant figures to represent numbers. For example, suppose the equations are $1\times10^{-10}x_1 + x_2 = 1$ and $x_1 - x_2 = 0$. Further suppose that the computer is limited to 8 significant figures for each number. The correct solution is $x_1 = x_2 = 1/(1+1\times10^{-10}) = 0.9999999999$. If we divide the first equation by the x_1 coefficient we get $x_1 + 10^{10}x_2 = 10^{10}$ (Eq. 1) and subtracting this equation from the second equation, we get $-(1+10^{10})x_2 = -10^{10}$ (Eq. 2). Because the computer is limited to 8 significant figures, the coefficient of x_2 (whose accurate value is $-1.0000000001\times10^{10}$) is stored as -1.0000000×10^{10} and Eq. 2 becomes $-10^{10}x_2 = -10^{10}$, with solution $x_2 = 1$. When this slightly inaccurate value is substituted into Eq. 1, we get $x_1 + 10^{10} = 10^{10}$, which gives the very inaccurate result $x_1 = 0$.

8.25

$$\begin{vmatrix} 2 & 5 & 1 & 3 \\ 8 & 0 & 4 & -1 \\ 6 & 6 & 6 & 1 \\ 5 & -2 & -2 & 2 \end{vmatrix} = 2\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 8 & 0 & 4 & -1 \\ 6 & 6 & 6 & 1 \\ 5 & -2 & -2 & 2 \end{vmatrix} = 2\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 0 & -20 & 0 & -13 \\ 0 & -9 & 3 & -8 \\ 0 & -14.5 & -4.5 & -5.5 \end{vmatrix} =$$

$$2(-20)\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 0 & 1 & 0 & 0.65 \\ 0 & -9 & 3 & -8 \\ 0 & -14.5 & -4.5 & -5.5 \end{vmatrix} = 2(-20)\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 0 & 1 & 0 & 0.65 \\ 0 & 0 & 3 & -2.15 \\ 0 & 0 & -4.5 & 3.925 \end{vmatrix} =$$

$$2(-20)3\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 0 & 1 & 0 & 0.65 \\ 0 & 0 & 1 & -0.7166\ldots \\ 0 & 0 & -4.5 & 3.925 \end{vmatrix} = -120\begin{vmatrix} 1 & 2.5 & 0.5 & 1.5 \\ 0 & 1 & 0 & 0.65 \\ 0 & 0 & 1 & -0.7166\ldots \\ 0 & 0 & 0 & 0.7 \end{vmatrix} = -120(0.7) = -84$$

8.26 **(a)** For a nontrivial solution to exist, the coefficient determinant must be zero. The coefficient determinant is 8(4) – (–3)(–15) = –13, so the solution is $x = 0$, $y = 0$.

(b) The coefficient determinant is $-4(\frac{15}{4}) - 5i(3i) = -15 + 15 = 0,$ so a nontrivial solution exists. (Note also that the second equation is the first equation multiplied by $-5i/4$.) Let $y = k.$ Then the first equation gives $x = \frac{3}{4}iy = \frac{3}{4}ik,$ so the solution is $x = \frac{3}{4}ik,\ \ y = k,$ where k is any number. (Alternatively, we can take $x = 3ic,\ \ y = 4c,$ where c is an arbitrary constant.) Use of the second equation instead of the first gives the same solution.

8.27 **(a)**

$$\begin{matrix} 1 & 2 & 3 & 0 \\ 3 & 1 & 2 & 0 \\ 2 & 3 & 1 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 2 & 3 & 0 \\ 0 & -5 & -7 & 0 \\ 0 & -1 & -5 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 2 & 3 & 0 \\ 0 & 1 & \frac{7}{5} & 0 \\ 0 & -1 & -5 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 0 & \frac{1}{5} & 0 \\ 0 & 1 & \frac{7}{5} & 0 \\ 0 & 0 & -\frac{18}{5} & 0 \end{matrix} \rightarrow$$

$$\begin{matrix} 1 & 0 & \frac{1}{5} & 0 \\ 0 & 1 & \frac{7}{5} & 0 \\ 0 & 0 & 1 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{matrix}$$

The last row gives $z = 0$. The first two rows give $x = 0$ and $y = 0$. As a check one finds that the coefficient determinant is nonzero.

(b)

$$\begin{matrix} 1 & 2 & 3 & 0 \\ 1 & -1 & 1 & 0 \\ 7 & -1 & 11 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 2 & 3 & 0 \\ 0 & -3 & -2 & 0 \\ 0 & -15 & -10 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 2 & 3 & 0 \\ 0 & 1 & \frac{2}{3} & 0 \\ 0 & -15 & -10 & 0 \end{matrix} \rightarrow \begin{matrix} 1 & 0 & \frac{5}{3} & 0 \\ 0 & 1 & \frac{2}{3} & 0 \\ 0 & 0 & 0 & 0 \end{matrix}$$

The last row reads 0 = 0, indicating that z can be assigned an arbitrary value. Let $z = k$, where k is an arbitrary constant. Then the first row gives $x = -5k/3$ and the second row gives $y = -2k/3$. As a check the coefficient determinant is zero, showing there is a nontrivial solution.

8.28 A C++ program that avoids division by a coefficient that is zero or very small (see Prob. 8.24) is the following:

```
#include <iostream>
#include <cmath>
using namespace std;
int i, j, n, s, w, k, r;
double a[11][11], b[11], x[11], temp[11][11], tt, fac, sum, denom;
int main() {
    cout  <<  "Enter N (less than 11):  ";
    cin  >>  n;
    for (i=1;  i<=n;  i=i+1)  {
       for (j=1;  j<=n;  j=j+1)  {
          cout  <<  "i =  "  <<  i  <<  "  j =  "  << j  <<  "  Enter coef. a(i,j)  ";
          cin  >> a[i][j];
       }
       cout   <<  "i =  "  << i  <<  "  Enter b(i) ";
       cin  >>  b[i];
    }
    for (i=1; i<=n-1; i=i+1) {
       if (fabs(a[i][i]) < 1e-6) {
          for (s=i+1;  s<=n;  s=s+1) {
```

```
            if (fabs(a[s][i])<1e-6)
               continue;
            for (w=i;  w<=n;  w=w+1) {
               temp[i][w] = a[i][w];
               a[i][w] = a[s][w];
               a[s][w] = temp[i][w];
            }
            tt = b[i];
            b[i] = b[s];
            b[s] = tt;
            goto label1;
         }
      cout  <<  "Failed; division by small number problem";
      return 0;
      }
      label1: denom=a[i][i];
      for (j=1; j<=n; j=j+1) {
         a[i][j]=a[i][j]/denom;
      }
      b[i]=b[i]/denom;
      for (k=1; k<= n-i; k=k+1) {
         fac=a[i+k][i];
         for (j=i;  j<=n;  j=j+1) {
            a[i+k][j]=a[i+k][j]-fac*a[i][j];
         }
         b[i+k]=b[i+k]-fac*b[i];
      }
   }
   x[n]=b[n]/a[n][n];
   for (k=1; k<=n-1;  k=k+1) {
      sum=0;
      for (r=n-k+1; r<=n; r=r+1) {
         sum=sum+a[n-k][r]*x[r];
      }
      x[n-k]=b[n-k] - sum;
   }
   for (k=1; k<=n; k=k+1) {
      cout <<  "k  =  " <<  k  <<  "  x(k) =  "  << x[k]  <<endl;
   }
   return 0;
```

}

8.29 **(a)** F; **(b)** T; **(c)** F; **(d)** F.

8.30 We have $\langle f_2 \mid f_1 \rangle = \langle f_1 \mid f_2 \rangle^* = b^* = b$, since b is real. Also,
$\langle f_2 \mid \hat{H} \mid f_1 \rangle = \langle f_1 \mid \hat{H} \mid f_2 \rangle^* = a^* = a$, since a is real and $\hat{H}$ is Hermitian. The secular equation (8.56) is

$$\begin{vmatrix} 4a-2bW & a-bW \\ a-bW & 6a-3bW \end{vmatrix} = 0 = (4a-2bW)(6a-3bW)-(a-bW)^2 =$$

$$5b^2W^2 - 22abW + 23a^2$$

$$W = \left(22ab \pm \sqrt{484a^2b^2 - 460b^2a^2}\right)\Big/10b^2. \quad W_1 = 1.710102a/b, \quad W_2 = 2.689898a/b\,.$$

The set of equations (8.54) for W_1 is

$$(4a-2bW_1)c_1 + (a-bW_1)c_2 = 0 \qquad 0.579796ac_1 - 0.710102ac_2 = 0$$
$$(a-bW_1)c_1 + (6a-3bW_1)c_2 = 0 \qquad -0.710102ac_1 + 0.869694ac_2 = 0$$

Either the first or the second equation gives $c_1 = 1.224745c_2$. Normalization gives
$\langle \phi \mid \phi \rangle = 1 = \langle c_1 f_1 + c_2 f_2 \mid c_1 f_1 + c_2 f_2 \rangle = c_1^2 \langle f_1 \mid f_1 \rangle + 2c_1c_2 \langle f_1 \mid f_2 \rangle + c_2^2 \langle f_2 \mid f_2 \rangle =$
$(1.224745)^2 c_2^2(2b) + 2(1.224745)c_2c_2b + c_2^2(3b)$ so $8.449491bc_2^2 = 1$ and
$c_2 = 0.344021b^{-1/2}$. $c_1 = 1.224745c_2 = 0.421338b^{-1/2}$. The approximation to the ground-state wave function is $\phi = 0.421338b^{-1/2} f_1 + 0.344021b^{-1/2} f_2$.
The set of equations (8.54) for W_2 is

$$-1.379796ac_1 - 1.689898ac_2 = 0$$
$$-1.689898ac_1 - 2.069694ac_2 = 0$$

Either the first or the second equation gives $c_1 = -1.224745c_2$. Normalization gives
$1 = c_1^2 \langle f_1 \mid f_1 \rangle + 2c_1c_2 \langle f_1 \mid f_2 \rangle + c_2^2 \langle f_2 \mid f_2 \rangle =$
$(-1.224745)^2 c_2^2(2b) - 2(1.224745)c_2c_2b + c_2^2(3b) = 2.050510bc_2^2$, so $c_2 = 0.698343b^{-1/2}$
and $c_1 = -0.855292b^{-1/2}$. The approximation to the first excited-state wave function is
$\phi = -0.855292b^{-1/2} f_1 + 0.698343b^{-1/2} f_2$.

8.31 We have $H_{21} = H_{12}^* = H_{12}$, since $\hat{H}$ is Hermitian and the basis functions are real. Also
$S_{21} = \langle f_2 \mid f_1 \rangle = \langle f_1 \mid f_2 \rangle^* = \langle f_1 \mid f_2 \rangle$. The secular equation is

$$\begin{vmatrix} H_{11}-S_{11}W & H_{12}-S_{12}W \\ H_{12}-S_{12}W & H_{11}-S_{11}W \end{vmatrix} = (H_{11}-S_{11}W)^2 - (H_{12}-S_{12}W)^2 = 0$$

$(H_{11}-S_{11}W)^2 = (H_{12}-S_{12}W)^2, \quad H_{11}-S_{11}W = \pm(H_{12}-S_{12}W)$ (Eq. 1),

$H_{11} \mp H_{12} = (S_{11} \mp S_{12})W$, $\quad W = (H_{11} \mp H_{12})/(S_{11} \mp S_{12})$ (Eq. 2)

The equations of (8.54) are

$(H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 = 0$

$(H_{12} - S_{12}W)c_1 + (H_{11} - S_{11}W)c_2 = 0$

The first equation gives $c_2/c_1 = -(H_{11} - S_{11}W)/(H_{12} - S_{12}W) = -1(\pm 1) = \mp 1$ (Eq. 3), where Eq. 1 was used. The upper sign in Eq. 3 goes with the upper sign in Eq. 2.

8.32 **(a)** The particle-in-a-box (PIB) wave functions f_1 and f_2 are even functions (Fig. 2.3) if the origin is put at the center of the box. The potential energy in Prob. 8.2 is an even function and each wave function in this one-dimensional problem will be either even or odd (Secs. 8.2 and 7.5), with the lowest state being even, the first excited state being odd, the second excited state being even, etc. Because f_1 and f_2 are even, we will get upper bounds to the lowest two states of even parity, which are the states with energies E_1 and E_3.

(b) The (PIB) wave functions f_1 and f_2 are eigenfunctions of a Hermitian operator $\hat{H}$ and have different eigenvalues, so they must be orthogonal.

(c) The PIB Hamiltonian has $V = 0$ inside the box so $\hat{H}_{\text{PIB}} = \hat{T}$ inside the box and since f_1 and f_2 are PIB eigenfunctions with quantum numbers $n = 1$ and 3, we have

$\hat{T}f_1 = \varepsilon_1 f_1 = (h^2/8ml^2)f_1$ and $\hat{T}f_2 = \varepsilon_2 f_2 = (9h^2/8ml^2)f_2$. So

$\varepsilon_1 = h^2/8ml^2 = 4\pi^2\hbar^2/8ml^2 = 4.934802\hbar^2/ml^2 = 4.934802V_0$ and

$\varepsilon_2 = 9h^2/8ml^2 = (9)4\pi^2\hbar^2/8ml^2 = 44.413220\hbar^2/ml^2 = 44.413220V_0$. Also

$\langle f_i | \hat{T} | f_j \rangle = \varepsilon_j \langle f_i | f_j \rangle = \varepsilon_j \delta_{ij}$, $i = 1, 2$.

(d) Because of orthonormality of the PIB functions, $S_{ij} = \delta_{ij}$. We have

$H_{ij} = T_{ij} + V_{ij} = \delta_{ij}\varepsilon_j + V_{ij}$ (Eq. 1). The integral $\langle f_1 | V | f_1 \rangle$ was found in Prob. 8.2 and is

$V_{11} = \langle f_1 | V | f_1 \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin^2(\pi x/l)\, dx = 0.818310V_0 = 0.818310\hbar^2/ml^2$.

$V_{22} = \langle f_2 | V | f_2 \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin^2(3\pi x/l)\, dx = (V_0/l)[x - (l/6\pi)\sin 6\pi x/l)]\Big|_{l/4}^{3l/4} =$

$V_0[\frac{3}{4} - \frac{1}{4} - (6\pi)^{-1}\sin(9\pi/2) + (6\pi)^{-1}\sin(3\pi/2)] = V_0[\frac{1}{2} - (3\pi)^{-1}] = 0.393897V_0 =$

$0.393897\hbar^2/ml^2$. Finally, $V_{12} = V_{21} = \langle f_1 | V | f_2 \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin(\pi x/l)\sin(3\pi x/l)\, dx =$

$(V_0/l)[(l/2\pi)\sin(2\pi x/l) - (l/4\pi)\sin(4\pi x/l)]\Big|_{l/4}^{3l/4} = -(V_0/\pi) = -0.318310\hbar^2/ml^2$.

Equation 1 gives $H_{11} = \varepsilon_1 + V_{11} = 4.934802V_0 + 0.818310V_0 = 5.753112V_0$,

$H_{12} = H_{21} = 0 + V_{12} = -0.318310V_0$,

$H_{22} = \varepsilon_2 + V_{22} = 44.413220V_0 + 0.393897V_0 = 44.807117V_0$. The secular equation is

$$\begin{vmatrix} H_{11}-S_{11}W & H_{12}-S_{12}W \\ H_{21}-S_{21}W & H_{22}-S_{22}W \end{vmatrix} = \begin{vmatrix} 5.753112V_0 - W & -0.318310V_0 \\ -0.318310V_0 & 44.807117V_0 - W \end{vmatrix} = 0 \text{ and}$$

$W^2 - 50.560229WV_0 + 257.6790V_0^2 = 0$. The roots are $44.80971V_0 = 44.80971\hbar^2/ml^2$ and $5.750517\hbar^2/ml^2$. The ground-state energy error is much less than when only f_1 was used. To find the ground-state ϕ_1, we solve (8.54) with $W = 5.750517V_0$, which is

$$0.002595V_0c_1 - 0.318310V_0c_2 = 0$$
$$-0.318310V_0c_1 + 39.056600V_0c_2 = 0$$

The second equation gives $c_2 = 0.0081500c_1$. The normalization condition is
$\langle\phi\,|\,\phi\rangle = 1 = \langle c_1f_1 + c_2f_2\,|\,c_1f_1 + c_2f_2\rangle = c_1^2\langle f_1\,|\,f_1\rangle + 2c_1c_2\langle f_1\,|\,f_2\rangle + c_2^2\langle f_2\,|\,f_2\rangle = c_1^2 + c_2^2$,
so $1 = c_1^2 + (0.0081500)^2c_1^2$ and $c_1 = 0.999967,\ c_2 = 0.0081497$.
$\phi_1 = 0.999967f_1 + 0.0081497f_2$.

To find ϕ for the E_3 state, we solve (8.54) with $W = 44.80971V_0$, which is

$$-39.05660V_0c_1 - 0.318310V_0c_2 = 0$$
$$-0.318310V_0c_1 - 0.00259V_0c_2 = 0$$

The first equation gives $c_1 = -0.00814996c_2$. The normalization condition gives
$1 = c_1^2 + c_2^2 = (-0.00814996)^2c_2^2 + c_2^2$, and $c_2 = 0.999967,\ c_1 = -0.0081497$.
$\phi = -0.0081497f_1 + 0.999967f_2$.

(e) We could take $f_1,\ f_2,\ f_3$ as the $n = 1, 2, 3$ PIB wave functions.

8.33 $f_1 = x^2(l-x), \quad f_2 = x(l-x)^2$

$S_{11} = \langle x^2(l-x)\,|\,x^2(l-x)\rangle = \int_0^l (x^4l^2 - 2lx^5 + x^6)\,dx = l^7(\frac{1}{5} - \frac{2}{6} + \frac{1}{7}) = l^7/105$

$S_{22} = \langle x(l-x)^2\,|\,x(l-x)^2\rangle = \int_0^l (x^2l^4 - 4l^3x^3 + 6l^2x^4 - 4lx^5 + x^6)\,dx = l^7(\frac{1}{3} - \frac{4}{4} + \frac{6}{5} - \frac{4}{6} + \frac{1}{7})$
$= l^7/105$

$S_{12} = S_{21} = \langle x^2(l-x)\,|\,x(l-x)^2\rangle = \int_0^l (l^3x^3 - 3l^2x^4 + 3lx^5 - x^6)\,dx = l^7(\frac{1}{4} - \frac{3}{5} + \frac{3}{6} - \frac{1}{7}) = l^7/140$

$\hat{H}f_1 = -(\hbar^2/2m)(d^2/dx^2)(x^2l - x^3) = (\hbar^2/m)(3x - l)$

$\hat{H}f_2 = -(\hbar^2/2m)(d^2/dx^2)(xl^2 - 2lx^2 + x^3) = (\hbar^2/m)(2l - 3x)$

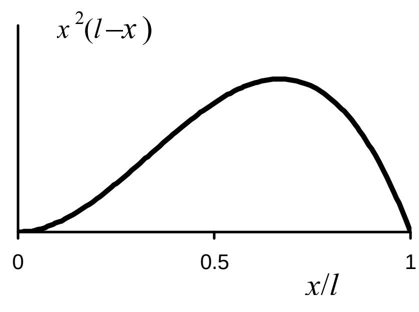
$H_{11} = \langle f_1\,|\,\hat{H}\,|\,f_1\rangle = (\hbar^2/m)\langle x^2(l-x)\,|\,3x - l\rangle = (\hbar^2/m)\int_0^l (-l^2x^2 + 4lx^3 - 3x^4)\,dx$
$= (\hbar^2l^5/m)(-\frac{1}{3} + \frac{4}{4} - \frac{3}{5}) = \frac{1}{15}l^5\hbar^2/m$

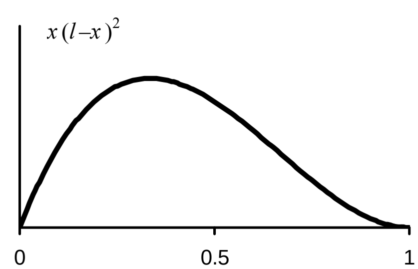
$H_{22} = \langle f_2\,|\,\hat{H}\,|\,f_2\rangle = (\hbar^2/m)\langle x(l-x)^2\,|\,2l - 3x\rangle = (\hbar^2/m)\int_0^l (2l^3x - 7l^2x^2 + 8lx^3 - 3x^4)\,dx$
$= (\hbar^2/m)l^5(\frac{2}{2} - \frac{7}{3} + \frac{8}{4} - \frac{3}{5}) = \frac{1}{15}l^5\hbar^2/m$

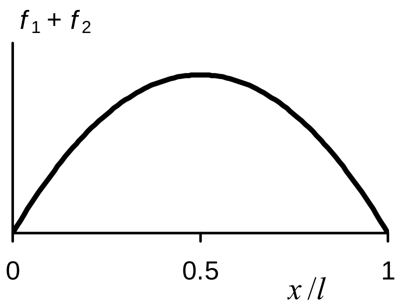
$H_{12} = \langle f_1 | \hat{H} | f_2 \rangle = (\hbar^2/m)\langle x^2(l-x) | 2l-3x \rangle = (\hbar^2/m)\int_0^l (2l^2x^2 - 5lx^3 + 3x^4)\, dx$
$= (\hbar^2/m)l^5(\frac{2}{3} - \frac{5}{4} + \frac{3}{5}) = \frac{1}{60}l^5\hbar^2/m$

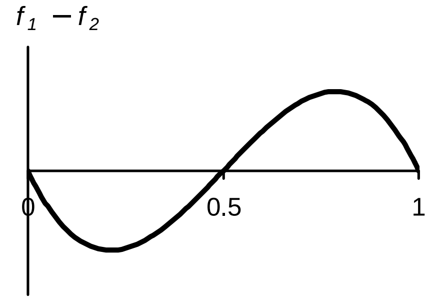
Since $H_{11} = H_{22}$ and $S_{11} = S_{22}$, the results of Prob. 8.30 apply. We have $W = (H_{11} - H_{12})/(S_{11} - S_{12}) = (\hbar^2 l^5/m)(\frac{1}{15} - \frac{1}{60})/(l^7/105 - l^7/140) = 21(\hbar^2/ml^2)$ and $W = (H_{11} + H_{12})/(S_{11} + S_{12}) = (\hbar^2 l^5/m)(\frac{1}{15} + \frac{1}{60})/(l^7/105 + l^7/140) = 5(\hbar^2/ml^2)$. The true energies are $E_1 = h^2/8ml^2 = 4\pi^2\hbar^2/8ml^2 = 4.93480\hbar^2/ml^2$ and $E_2 = 4E_1 = 19.73921\hbar^2/ml^2$. The errors are 1.3% and 6.4%.

From Eq. 3 of Prob. 8.30, the ground-state ϕ has $c_2/c_1 = \mp 1$, where the plus sign goes with the ground state. Normalization gives $\langle \phi | \phi \rangle = 1 = \langle c_1 f_1 + c_2 f_2 | c_1 f_1 + c_2 f_2 \rangle = c_1^2 S_{11} + 2c_1c_2S_{12} + c_2^2 S_{22} = c_1^2(S_{11} \mp 2S_{12} + S_{22}) = 2c_1^2(S_{11} \mp S_{12})$, so $c_1 = [2(S_{11} \mp S_{12})]^{-1/2}$. For the ground state, $\phi_1 = (f_1 + f_2)/[2(S_{11} + S_{12})]^{1/2}$. For the first excited state $\phi_2 = (f_1 - f_2)/[2(S_{11} - S_{12})]^{1/2}$. The nodes of $f_1 = x^2(l-x)$ are at 0 and *l*. To find its extrema, we set $f_1' = 0 = 2xl - 3x^2$ and we get $x = 0$ and $x = \frac{2}{3}l$. Since f_1 is zero at the ends of the box and is positive everywhere inside the box, $x = \frac{2}{3}l$ must be a maximum. The nodes of $f_2 = x(l-x)^2$ are at 0 and *l*. We set $f_2' = 0 = 3x^2 - 4lx + l^2$ and get $x = l$ and $x = \frac{1}{3}l$. Since f_2 is zero at the ends of the box and is positive everywhere inside the box, $x = \frac{1}{3}l$ must be a maximum. (A little thought shows that if we flip the f_1 graph about the center of the box, we get the f_2 graph.) The ground state is $N(f_1 + f_2) = N[x^2(l-x) + x(l-x)^2] = Nx(l-x)[x + (l-x)] = Nlx(l-x)$. This parabolic function has nodes at 0 and *l* and by setting its derivative equal to zero, we find a maximum at the center of the box. The first excited state is $N'(f_1 - f_2) = N'[x^2(l-x) - x(l-x)^2] = N'x(l-x)[x - (l-x)] = N'x(l-x)(2x-l)$. This function has nodes at 0, *l*, and *l*/2. Its derivative is zero at $x = (\frac{1}{2} + \sqrt{3}/6)l = 0.79l$ and at $x = (\frac{1}{2} - \sqrt{3}/6)l = 0.21l$. Since this function is zero at *x* = 0 and is negative for very small *x*, 0.21*l* is a minimum. Sketches (not to scale) are









8.34 $x = x' + \frac{1}{2}l$ and the functions are $f_1 = (x' + \frac{1}{2}l)(\frac{1}{2}l - x')$, $f_2 = (x' + \frac{1}{2}l)^2(\frac{1}{2}l - x')^2$, $f_3 = (x' + \frac{1}{2}l)(\frac{1}{2}l - x')(-x')$, $f_4 = (x' + \frac{1}{2}l)^2(\frac{1}{2}l - x')^2(-x')$. Replacing x' by $-x'$, we see that f_1 is even, f_2 is even, f_3 is odd, and f_4 is odd.

8.35 $S_{12} = \langle f_1 | f_2 \rangle = \langle x(l-x) | x^2(l-x)^2 \rangle = \int_0^l (-x^6 + 3lx^5 - 3l^2x^4 + l^3x^3)\, dx =$
$l^7(-\frac{1}{7} + \frac{3}{6} - \frac{3}{5} + \frac{1}{4}) = l^7/140.$
$S_{22} = \langle f_2 | f_2 \rangle = \langle x^2(l-x)^2 | x^2(l-x)^2 \rangle = \int_0^l (x^8 - 4lx^7 + 6l^2x^6 - 4l^3x^5 + l^4x^4)\, dx =$
$l^9(\frac{1}{9} - \frac{4}{8} + \frac{6}{7} - \frac{4}{6} + \frac{1}{5}) = l^9/630$.
$\hat{H}f_1 = -(\hbar^2/2m)(d^2/dx^2)(xl - x^2) = \hbar^2/m$.
$H_{12} = H_{21} = \langle f_2 | \hat{H} | f_1 \rangle = \langle x^2(l-x)^2 | \hbar^2/m \rangle = (\hbar^2/m)\int_0^l (x^4 - 2lx^3 + l^2x^2)\, dx =$
$(\hbar^2 l^5/m)(\frac{1}{5} - \frac{2}{4} + \frac{1}{3}) = \hbar^2 l^5/30m$.
$\hat{H}f_2 = -(\hbar^2/2m)(d^2/dx^2)(x^2l^2 - 2x^3l + x^4) = -(\hbar^2/m)(l^2 - 6xl + 6x^2)$
$H_{22} = \langle f_2 | \hat{H} | f_2 \rangle = -(\hbar^2/m)\langle x^2(l-x)^2 | l^2 - 6xl + 6x^2 \rangle =$
$-(\hbar^2/m)\int_0^l (6x^6 - 18lx^5 + 19l^2x^4 - 8l^3x^3 + l^4x^2)\, dx =$
$-(\hbar^2 l^7/m)(\frac{6}{7} - \frac{18}{6} + \frac{19}{5} - \frac{8}{4} + \frac{1}{3}) = \hbar^2 l^7/105m$.

8.36

$$0 = \begin{vmatrix} H_{33} - S_{33}W & H_{34} - S_{34}W \\ H_{43} - S_{43}W & H_{44} - S_{44}W \end{vmatrix} = \begin{vmatrix} \dfrac{\hbar^2 l^5}{40m} - \dfrac{l^7}{840}W & \dfrac{\hbar^2 l^7}{280m} - \dfrac{l^9}{5040}W \\ \dfrac{\hbar^2 l^7}{280m} - \dfrac{l^9}{5040}W & \dfrac{\hbar^2 l^9}{1260m} - \dfrac{l^{11}}{27720}W \end{vmatrix}$$

We multiply row 1 by $5040m/l^5$ and row 2 by $55440m/l^7$ to get

$$0 = \begin{vmatrix} 126\hbar^2 - 6ml^2W & 18\hbar^2 l^2 - ml^4 W \\ 198\hbar^2 - 11ml^2W & 44\hbar^2 l^2 - 2ml^4 W \end{vmatrix} = m^2 l^6 W^2 - 120ml^4\hbar^2 W + 1980\hbar^4 l^2 \text{ (Eq. 1)}$$

The quadratic formula gives

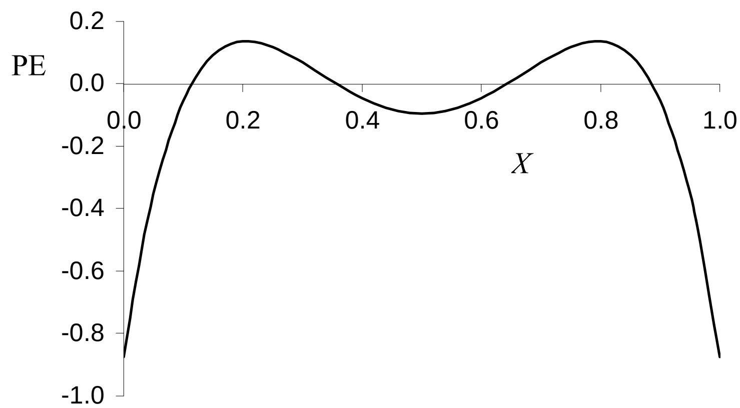
$W = (\hbar^2/ml^2)[60 \pm \frac{1}{2}\sqrt{(120)^2 - 4(1980)}] = 19.75078\hbar^2/ml^2,\ 100.2492\hbar^2/ml^2$

$W = 0.5002930h^2/ml^2,\ 2.5393425h^2/ml^2$.

8.37 The percent error (PE) is $\text{PE} = 100(\phi_1 - \psi_1)/\psi_1$. Letting $X \equiv x/l$, we have

$$\text{PE} = \frac{100[4.404X(1-X) + 4.990X^2(1-X)^2 - 2^{1/2}\sin(\pi X)}{2^{1/2}\sin(\pi X)}$$

provided $X \neq 0$. In making the graph, we start and end at numbers like X = 0.000001 and 0.999999 to avoid the indeterminate number 0/0 at 0 and 1. We get



8.38 The form of ϕ_2 is shown in Eq. (8.69). We use the form of the coefficients given in the determinant of Eq. 1 in Prob. 8.35. Substitution of $W_2 = 0.50029030h^2/ml^2$ gives

$0.189859h^2 c_3^{(2)} - 0.044348h^2 l^2 c_4^{(2)} = 0$

$-0.487824h^2 c_3^{(2)} + 0.113947h^2 l^2 c_4^{(2)} = 0$

We get $c_3^{(2)} = 0.233582l^2 c_4^{(2)}$. The normalization condition gives

$\langle \phi | \phi \rangle = 1 = \langle c_3 f_3 + c_4 f_4 | c_3 f_3 + c_4 f_4 \rangle = c_3^2 \langle f_3 | f_3 \rangle + 2c_3 c_4 \langle f_3 | f_4 \rangle + c_4^2 \langle f_4 | f_4 \rangle =$
$(0.233582)^2 c_4^2 l^4 l^7/840 + 2(0.233582)c_4 c_4 l^2 l^9/5040 + c_4^2 l^{11}/27720$. We get
$c_4 = 71.848l^{-11/2}$. Then $c_3 = 0.233582l^2 c_4 = 16.782l^{-7/2}$. So
$\phi_2 = 16.78l^{-7/2} x(l-x)(\frac{1}{2}l - x) + 71.848l^{-11/2} x^2 (l-x)^2 (\frac{1}{2}l - x)$.

The form of ϕ_3 is shown in Eq. (8.69). We use the form of the coefficients given in the determinant that precedes Eq. (8.71). Substitution of $W_3 = 1.293495h^2/ml^2$ gives

$-16.33581h^2 c_1^{(3)} - 3.525861h^2 l^2 c_2^{(3)} = 0$

$-10.57758h^2 c_1^{(3)} - 2.283026h^2 l^2 c_2^{(3)} = 0$

We get $c_1^{(3)} = -0.215836 l^2 c_2^{(3)}$. The normalization condition gives $\langle \phi \mid \phi \rangle = 1 = \langle c_1 f_1 + c_2 f_2 \mid c_1 f_1 + c_2 f_2 \rangle = c_1^2 \langle f_1 \mid f_1 \rangle + 2c_1 c_2 \langle f_1 \mid f_2 \rangle + c_2^2 \langle f_2 \mid f_2 \rangle =$ $(-0.215836)^2 c_2^2 l^4 l^5/30 + 2(-0.215836) c_2 c_2 l^2 l^7/140 + c_2^2 l^9/630$. We get $c_2 = 132.72 l^{-9/2}$. Then $c_1 = -0.215836 l^2 c_2 = -28.646 l^{-5/2}$. So $\phi_3 = -28.646 l^{-5/2} x(l-x) + 132.72 l^{-9/2} x^2 (l-x)^2$.

8.39 **(a)** We have $c_i = a_i + ib_i$ and $c_i^* = a_i - ib_i$. We start with W as a function of the a_i's and b_i's, and then make the substitutions $a_i = (c_i + c_i^*)/2$ and $b_i = (c_i - c_i^*)/2i$ for each a_i and b_i. This converts W to a function of the c_i's and c_i^*'s, where we consider c_i and c_i^* as independent of each other. The chain rule [Eq. (5.53)] gives

$\dfrac{\partial W}{\partial c_i} = \dfrac{\partial W}{\partial a_i}\dfrac{\partial a_i}{\partial c_i} + \dfrac{\partial W}{\partial b_i}\dfrac{\partial b_i}{\partial c_i} = \dfrac{1}{2}\dfrac{\partial W}{\partial a_i} + \dfrac{1}{2i}\dfrac{\partial W}{\partial b_i}$ and

$\dfrac{\partial W}{\partial c_i^*} = \dfrac{\partial W}{\partial a_i}\dfrac{\partial a_i}{\partial c_i^*} + \dfrac{\partial W}{\partial b_i}\dfrac{\partial b_i}{\partial c_i^*} = \dfrac{1}{2}\dfrac{\partial W}{\partial a_i} - \dfrac{1}{2i}\dfrac{\partial W}{\partial b_i}$.

(Terms involving $\partial W/\partial a_j$ and $\partial W/\partial b_j$ with $j \neq i$ do not occur because $\partial a_j/\partial c_i = 0$ and $\partial b_j/\partial c_i = 0$.) Setting $\partial W/\partial a_i = 0$ and $\partial W/\partial b_i = 0$, we get $\partial W/\partial c_i = 0$ and $\partial W/\partial c_i^* = 0$.

(b) Since the coefficients can be complex, each c_j in (8.45) is changed to c_j^* to give $W \sum_j \sum_k c_j^* c_k S_{jk} = \sum_j \sum_k c_j^* c_k H_{jk}$ (Eq. 1). Taking $\partial/\partial c_i$ of Eq. 1 with the c_j^*'s being considered as independent of the c_i's and hence being held constant, we have

$(\partial W/\partial c_i) \sum_j \sum_k c_j^* c_k S_{jk} + W \sum_j \sum_k c_j^* (\partial c_k/\partial c_i) S_{jk} = \sum_j \sum_k c_j^* (\partial c_k/\partial c_i) H_{jk}$

$(\partial W/\partial c_i) \sum_j \sum_k c_j^* c_k S_{jk} + W \sum_j \sum_k c_j^* \delta_{ki} S_{jk} = \sum_j \sum_k c_j^* \delta_{ki} H_{jk}$

$0 + W \sum_j c_j^* S_{ji} = \sum_j c_j^* H_{ji}$ [where (8.46) was used] so $\sum_j [(H_{ji} - WS_{ji}) c_j^*] = 0$, which is the complex conjugate of (8.53). Taking $\partial/\partial c_i^*$ of Eq. 1 with the c_i's being considered as independent of the c_i^*'s, we have

$(\partial W/\partial c_i^*) \sum_j \sum_k c_j^* c_k S_{jk} + W \sum_j \sum_k (\partial c_j^*/\partial c_i^*) c_k S_{jk} = \sum_j \sum_k (\partial c_j^*/\partial c_i^*) c_k H_{jk}$

$(\partial W/\partial c_i^*) \sum_j \sum_k c_j^* c_k S_{jk} + W \sum_j \sum_k \delta_{ji} c_k S_{jk} = \sum_j \sum_k \delta_{ji} c_k H_{jk}$

$0 + W \sum_k c_k S_{ik} = \sum_k c_k H_{ik}$ so $\sum_k (H_{ik} - S_{ik} W) c_k = 0$, which is (8.53).

8.40 **(a)** Use of (8.40) gives $\langle f_i \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle = \langle f_i \mid \hat{H} - W_\alpha \mid \sum_k c_k^{(\alpha)} f_k \rangle =$
$\sum_k \langle f_i \mid \hat{H} - W_\alpha \mid f_k \rangle c_k^{(\alpha)} = \sum_k [\langle f_i \mid \hat{H} \mid f_k \rangle - W_\alpha \langle f_i \mid f_k \rangle] c_k^{(\alpha)} = 0$ for $i = 1, 2, \ldots, n$.

(b) Use of (8.40) gives
$\langle \phi_\beta \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle = \langle \sum_k c_k^{(\beta)} f_k \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle = \sum_k c_k^{(\beta)*} \langle f_k \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle = 0$, since $\langle f_k \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle$ was shown to be zero in (a) for all *k*. The labels α and β are arbitrary, and interchange of α and β gives $\langle \phi_\alpha \mid \hat{H} - W_\beta \mid \phi_\beta \rangle = 0$. Taking the complex conjugate, we get $\langle \phi_\alpha \mid \hat{H} - W_\beta \mid \phi_\beta \rangle^* = 0$.

(c) We have $\langle \phi_\beta \mid \hat{H} - W_\alpha \mid \phi_\alpha \rangle = \langle \phi_\alpha \mid \hat{H} - W_\beta \mid \phi_\beta \rangle^*$ (Eq. 1). The left side of Eq. 1 is $\langle \phi_\beta \mid \hat{H} \mid \phi_\alpha \rangle - W_\alpha \langle \phi_\beta \mid \phi_\alpha \rangle$ (Eq. 1-ls). The right side of Eq. 1 is
$\langle \phi_\alpha \mid \hat{H} - W_\beta \mid \phi_\beta \rangle^* = [\langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle - W_\beta \langle \phi_\alpha \mid \phi_\beta \rangle]^* = \langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle^* - W_\beta \langle \phi_\alpha \mid \phi_\beta \rangle^* =$
$\langle \phi_\beta \mid \hat{H} \mid \phi_\alpha \rangle - W_\beta \langle \phi_\beta \mid \phi_\alpha \rangle$ (Eq. 1-rs). Equating the last expression in Eq. 1-rs to the last expression in Eq. 1-ls, we have $\langle \phi_\beta \mid \hat{H} \mid \phi_\alpha \rangle - W_\beta \langle \phi_\beta \mid \phi_\alpha \rangle = \langle \phi_\beta \mid \hat{H} \mid \phi_\alpha \rangle - W_\alpha \langle \phi_\beta \mid \phi_\alpha \rangle$, which becomes $(W_\alpha - W_\beta) \langle \phi_\beta \mid \phi_\alpha \rangle = 0$. So if $W_\beta \neq W_\alpha$, we have $\langle \phi_\beta \mid \phi_\alpha \rangle = 0$.

(d) The result $\langle g \mid \hat{H} \mid g \rangle \geq E_m$ follows from $\langle g \mid g \rangle = 1$ and Eq. (8.19) with $k = m - 1$ and $\phi = g$.

(e) We showed in part (b) that $\langle \phi_\alpha \mid \hat{H} - W_\beta \mid \phi_\beta \rangle = 0$, so $0 = \langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle - W_\beta \langle \phi_\alpha \mid \phi_\beta \rangle$ (Eq. 2). We showed in (c) that $\langle \phi_\beta \mid \phi_\alpha \rangle = 0$ if $W_\beta \neq W_\alpha$, and the ϕ functions can be chosen to be orthogonal when $W_\beta = W_\alpha$. So Eq. 2 becomes $0 = \langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle$ for $\alpha \neq \beta$.

(f) $\langle g \mid \hat{H} \mid g \rangle = \langle \sum_{\alpha=1}^m b_\alpha \phi_\alpha \mid \hat{H} \mid \sum_{\beta=1}^m b_\beta \phi_\beta \rangle = \sum_{\alpha=1}^m \sum_{\beta=1}^m b_\alpha^* b_\beta \langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle$. Since $\langle \phi_\alpha \mid \hat{H} \mid \phi_\beta \rangle = 0$ for $\alpha \neq \beta$, when we do the sum over β, only the term with $\beta = \alpha$ is nonzero, and $\langle g \mid \hat{H} \mid g \rangle = \sum_{\alpha=1}^m b_\alpha^* b_\alpha \langle \phi_\alpha \mid \hat{H} \mid \phi_\alpha \rangle = \sum_{\alpha=1}^m |b_\alpha|^2 W_\alpha$ (Eq. 3), where the first equation in (8.44) with ϕ normalized was used.

(g) Since *g* is normalized, we have
$1 = \langle g \mid g \rangle = \langle \sum_{\alpha=1}^m b_\alpha \phi_\alpha \mid \sum_{\beta=1}^m b_\beta \phi_\beta \rangle = \sum_{\alpha=1}^m \sum_{\beta=1}^m b_\alpha^* b_\beta \langle \phi_\alpha \mid \phi_\beta \rangle = \sum_{\alpha=1}^m \sum_{\beta=1}^m b_\alpha^* b_\beta \delta_{\alpha\beta} =$
$\sum_{\alpha=1}^m |b_\alpha|^2$.

(h) Since α goes from 1 to *m* in the sums in (f) and (g) and since the *W*'s are numbered in order of increasing value, we have $W_\alpha \leq W_m$ and $\sum_{\alpha=1}^m |b_\alpha|^2 W_\alpha \leq \sum_{\alpha=1}^m |b_\alpha|^2 W_m$. Hence Eq. 3 in part (f) gives $\langle g \mid \hat{H} \mid g \rangle \leq \sum_{\alpha=1}^m |b_\alpha|^2 W_m = W_m \sum_{\alpha=1}^m |b_\alpha|^2 = W_m$.

(i) From parts (h) and (d), $W_m \geq \langle g \mid \hat{H} \mid g \rangle \geq E_m$.

8.41

$$\mathbf{A}^* = \begin{pmatrix} 7 & 3 & 0 \\ 2+i & -2i & -i \\ 1-i & 4 & 2 \end{pmatrix} \qquad \mathbf{A}^{\mathrm{T}} = \begin{pmatrix} 7 & 2-i & 1+i \\ 3 & 2i & 4 \\ 0 & i & 2 \end{pmatrix} \qquad \mathbf{A}^{\dagger} = \begin{pmatrix} 7 & 2+i & 1-i \\ 3 & -2i & 4 \\ 0 & -i & 2 \end{pmatrix}$$

8.42 **(a)** Only **F** is real. **(b)** **C** and **F** are symmetric. **(c)** **D** and **F** are Hermitian.

8.43 Since $\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{I}$, we have $\delta_{ij} = (\mathbf{I})_{ij} = (\mathbf{U}^{\dagger}\mathbf{U})_{ij} = \sum_k (\mathbf{U}^{\dagger})_{ik}(\mathbf{U})_{kj} = \sum_k u_{ki}^* u_{kj}$, where (8.90) was used.

8.44 $1 = \langle \mathsf{v} \mid \mathsf{v} \rangle = \langle \sum_i \mathsf{v}_i f_i \mid \sum_j \mathsf{v}_j f_j \rangle = \sum_i \sum_j \langle \mathsf{v}_i f_i \mid \mathsf{v}_j f_j \rangle = \sum_i \sum_j \mathsf{v}_i^* \mathsf{v}_j \langle f_i \mid f_j \rangle = \sum_i \sum_j \mathsf{v}_i^* \mathsf{v}_j \delta_{ij}$ $= \sum_i |\mathsf{v}_i|^2$. Similarly, $\sum_i |w_i|^2 = 1$.

Also, $0 = \langle w \mid \mathsf{v} \rangle = \langle \sum_i w_i f_i \mid \sum_j \mathsf{v}_j f_j \rangle = \sum_i \sum_j w_i^* \mathsf{v}_j \langle f_i \mid f_j \rangle = \sum_i \sum_j w_i^* \mathsf{v}_j \delta_{ij} = \sum_i w_i^* \mathsf{v}_i$.

8.45 The characteristic equation (8.81) for **A** is

$$\det(A_{ij} - \lambda\delta_{ij}) = 0 = \begin{vmatrix} 0-\lambda & -1 \\ 3 & 2-\lambda \end{vmatrix} = \lambda^2 - 2\lambda + 3$$

The roots are $\lambda = \frac{1}{2}[2 \pm \sqrt{4-12}] = 1+\sqrt{2}i,\ 1-\sqrt{2}i$. The sum of the eigenvalues is 2, which is the trace of the matrix.

For $\lambda_1 = 1+\sqrt{2}i,$ the equations (8.82) are

$$-\lambda c_1^{(1)} - c_2^{(1)} = -(1+\sqrt{2}i)c_1^{(1)} - c_2^{(1)} = 0$$
$$3c_1^{(1)} + (2-\lambda)c_2^{(1)} = 3c_1^{(1)} + (1-\sqrt{2}i)c_2^{(1)} = 0$$

The first equation gives $c_2^{(1)} = -(1+\sqrt{2}i)c_1^{(1)}$. As a check, the second equation gives

$$c_2^{(1)} = -\frac{3}{1-\sqrt{2}i}c_1^{(1)} = -\frac{3}{1-\sqrt{2}i}\frac{1+\sqrt{2}i}{1+\sqrt{2}i}c_1^{(1)} = -(1+\sqrt{2}i)c_1^{(1)}$$

The normalization condition (8.83) is

$1 = |c_1^{(1)}|^2 + |c_2^{(1)}|^2 = |c_1^{(1)}|^2 + (-1-\sqrt{2}i)(-1+\sqrt{2}i)\,|c_1^{(1)}|^2 = 4\,|c_1^{(1)}|^2$. So $|c_1^{(1)}| = \frac{1}{2}$. If we take $c_1^{(1)} = \frac{1}{2}$, then $c_2^{(1)} = -(1+\sqrt{2}i)c_1^{(1)} = -\frac{1}{2} - \frac{1}{2}\sqrt{2}i$. Infinitely many other choices are possible. For example, $|c_1^{(1)}|^2 = \frac{1}{4}$ so normalization means that $|c_2^{(1)}|^2 = \frac{3}{4}$. If we take $c_2^{(1)} = \frac{1}{2}\sqrt{3}$, then $c_1^{(1)} = -\dfrac{1-\sqrt{2}i}{3}c_2^{(1)} = -\frac{1}{6}\sqrt{3} + \frac{1}{6}\sqrt{6}i$.

For $\lambda_2 = 1-\sqrt{2}i,$ the equations (8.82) are

$$-\lambda c_1^{(2)} - c_2^{(2)} = -(1-\sqrt{2}i)c_1^{(2)} - c_2^{(2)} = 0$$
$$3c_1^{(2)} + (2-\lambda)c_2^{(2)} = 3c_1^{(2)} + (1+\sqrt{2}i)c_2^{(2)} = 0$$

The first equation gives $c_2^{(2)} = -(1-\sqrt{2}i)c_1^{(2)}$. As a check, the second equation gives

$$c_2^{(2)} = -\frac{3}{1+\sqrt{2}i}c_1^{(2)} = -\frac{3}{1+\sqrt{2}i}\frac{1-\sqrt{2}i}{1-\sqrt{2}i}c_1^{(2)} = -(1-\sqrt{2}i)c_1^{(2)}$$

The normalization condition (8.83) is $1 = |c_1^{(2)}|^2 + |c_2^{(2)}|^2 = |c_1^{(2)}|^2 + (-1-\sqrt{2}i)(-1+\sqrt{2}i)\,|c_1^{(2)}|^2 = 4\,|c_1^{(2)}|^2$. So $|c_1^{(2)}| = \frac{1}{2}$. If we take $c_1^{(2)} = \frac{1}{2}$, then $c_2^{(2)} = -(1-\sqrt{2}i)c_1^{(2)} = -\frac{1}{2} + \frac{1}{2}\sqrt{2}i$. (Other choices are possible.)

The eigenvectors of **A** are

$$\mathbf{c}^{(1)} = \begin{pmatrix} \frac{1}{2} \\ -\frac{1}{2} - \frac{1}{2}\sqrt{2}i \end{pmatrix} \qquad \mathbf{c}^{(2)} = \begin{pmatrix} \frac{1}{2} \\ -\frac{1}{2} + \frac{1}{2}\sqrt{2}i \end{pmatrix}$$

The characteristic equation (8.81) for **B** is

$$\det(B_{ij} - \lambda\delta_{ij}) = 0 = \begin{vmatrix} 2-\lambda & 0 \\ 9 & 2-\lambda \end{vmatrix} = \lambda^2 - 4\lambda + 4$$

The roots are $\lambda = \frac{1}{2}[4 \pm \sqrt{16-16}] = 2,\ 2$. The sum of the eigenvalues is 4, which is the trace of the matrix.

For $\lambda_1 = 2,$ the equations (8.82) are

$$(2-\lambda)c_1^{(1)} + 0c_2^{(1)} = 0c_1^{(1)} + 0c_2^{(1)} = 0$$
$$9c_1^{(1)} + (2-\lambda)c_2^{(1)} = 9c_1^{(1)} + 0c_2^{(1)} = 0$$

The second equation gives $c_1^{(1)} = 0$. Normalization gives $|c_2^{(1)}| = 1$ and we can take $c_2^{(1)} = 1$. The second root equals the first root and the second eigenvector is the same as the first eigenvector.

The characteristic equation (8.81) for **C** is

$$\det(C_{ij} - \lambda\delta_{ij}) = 0 = \begin{vmatrix} 4-\lambda & 0 \\ 0 & 4-\lambda \end{vmatrix} = (4-\lambda)(4-\lambda)$$

The roots are $\lambda = 4,\ 4$. The sum of the eigenvalues is 8, which is the trace of the matrix.

For $\lambda_1 = 4,$ the equations (8.82) are

$$(4-\lambda)c_1^{(1)} + 0c_2^{(1)} = 0c_1^{(1)} + 0c_2^{(1)} = 0$$
$$0c_1^{(1)} + (4-\lambda)c_2^{(1)} = 0c_1^{(1)} + 0c_2^{(1)} = 0$$

These equations give no information. Normalization requires that $1 = |c_1^{(1)}|^2 + |c_2^{(1)}|^2$. Any values of $c_1^{(1)}$ and $c_2^{(1)}$ that satisfy this condition can be used. A simple choice is $c_1^{(1)} = 1$ and $c_2^{(1)} = 0$. A simple choice of the second eigenvector is $c_1^{(1)} = 0$ and $c_2^{(1)} = 1$. (Any two normalized linear combinations of these two eigenvectors can be used.)

8.46 The characteristic equation (8.81) is

$$\begin{vmatrix} a_{11}-\lambda & 0 & 0 \\ 0 & a_{22}-\lambda & 0 \\ 0 & 0 & a_{33}-\lambda \end{vmatrix} = 0 = (a_{11}-\lambda)(a_{22}-\lambda)(a_{33}-\lambda)$$

The roots are $\lambda = a_{11},\ a_{22},\ a_{33}$. For $\lambda = a_{11}$, the equations (8.82) are

$$(a_{11}-a_{11})c_1^{(1)} + 0c_2^{(1)} + 0c_3^{(1)} = 0$$
$$0c_1^{(1)} + (a_{22}-a_{11})c_2^{(1)} + 0c_3^{(1)} = 0$$
$$0c_1^{(1)} + 0c_2^{(1)} + (a_{33}-a_{11})c_3^{(1)} = 0$$

Since $a_{11} \neq a_{22} \neq a_{33}$, we have $c_2^{(1)} = 0$ and $c_3^{(1)} = 0$. To satisfy normalization, we take $c_1^{(1)} = 1$. Similarly, the components of the eigenvector for $\lambda = a_{22}$ are $0,\ 1,\ 0$ and the components of the $\lambda = a_{33}$ eigenvector are $0,\ 0,\ 1$.

8.47 **(a)** The characteristic equation (8.81) is

$$\det(A_{ij} - \lambda\delta_{ij}) = 0 = \begin{vmatrix} 2-\lambda & 2 \\ 2 & -1-\lambda \end{vmatrix} = \lambda^2 - \lambda - 6$$

The roots are $\lambda = 3,\ -2$. For $\lambda_1 = 3$, the equations (8.82) are

$$(2-\lambda)c_1^{(1)} + 2c_2^{(1)} = -1c_1^{(1)} + 2c_2^{(1)} = 0$$
$$2c_1^{(1)} + (-1-\lambda)c_2^{(1)} = 2c_1^{(1)} - 4c_2^{(1)} = 0$$

These equations give $c_1^{(1)} = 2c_2^{(1)}$. The normalization condition (8.83) is $1 = |c_1^{(1)}|^2 + |c_2^{(1)}|^2 = 4|c_2^{(1)}|^2 + |c_2^{(1)}|^2 = 5|c_2^{(1)}|^2$. So $|c_2^{(1)}| = 1/5^{1/2}$. We take $c_2^{(1)} = 1/5^{1/2}$. Then $c_1^{(1)} = 2c_2^{(1)} = 2/5^{1/2}$. For $\lambda_2 = -2$, the equations (8.82) are

$$(2-\lambda)c_1^{(2)} + 2c_2^{(2)} = 4c_1^{(2)} + 2c_2^{(2)} = 0$$
$$2c_1^{(2)} + (-1-\lambda)c_2^{(2)} = 2c_1^{(2)} + c_2^{(2)} = 0$$

These equations give $c_1^{(2)} = -\frac{1}{2}c_2^{(2)}$. The normalization condition (8.83) is $1 = |c_1^{(2)}|^2 + |c_2^{(2)}|^2 = \frac{1}{4}|c_2^{(2)}|^2 + |c_2^{(2)}|^2 = \frac{5}{4}|c_2^{(2)}|^2$. So $|c_2^{(2)}| = 2/5^{1/2}$. We take $c_2^{(2)} = 2/5^{1/2}$. Then $c_1^{(2)} = -\frac{1}{2}c_2^{(2)} = -1/5^{1/2}$.

(b) **A** is real and symmetric. It is also Hermitian.

(c) As noted in Sec. 8.6, the eigenvector matrix

$$\mathbf{C} = \begin{pmatrix} \frac{2}{5^{1/2}} & -\frac{1}{5^{1/2}} \\ \frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix} = \begin{pmatrix} 0.89442719 & -0.447213595 \\ 0.447213595 & 0.89442719 \end{pmatrix}$$

for the real symmetric matrix **A** is orthogonal and is unitary. The orthogonality of the two eigenvectors is readily verified. Also

$$\mathbf{C}^\dagger\mathbf{C} = \mathbf{C}^\mathrm{T}\mathbf{C} = \begin{pmatrix} \frac{2}{5^{1/2}} & \frac{1}{5^{1/2}} \\ -\frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix}\begin{pmatrix} \frac{2}{5^{1/2}} & -\frac{1}{5^{1/2}} \\ \frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(d)

$$\mathbf{C}^{-1} = \mathbf{C}^\mathrm{T} = \begin{pmatrix} \frac{2}{5^{1/2}} & \frac{1}{5^{1/2}} \\ -\frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix}$$

(e) $\mathbf{C}^{-1}\mathbf{AC} =$

$$\begin{pmatrix} \frac{2}{5^{1/2}} & \frac{1}{5^{1/2}} \\ -\frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix}\begin{pmatrix} 2 & 2 \\ 2 & -1 \end{pmatrix}\begin{pmatrix} \frac{2}{5^{1/2}} & -\frac{1}{5^{1/2}} \\ \frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix} = \begin{pmatrix} \frac{2}{5^{1/2}} & \frac{1}{5^{1/2}} \\ -\frac{1}{5^{1/2}} & \frac{2}{5^{1/2}} \end{pmatrix}\begin{pmatrix} \frac{6}{5^{1/2}} & \frac{2}{5^{1/2}} \\ \frac{3}{5^{1/2}} & -\frac{4}{5^{1/2}} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 0 & -2 \end{pmatrix}$$

8.48 **(a)** The characteristic equation (8.81) is

$$\det(A_{ij} - \lambda\delta_{ij}) = 0 = \begin{vmatrix} 2-\lambda & -2i \\ 2i & 2-\lambda \end{vmatrix} = \lambda^2 - 4\lambda = \lambda(\lambda - 4)$$

The roots are $\lambda = 0,\ 4$. For $\lambda = 0$, the equations (8.82) are

$$(2-\lambda)c_1^{(1)} - 2ic_2^{(1)} = 2c_1^{(1)} - 2ic_2^{(1)} = 0$$

$$2ic_1^{(1)} + (2-\lambda)c_2^{(1)} = 2ic_1^{(1)} + 2c_2^{(1)} = 0$$

These equations give $c_1^{(1)} = ic_2^{(1)}$. The normalization condition (8.83) is $1 = |c_1^{(1)}|^2 + |c_2^{(1)}|^2 = |c_2^{(1)}|^2 + |c_2^{(1)}|^2 = 2|c_2^{(1)}|^2$. So $|c_2^{(1)}| = 1/2^{1/2}$. We take $c_2^{(1)} = 1/2^{1/2}$. Then $c_1^{(1)} = ic_2^{(1)} = i/2^{1/2}$. For $\lambda = 4$, the equations (8.82) are

$$(2-\lambda)c_1^{(2)} - 2ic_2^{(2)} = -2c_1^{(2)} - 2ic_2^{(2)} = 0$$

$$2ic_1^{(2)} + (2-\lambda)c_2^{(2)} = 2ic_1^{(2)} - 2c_2^{(2)} = 0$$

These equations give $c_1^{(2)} = -ic_2^{(2)}$. The normalization condition (8.83) is $1 = |c_1^{(2)}|^2 + |c_2^{(2)}|^2 = |c_2^{(2)}|^2 + |c_2^{(2)}|^2 = 2|c_2^{(2)}|^2$. So $|c_2^{(2)}| = 1/2^{1/2}$. We take $c_2^{(2)} = 1/2^{1/2}$. Then $c_1^{(2)} = -ic_2^{(2)} = -i/2^{1/2}$.

(b) **A** is not real and is not symmetric. It is Hermitian.

(c) The eigenvector matrix **C** for the Hermitian matrix **A** is unitary. The orthogonality of the eigenvectors is readily verified. Also

$$\mathbf{C}^{\dagger}\mathbf{C} = \begin{pmatrix} -\frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \\ \frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix}\begin{pmatrix} \frac{i}{2^{1/2}} & -\frac{i}{2^{1/2}} \\ \frac{1}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(d)

$$\mathbf{C}^{-1} = \mathbf{C}^{\dagger} = \begin{pmatrix} -\frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \\ \frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix}$$

(e)

$$\mathbf{C}^{-1}\mathbf{AC} = \begin{pmatrix} -\frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \\ \frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix}\begin{pmatrix} 2 & -2i \\ 2i & 2 \end{pmatrix}\begin{pmatrix} \frac{i}{2^{1/2}} & -\frac{i}{2^{1/2}} \\ \frac{1}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix} = \begin{pmatrix} -\frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \\ \frac{i}{2^{1/2}} & \frac{1}{2^{1/2}} \end{pmatrix}\begin{pmatrix} 0 & \frac{-4i}{2^{1/2}} \\ 0 & \frac{4}{2^{1/2}} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 4 \end{pmatrix}$$

8.49 For $\lambda_2 = -1$, the equations (8.82) are

$$(3-\lambda)c_1^{(2)} + 2ic_2^{(2)} = 4c_1^{(2)} + 2ic_2^{(2)} = 0$$
$$-2ic_1^{(2)} + (0-\lambda)c_2^{(2)} = -2ic_1^{(2)} + c_2^{(2)} = 0$$

So $c_1^{(2)} = -\frac{1}{2}ic_2^{(2)}$. Normalization gives $1 = |c_1^{(2)}|^2 + |c_2^{(2)}|^2 = \frac{1}{4}|c_2^{(2)}|^2 + |c_2^{(2)}|^2 = \frac{5}{4}|c_2^{(2)}|^2$. So $|c_2^{(2)}| = 2/5^{1/2}$. We take $c_2^{(2)} = 2/5^{1/2}$. Then $c_1^{(2)} = -\frac{1}{2}ic_2^{(2)} = -i/5^{1/2}$.

8.50 The characteristic equation (8.81) is

$$0 = \begin{vmatrix} -1-\lambda & 0 & -2 \\ 0 & 5-\lambda & 0 \\ -2 & 4 & 2-\lambda \end{vmatrix} = (5-\lambda)\begin{vmatrix} -1-\lambda & -2 \\ -2 & 2-\lambda \end{vmatrix} = (5-\lambda)(\lambda^2-\lambda-6)$$

One root is $\lambda = 5$. The other roots are found from $\lambda^2 - \lambda - 6 = 0$ and are $\lambda = 3$ and $\lambda = -2$.

For $\lambda_1 = 5$, the equations (8.82) are

$$(-1-\lambda)c_1^{(1)} + 0c_2^{(1)} - 2c_3^{(1)} = -6c_1^{(1)} + 0c_2^{(1)} - 2c_3^{(1)} = 0$$
$$0c_1^{(1)} + (5-\lambda)c_2^{(1)} + 0c_3^{(1)} = 0c_1^{(1)} + 0c_2^{(1)} + 0c_3^{(1)} = 0$$
$$-2c_1^{(1)} + 4c_2^{(1)} + (2-\lambda)c_3^{(1)} = -2c_1^{(1)} + 4c_2^{(1)} - 3c_3^{(1)} = 0$$

We set $c_3^{(1)} = k$, where the constant k will be found from normalization. The first equation gives $c_1^{(1)} = -\frac{1}{3}c_3^{(1)} = -\frac{1}{3}k$. The third equation gives

$c_2^{(1)} = \frac{1}{2}c_1^{(1)} + \frac{3}{4}c_3^{(1)} = -\frac{1}{6}k + \frac{3}{4}k = \frac{7}{12}k$. Normalization gives $1 = |c_1^{(1)}|^2 + |c_2^{(1)}|^2 + |c_3^{(1)}|^2 = \frac{1}{9}|k|^2 + \frac{49}{144}|k|^2 + |k|^2 = \frac{209}{144}|k|^2$ and $|k| = 12/(209)^{1/2} = 0.8300574$. We take $k = 0.8300574$. So $c_1^{(1)} = -\frac{1}{3}k = -0.2766858$, $c_2^{(1)} = \frac{7}{12}k = 0.4842001$, $c_3^{(1)} = k = 0.8300574$.

For $\lambda_2 = 3$, the equations (8.82) are

$$(-1-\lambda)c_1^{(2)} + 0c_2^{(2)} - 2c_3^{(2)} = -4c_1^{(2)} + 0c_2^{(2)} - 2c_3^{(2)} = 0$$
$$0c_1^{(2)} + (5-\lambda)c_2^{(2)} + 0c_3^{(2)} = 0c_1^{(2)} + 2c_2^{(2)} + 0c_3^{(2)} = 0$$
$$-2c_1^{(2)} + 4c_2^{(2)} + (2-\lambda)c_3^{(2)} = -2c_1^{(2)} + 4c_2^{(2)} - c_3^{(2)} = 0$$

The second equation gives $c_2^{(2)} = 0$. The first equation gives $c_1^{(2)} = -\frac{1}{2}c_3^{(2)}$. Normalization gives $1 = |c_1^{(2)}|^2 + |c_2^{(2)}|^2 + |c_3^{(2)}|^2 = \frac{1}{4}|c_3^{(2)}|^2 + |c_3^{(2)}|^2 = \frac{5}{4}|c_3^{(2)}|^2$ and $|c_3^{(2)}| = 2/5^{1/2}$. We take $c_3^{(2)} = 2/5^{1/2} = 0.8944272$. So $c_1^{(2)} = -1/5^{1/2} = -0.4472136$.

For $\lambda_3 = -2$, the equations (8.82) are

$$(-1-\lambda)c_1^{(3)} + 0c_2^{(3)} - 2c_3^{(3)} = c_1^{(3)} + 0c_2^{(3)} - 2c_3^{(3)} = 0$$
$$0c_1^{(3)} + (5-\lambda)c_2^{(3)} + 0c_3^{(3)} = 0c_1^{(3)} + 7c_2^{(3)} + 0c_3^{(3)} = 0$$
$$-2c_1^{(3)} + 4c_2^{(3)} + (2-\lambda)c_3^{(3)} = -2c_1^{(3)} + 4c_2^{(3)} + 4c_3^{(3)} = 0$$

The second equation gives $c_2^{(3)} = 0$. The first equation gives $c_1^{(3)} = 2c_3^{(3)}$. Normalization gives $1 = |c_1^{(3)}|^2 + |c_2^{(3)}|^2 + |c_3^{(3)}|^2 = 4|c_3^{(3)}|^2 + |c_3^{(3)}|^2 = 5|c_3^{(3)}|^2$ and $|c_3^{(3)}| = 1/5^{1/2}$. We take $c_3^{(3)} = 1/5^{1/2} = 0.4472136$. So $c_1^{(3)} = 2/5^{1/2} = 0.8944272$. The eigenvectors are

$$\begin{pmatrix} -0.2766858 \\ 0.4842001 \\ 0.8300574 \end{pmatrix} \qquad \begin{pmatrix} -0.4472136 \\ 0 \\ 0.8944272 \end{pmatrix} \qquad \begin{pmatrix} 0.8944272 \\ 0 \\ 0.4472136 \end{pmatrix}$$

8.51 $$\begin{pmatrix} -1 & 0 & -2 & 1 & 0 & 0 \\ 0 & 5 & 0 & 0 & 1 & 0 \\ -2 & 4 & 2 & 0 & 0 & 1 \end{pmatrix} \to \begin{pmatrix} 1 & 0 & 2 & -1 & 0 & 0 \\ 0 & 5 & 0 & 0 & 1 & 0 \\ -2 & 4 & 2 & 0 & 0 & 1 \end{pmatrix} \to \begin{pmatrix} 1 & 0 & 2 & -1 & 0 & 0 \\ 0 & 5 & 0 & 0 & 1 & 0 \\ 0 & 4 & 6 & -2 & 0 & 1 \end{pmatrix} \to$$

$$\begin{pmatrix} 1 & 0 & 2 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{5} & 0 \\ 0 & 4 & 6 & -2 & 0 & 1 \end{pmatrix} \to \begin{pmatrix} 1 & 0 & 2 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{5} & 0 \\ 0 & 0 & 6 & -2 & -\frac{4}{5} & 1 \end{pmatrix} \to \begin{pmatrix} 1 & 0 & 2 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{5} & 0 \\ 0 & 0 & 1 & -\frac{1}{3} & -\frac{2}{15} & \frac{1}{6} \end{pmatrix} \to$$

$$\begin{pmatrix} 1 & 0 & 0 & -\frac{1}{3} & \frac{4}{15} & -\frac{1}{3} \\ 0 & 1 & 0 & 0 & \frac{1}{5} & 0 \\ 0 & 0 & 1 & -\frac{1}{3} & -\frac{2}{15} & \frac{1}{6} \end{pmatrix}$$

The inverse is

$$\mathbf{A}^{-1} = \begin{pmatrix} -\frac{1}{3} & \frac{4}{15} & -\frac{1}{3} \\ 0 & \frac{1}{5} & 0 \\ -\frac{1}{3} & -\frac{2}{15} & \frac{1}{6} \end{pmatrix}$$

8.52 The matrix is

$$\mathbf{B} = \begin{pmatrix} 1 & \frac{5}{3} & 2.5 & \frac{17}{5} & \frac{26}{6} & \frac{37}{7} \\ \frac{5}{3} & 2 & \frac{13}{5} & \frac{20}{6} & \frac{29}{7} & 5 \\ 2.5 & \frac{13}{5} & 3 & \frac{25}{7} & \frac{34}{8} & 5 \\ \frac{17}{5} & \frac{20}{6} & \frac{25}{7} & 4 & \frac{41}{9} & \frac{52}{10} \\ \frac{26}{6} & \frac{29}{7} & \frac{34}{8} & \frac{41}{9} & 5 & \frac{61}{11} \\ \frac{37}{7} & 5 & 5 & \frac{52}{10} & \frac{61}{11} & 6 \end{pmatrix}$$

A graphing calculator with eigenvalue capability or a computer-algebra program gives the eigenvalues as –3.3664014, 24.5567896, –0.00499050, –0.1852766, -1.0597948×10^{-6}, –0.0001200235 and gives the eigenvector matrix as

$$\begin{pmatrix} 0.6695666 & -0.3237631 & 0.3036389 & -0.5896587 & 0.0136789 & 0.0823222 \\ 0.4293335 & -0.3276050 & -0.6635074 & 0.2630438 & -0.1242886 & -0.4283293 \\ 0.1791639 & -0.3583884 & -0.0015726 & 0.4983841 & 0.4297147 & 0.6375061 \\ -0.0604158 & -0.4055325 & -0.4559910 & 0.3688083 & -0.697981 & -0.0277208 \\ -0.2863645 & -0.4635497 & 0.315732 & 0.0260194 & 0.536420 & -0.562548 \\ -0.4995987 & -0.5292213 & -0.3999305 & -0.4450026 & -0.1574374 & 0.2959183 \end{pmatrix}$$

where the columns are in the order of the eigenvalues given above.

8.53 With 1, 1 as the initial guess for the elements of **x**, Excel gives $\lambda_1 = -2.0000006$. The elements of the **x** that gives this eigenvalue are –0.4473249 and 0.8943717, and these are the elements of the λ_1 eigenvector. With an initial guess of 1, 1 for the elements of **y**, and with the constraints that **y** be normalized and orthogonal to the **x** previously found, Excel gives $\lambda_2 = 2.99999998$ and gives the **y** eigenvector elements as 0.8943716 and 0.4473248. (When entering matrix elements into Excel, hold down Control and Shift and then press Enter.) More-accurate values can be found by using Options in the Solver Parameters box to decrease the Precision to 10^{-10} *after* the preceding eigenvalues and eigenvectors have been found with the default precision of 10^{-6}. Excel then gives $\lambda_1 = -1.9999999999988$ with eigenvector components –0.447213850 and 0.894427064 and gives $\lambda_2 = 2.999999999954$ with eigenvector components 0.894427064 and 0.447213850.

8.54 In Excel, after viewing the initial graphs, double-click on the *y* axis and set the maximum and minimum on the *y* axis scale to something like 1E13 and –1E13. The graph of the altered polynomial shows only 10 roots (as compared with 20 for the original polynomial). The missing 10 roots are imaginary numbers (as can be verified using a computer-algebra program or a calculator with root-finding capability).

8.55 Multiplication of $\mathbf{B} = \mathbf{M}^{-1}\mathbf{AM}$ by **M** on the left gives $\mathbf{MB} = \mathbf{MM}^{-1}\mathbf{AM} = \mathbf{IAM} = \mathbf{AM}$. Multiplication of $\mathbf{MB} = \mathbf{AM}$ by $\mathbf{M}^{-1}$ on the right gives $\mathbf{MBM}^{-1} = \mathbf{A}$. Substitution of this expression for **A** in the eigenvalue equation $\mathbf{Ac}_i = \lambda_i\mathbf{c}_i$ gives $\mathbf{MBM}^{-1}\mathbf{c}_i = \lambda_i\mathbf{c}_i$. Multiplication of this equation by $\mathbf{M}^{-1}$ on the left gives $\mathbf{B}(\mathbf{M}^{-1}\mathbf{c}_i) = \lambda_i(\mathbf{M}^{-1}\mathbf{c}_i)$, so the eigenvalues of **B** are the same as those of **A** and the eigenvectors of **B** are $\mathbf{M}^{-1}\mathbf{c}_i$, where $\mathbf{c}_i$ are the eigenvectors of **A**.

8.56 We have $\mathbf{Ac}_i = \lambda_i\mathbf{c}_i$. Multiplication of this equation by **A** on the left gives $\mathbf{A}^2\mathbf{c}_i = \lambda_i\mathbf{Ac}_i = \lambda_i\lambda_i\mathbf{c}_i = \lambda_i^2\mathbf{c}_i$, so the eigenvalues of $\mathbf{A}^2$ are λ_i^2 and the eigenvectors are the same as those of **A**.

8.57 **(a)** $\delta_{jm} = \langle g_j \mid g_m\rangle = \langle \sum_i a_{ij}f_i \mid \sum_k a_{km}f_k\rangle = \sum_i \sum_k \langle a_{ij}f_i \mid a_{km}f_k\rangle = \sum_i a_{ij}^*[\sum_k \langle f_i \mid f_k\rangle a_{km}]$ (Eq. 1). We have $\sum_k \langle f_i \mid f_k\rangle a_{km} = \sum_k S_{ik}a_{km} = (\mathbf{SA})_{im}$, where the matrix-multiplication rule (7.110) was used. From (8.90), $(\mathbf{A}^\dagger)_{ji} = a_{ij}^*$. Also $(\mathbf{I})_{jm} = \delta_{jm}$. Hence Eq. 1 becomes $(\mathbf{I})_{jm} = \sum_i (\mathbf{A}^\dagger)_{ji}(\mathbf{SA})_{im} = (\mathbf{A}^\dagger\mathbf{SA})_{jm}$. Therefore $\mathbf{I} = \mathbf{A}^\dagger\mathbf{SA}$.

(b) Equation (8.53) gives $\sum_{k=1}^n H_{ik}c_k = W\sum_{k=1}^n S_{ik}c_k$ (Eq. 2). By the matrix-multiplication rule (7.110), $\sum_{k=1}^n H_{ik}c_k$ is the *i*th element of the column vector **Hc** and $\sum_{k=1}^n S_{ik}c_k$ is the *i*th element of the column vector **Sc**, so **Hc** = W**Sc**. Adding the index *j* to label the eigenvalues and eigenvectors, we rewrite this last equation as $\mathbf{Hc}^{(j)} = W_j\mathbf{Sc}^{(j)}$ and rewrite Eq. 2 as $\sum_{k=1}^n H_{ik}c_k^{(j)} = W_j\sum_{k=1}^n S_{ik}c_k^{(j)}$ (Eq. 3). As in the text and equations following Eq. (8.87), we have $(\mathbf{HC})_{ij} = \sum_k H_{ik}c_k^{(j)}$ and $(\mathbf{CW})_{kj} = c_k^{(j)}W_j$. Then $(\mathbf{SCW})_{ij} = \sum_k S_{ik}(\mathbf{CW})_{kj} = \sum_k S_{ik}c_k^{(j)}W_j$. Use of Eq. 3 shows $(\mathbf{HC})_{ij} = (\mathbf{SCW})_{ij}$, so $\mathbf{HC} = \mathbf{SCW}$.

(c) We have $\mathbf{A}^\dagger\mathbf{HAA}^{-1}\mathbf{C} = \mathbf{A}^\dagger\mathbf{SAA}^{-1}\mathbf{CW} = \mathbf{IA}^{-1}\mathbf{CW} = \mathbf{A}^{-1}\mathbf{CW}$ (Eq. 4). Defining $\mathbf{H}' \equiv \mathbf{A}^\dagger\mathbf{HA}$ and $\mathbf{C}' \equiv \mathbf{A}^{-1}\mathbf{C}$, we write Eq. 4 as $\mathbf{H}'\mathbf{C}' = \mathbf{C}'\mathbf{W}$.

8.58 **(a)** Since $\mathbf{U}$ is unitary, $\mathbf{U}^{-1} = \mathbf{U}^\dagger$ and $\mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$. Multiplication of $\mathbf{s} = \mathbf{U}^\dagger\mathbf{S}\mathbf{U}$ by $\mathbf{U}$ on the left and by $\mathbf{U}^\dagger$ on the right gives $\mathbf{U}\mathbf{s}\mathbf{U}^\dagger = \mathbf{U}\mathbf{U}^\dagger\mathbf{S}\mathbf{U}\mathbf{U}^\dagger = \mathbf{I}\mathbf{S}\mathbf{I} = \mathbf{S}$.

(b) We have $\mathbf{M}^2 = \mathbf{M}\mathbf{M} = \mathbf{U}\mathbf{s}^{1/2}\mathbf{U}^\dagger\mathbf{U}\mathbf{s}^{1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{s}^{1/2}\mathbf{I}\mathbf{s}^{1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{s}^{1/2}\mathbf{s}^{1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{s}\mathbf{U}^\dagger = \mathbf{S}$, where the result of part (a) was used. So $\mathbf{M} = \mathbf{S}^{1/2}$.

(c) $\mathbf{M}\mathbf{N} = \mathbf{U}\mathbf{s}^{1/2}\mathbf{U}^\dagger\mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{s}^{1/2}\mathbf{I}\mathbf{s}^{-1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{s}^{1/2}\mathbf{s}^{-1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{I}\mathbf{U}^\dagger = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$.

(d) $((\mathbf{BC})^\dagger)_{ij} = (\mathbf{BC})^*_{ji} = (\sum_k b_{jk}c_{ki})^* = \sum_k b^*_{jk}c^*_{ki}$ and $(\mathbf{C}^\dagger\mathbf{B}^\dagger)_{ij} = \sum_k (\mathbf{C}^\dagger)_{ik}(\mathbf{B}^\dagger)_{kj} = \sum_k c^*_{ki}b^*_{jk}$. Since the (i, j)th elements of $(\mathbf{BC})^\dagger$ and $\mathbf{C}^\dagger\mathbf{B}^\dagger$ are equal, we have $(\mathbf{BC})^\dagger = \mathbf{C}^\dagger\mathbf{B}^\dagger$ (Eq. 1). Setting $\mathbf{C} = \mathbf{DE}$ in $(\mathbf{BC})^\dagger = \mathbf{C}^\dagger\mathbf{B}^\dagger$, we have $(\mathbf{BDE})^\dagger = (\mathbf{DE})^\dagger\mathbf{B}^\dagger = \mathbf{E}^\dagger\mathbf{D}^\dagger\mathbf{B}^\dagger$ (Eq. 2), where Eq. 1 was used. The matrix $\mathbf{A}$ is chosen as $\mathbf{A} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$, so $\mathbf{A}^\dagger = (\mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger)^\dagger = (\mathbf{U}^\dagger)^\dagger(\mathbf{s}^{-1/2})^\dagger\mathbf{U}^\dagger$ (Eq. 3), where Eq. 2 was used. The conjugate transpose is formed by taking the transpose of the matrix and replacing each element by its complex conjugate. The matrix $\mathbf{s}^{-1/2}$ is a diagonal square matrix, so taking its transpose does not change it; the matrix elements of $\mathbf{s}^{-1/2}$ are real numbers, so taking the complex conjugates of the elements does nothing. Hence $(\mathbf{s}^{-1/2})^\dagger = \mathbf{s}^{-1/2}$. Also, taking the conjugate transpose twice takes the transpose twice and takes the complex conjugate twice; the net effect is to bring us back to the original matrix. Hence $(\mathbf{U}^\dagger)^\dagger = \mathbf{U}$. So Eq. 3 becomes $\mathbf{A}^\dagger = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$. So $\mathbf{A}^\dagger\mathbf{S}\mathbf{A} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger\mathbf{S}\mathbf{A} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$. But from part (a), $\mathbf{U}^\dagger\mathbf{S}\mathbf{U} = \mathbf{s}$, so $\mathbf{A}^\dagger\mathbf{S}\mathbf{A} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{s}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$. The matrices $\mathbf{s}^{-1/2}$ and $\mathbf{s}$ are diagonal square matrices of the same order. The product $\mathbf{C}$ of two diagonal matrices $\mathbf{A}$ and $\mathbf{B}$ is a diagonal matrix whose diagonal elements are the products of the corresponding elements of $\mathbf{A}$ and $\mathbf{B}$; $c_{ij} = \sum_k a_{ik}b_{kj} = \sum_k (\delta_{ik}a_{ik})(\delta_{kj}b_{kj})$; each term in the sum is zero unless $i = k = j$, so c_{ij} is zero unless $i = j$ and $c_{ii} = a_{ii}b_{ii}$. The matrix product $\mathbf{s}\mathbf{s}^{-1/2}$ is thus a diagonal matrix with diagonal elements $s_i s_i^{-1/2} = s_i^{1/2}$, so the matrix product $\mathbf{s}^{-1/2}(\mathbf{s}\mathbf{s}^{-1/2})$ is diagonal with diagonal elements $s_i^{-1/2}s_i^{1/2} = 1$. Hence $\mathbf{s}^{-1/2}\mathbf{s}\mathbf{s}^{-1/2}$ is the unit matrix of order n. Hence $\mathbf{A}^\dagger\mathbf{S}\mathbf{A} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{s}\mathbf{s}^{-1/2}\mathbf{U}^\dagger = \mathbf{U}\mathbf{I}\mathbf{U}^\dagger = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$.

8.59 Use of the linearity of $\hat{A}$ gives $\hat{A}\sum_k c_k^{(n)} f_k = \sum_k c_k^{(n)}\hat{A}f_k = a_n \sum_k c_k^{(n)} f_k$. Multiplication by f_i^* followed by integration over all space gives $\sum_k c_k^{(n)}\langle f_i \mid \hat{A} \mid f_k\rangle = a_n \sum_k c_k^{(n)}\langle f_i \mid f_k\rangle$ and $\sum_k c_k^{(n)} A_{ik} = \sum_k a_n c_k^{(n)}\delta_{ik}$, which can be written as $\sum_k (A_{ik} - a_n\delta_{ik})c_k^{(n)} = 0$.

8.60 **(a)** In $T_{jk} = \langle f_j \mid \hat{T} \mid f_k\rangle$, the kinetic-energy operator equals the particle-in-a-box (PIB) Hamiltonian operator $(\hat{T} = \hat{H}_{\mathrm{PIB}})$ and the f functions are PIB wave functions. Hence

$T_{jk} = \langle f_j \mid \hat{H}_{\text{PIB}} \mid f_k \rangle = E_{\text{PIB}} \langle f_j \mid f_k \rangle = (k^2 4\pi^2 \hbar^2 / 8ml^2)\delta_{jk}$. The reduced energy and length are $E_r = E/(\hbar^2/ml^2)$ and $x_r = x/l$. One has the program evaluate $H_{jk} = T_{jk} + V_{jk}$. Because the PIB basis functions are orthonormal, $S_{ij} = \delta_{ij}$ in (8.55) and (8.58), and (8.79) applies. The eigenvalues of the **H** matrix give the optimized values W_i of the variational integral and the eigenvectors of **H** give the coefficients of the PIB basis functions. Before graphing the variational functions, normalize them by dividing by the square root of the sum of the squares of the coefficients. Using Mathcad with TOL set as 10^{-9}, one finds the following results. For 4 basis functions, the E_r values in the variation function are 47.599135, 53.418896, 117.149785, 151.09691. For 8 basis functions, we get as the lowest four energies 46.281200, 46.309366, 113.994381, 143.584363. For 16 basis functions, we get 45.850738, 46.138686, 113.944461, 143.384175. For 32 basis functions, 45.807849, 46.111840, 113.938854, 143.358149. The coefficients for the 32-basis-function case show that for the ground state, the coefficients are 0.64118 for the $n = 1$ PIB ψ, 0.73485 for $n = 3$, 0.21774 for $n = 5$; all other coefficients are less than 0.03 in magnitude. For the first excited state, the 32 basis-function calculation has coefficients 0.88039 for the $n = 2$ PIB ψ, 0.46888 for $n = 4$, and less than 0.06 in magnitude for all other coefficients. The figure on the next page shows a Mathcad sheet with 4 basis functions.

(b) For 4 basis functions, one finds the following. The function corresponding to the lowest-energy eigenvalue of 47.599 is $u \equiv 0.887\psi_2 + 0.463\psi_4$ (where ψ_n is a PIB wave function with quantum number *n*) and the function corresponding to the next-lowest eigenvalue 53.419 is $w \equiv 0.690\psi_1 + 0.723\psi_3$. With the origin at the center of the box, *u* is an odd function with one interior node [see the graph of phim(1,xr) on the next page] and *w* is an even function. (The function *w* dips slightly below the xr axis at the center of the box, so *w* has two interior nodes, one slightly to the left of the box center, and one slightly to the right of the center. When more basis functions are added, the function corresponding to *w* remains above the xr axis at the center of the box and has no interior nodes.) Hence *w* corresponds to the ground state, even though its variational energy is larger than that of *u*. The linear-variation theorem (8.61) is not violated by this result. We have $E_1 = 45.802$, $E_2 = 46.107$ (where the numbering on the true energies corresponds to the true ordering of the states) and $W_1 = 47.599$, $W_2 = 53.419$ (where the numbering corresponds to the ordering of the *W* values, which is not necessarily the true ordering of the states). Hence the (8.61) relations $W_1 \geq E_1$ and $W_2 \geq E_2$ are not violated, even though the states are incorrectly ordered with this small number of basis functions. It makes the most sense to apply the linear variation method separately to the even states and to the odd states (as is done in Prob. 8.60).

Double well (barrier of height V0 from L/4 to 3L/4)--Linear Variation-PIB basis

$\text{ORIGIN} := 1 \qquad \text{TOL} := 1\cdot10^{-9} \qquad \text{V0r} := 100. \qquad n := 4 \qquad j := 1,2..n \qquad k := 1,2..n$

$fj(j,xr) := 2^{0.5}\cdot\sin(j\cdot\pi\cdot xr) \qquad fk(k,xr) := 2^{0.5}\cdot\sin(k\cdot\pi\cdot xr)$

$$Tr_{j,k} := j^2\cdot\pi^2\cdot\frac{\delta(j,k)}{2} \qquad Vr_{j,k} := \int_{\frac{1}{4}}^{\frac{3}{4}} V0r\cdot fj(j,xr)\cdot fk(k,xr)\,dxr \qquad Hr_{j,k} := Tr_{j,k} + Vr_{j,k}$$

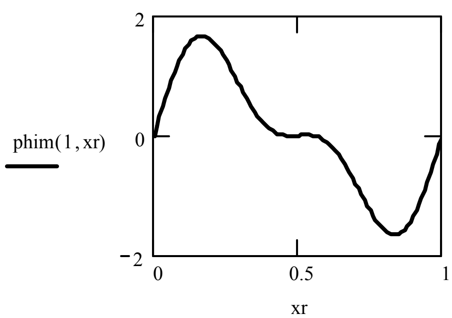
$$Hr = \begin{pmatrix} 86.766 & -2.063\times10^{-15} & -31.831 & 1.012\times10^{-14} \\ -2.495\times10^{-15} & 69.739 & 6.213\times10^{-15} & -42.441 \\ -31.831 & 6.977\times10^{-15} & 83.803 & -1.767\times10^{-15} \\ 9.793\times10^{-15} & -42.441 & -1.073\times10^{-15} & 128.957 \end{pmatrix}$$

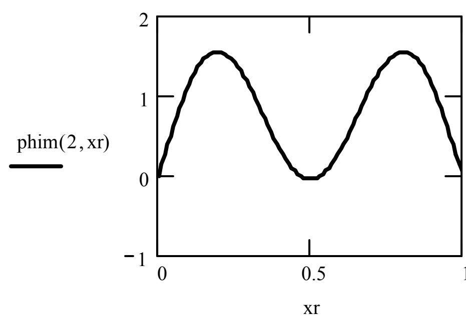
$$eig := \text{sort}(\text{eigenvals}(Hr)) \qquad eig = \begin{pmatrix} 47.59913500 \\ 53.41889638 \\ 117.14978470 \\ 151.09690901 \end{pmatrix}$$

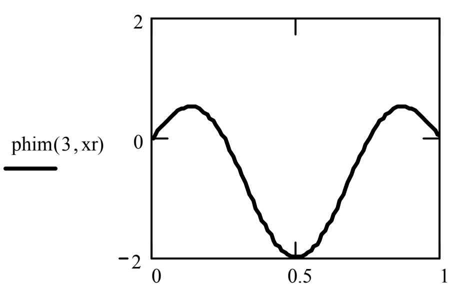
$$m := 1,2..n \qquad C^{\langle m\rangle} := \text{eigenvec}(Hr, eig_m) \qquad C = \begin{pmatrix} 0 & 0.69047 & -0.72336 & 0 \\ 0.88661 & 0 & 0 & -0.46251 \\ 0 & 0.72336 & 0.69047 & 0 \\ 0.46251 & 0 & 0 & 0.88661 \end{pmatrix}$$

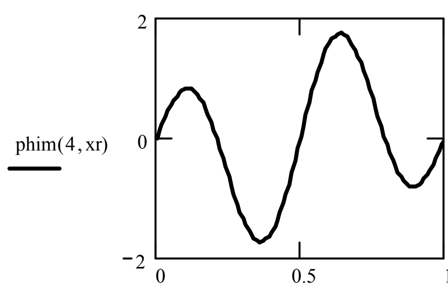
$xr := 0, .01..1$

$$phim(m,xr) := \frac{\sum_{j=1}^{n} C_{j,m}\cdot fj(j,xr)}{\left[\sum_{j=1}^{n}(C_{m,j})^2\right]^{0.5}} \qquad phim(2,0.5) = -0.047$$



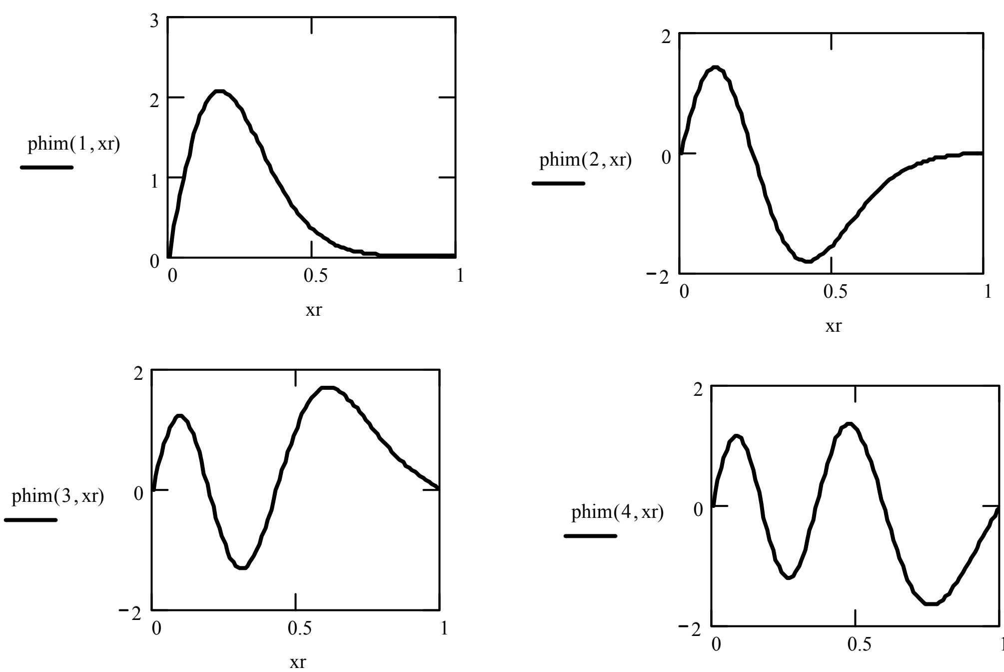






8.61 We modify the Mathcad sheet for Prob. 8.60 by adding the definition p:=0 if we want to include only basis functions with PIB quantum number $n = 2, 4, 6, \ldots$ (the odd-function states) or by adding p:=1 to include only the $n = 1, 3, 5, \ldots$ PIB states (the even-function states). In the fj, fk, and $\mathrm{Tr}_{j,k}$ definitions, j is replaced by 2j – p and k is replaced by 2k – p. With 16 even basis functions, the lowest two eigenvalues are 45.807849 and 113.938854. With 16 odd basis functions, the lowest two eigenvalues are 46.111840 and 143.358149. These numbers agree with those found in Prob. 8.59 using 32 basis functions.

8.62 The Mathcad sheet for Prob. 8.60 is modified by changing V0r to 200, by changing the limits in the $\mathrm{Vr}_{j,k}$ integral to 0 and 1, and by inserting a factor of xr in the integrand of the $\mathrm{Vr}_{j,k}$ integral. With 8 basis functions, one finds the four lowest eigenvalues 63.468669, 110.971574, 150.048599, 187.092431; with 12 basis functions, one finds 63.466117, 110.966517, 150.039184, 187.068173. The lowest four approximate wave functions have 0, 1, 2, and 3 interior nodes. Graphs of the 12-basis-function four lowest variational functions are



The plots show that as the energy of the state increases, the probability of finding the particle in the right half of the box (where *V* is greatest) increases. In the normalized variation functions, PIB functions whose coefficient is greater than 0.1 in magnitude are $n = 1, 2, 3$, and 4 for the ground state and $n = 1, 3, 4$, and 5 for the first excited state.

8.63 The fj and fk definitions are revised as indicated in the text. In the $\mathrm{Tr}_{j,k}$ definition, the 2 in the denominator is changed to 200. In the $\mathrm{Vr}_{j,k}$ definition, V0r is replaced by $(\mathrm{xr}^2/2)$ and the limits are changed to –5 and 5. The xr definition becomes xr:= –5,–4.95..5. One finds 13 basis functions are needed to get three-decimal-place accuracy; the lowest 5 eigenvalues are 0.500000002, 1.50000125, 2.5000019, 3.5002147, 4.500204. In the normalized variation functions, PIB functions whose coefficient is greater than 0.1 in magnitude are n = 1, 3, and 5 for the ground state and n =2, 4, 6, and 8 for the first excited state.

8.64 The fj and fk definitions are modified to resemble those in Prob. 8.63. In the $\mathrm{Tr}_{\mathrm{j,k}}$ definition, the 2 in the denominator is changed to 98 or 162 for the box lengths of 7 and 9 units, respectively. In the $\mathrm{Vr}_{\mathrm{j,k}}$ definition, V0r is replaced by xr^4 and the limits are appropriately modified. The xr definition is suitably modified. When the number of basis functions is increased from 9 to 10, an odd basis function is being added, and this changes the energy of the second lowest state (which is an odd function) but has no effect whatever on the energies of the first and third states (which are even functions). Hence, to be sure the three lowest energies are not changing in the third decimal place, one must check that these energies remain unchanged in the third decimal place for three successive values of the number of basis functions. For a box length of 7 units, this first occurs for 13, 14, and 15 basis functions. With 15 basis functions, the three lowest reduced energies are 0.6680, 2.3936_5, and 4.6968, in good agreement with the values in Prob. 4.32. For a box length of 9 units, stability in the third decimal place first occurs with 16, 17, and 18 basis functions. The 18-basis-function lowest energies are 0.6680. 2.3936_5, and 4.6978. The wave functions resemble those for the harmonic oscillator.

8.65 $\phi = r^{-1}F(r)Y_l^m(\theta,\phi) = r^{-1}[\sum_j c_j\psi_{\mathrm{PIB},j}(r)]Y_l^m(\theta,\phi) = \sum_j c_j\psi_{\mathrm{PIB},j}(r)r^{-1}Y_l^m(\theta,\phi) = \sum_j c_j f_j$, so $f_j = \psi_{\mathrm{PIB},j}(r)r^{-1}Y_l^m(\theta,\phi)$. Then $S_{jk} = \langle f_j \mid f_k\rangle = \int_0^\infty \psi_{\mathrm{PIB},j}(r)\psi_{\mathrm{PIB},k}(r)r^{-2}r^2\,dr\int_0^{2\pi}\int_0^\pi Y_l^{m}{}^*\,Y_l^m\sin\theta\,d\theta\,d\phi = \delta_{jk}$, since the spherical harmonics are normalized and the PIB functions are orthonormal.

Also, $H_{jk} = \langle f_j \mid \hat{H} \mid f_k\rangle$. The H-atom Hamiltonian has the form (6.8) and f_k has the form (6.16), with R in (6.16) replaced by $\psi_{\mathrm{PIB},k}r^{-1}$. So $\hat{H}f_k$ is given by the left side of (6.17) with R in (6.17) replaced by $\psi_{\mathrm{PIB},k}r^{-1}$, with R' replaced by $(d/dr)(\psi_{\mathrm{PIB},k}r^{-1}) =$ $-r^{-2}\psi_{\mathrm{PIB},k} + r^{-1}\psi'_{\mathrm{PIB},k}$ with R'' replaced by $(d^2/dr^2)(\psi_{\mathrm{PIB},k}r^{-1}) =$ $2r^{-3}\psi_{\mathrm{PIB},k} - 2r^{-2}\psi'_{\mathrm{PIB},k} + r^{-1}\psi''_{\mathrm{PIB},k}$, with $V = -e'^2/r$, and with $l = 0$, since we consider only the $l = 0$ states. With these substitutions, the left side of (6.17) becomes $\hat{H}f_k =$

$$-\frac{\hbar^2}{2\mu}\{2r^{-3}\psi_{\mathrm{PIB},k} - 2r^{-2}\psi'_{\mathrm{PIB},k} + r^{-1}\psi''_{\mathrm{PIB},k} + 2r^{-1}(-r^{-2}\psi_{\mathrm{PIB},k} + r^{-1}\psi'_{\mathrm{PIB},k})\} - Ze'^2r^{-1}\psi_{\mathrm{PIB},k}r^{-1} =$$

$r^{-1}[-(\hbar^2/2\mu)\psi''_{\mathrm{PIB},k} - (Ze'^2/r)\psi_{\mathrm{PIB},k}]$. Then $H_{jk} = \langle f_j \mid \hat{H} \mid f_k\rangle$ =

$\int_0^\infty \psi_{\text{PIB},j}(r)[-(\hbar^2/2\mu)\psi''_{\text{PIB},k} - (Ze'^2/r)\psi_{\text{PIB},k}]r^{-2}r^2\,dr \int_0^{2\pi}\int_0^\pi Y_l^m * Y_l^m \sin\theta\,d\theta\,d\phi =$
$\int_0^l \psi_{\text{PIB},j}(r)[-(\hbar^2/2\mu)\psi''_{\text{PIB},k}]\,dr - \int_0^l \psi_{\text{PIB},j}(r)[-(Ze'^2/r)\psi_{\text{PIB},k}]\,dr = T_{jk} + V_{jk}$ (ψ_{PIB} is zero for r greater than the box length).

Since $-(\hbar^2/2\mu)(d^2/dr^2)$ in T_{jk} is the PIB Hamiltonian operator, we have $T_{jk} = \langle\psi_{\text{PIB},j}|\hat{H}_{\text{PIB}}|\psi_{\text{PIB},k}\rangle = E_{\text{PIB}}\langle\psi_{\text{PIB},j}|\psi_{\text{PIB},k}\rangle = (k^2 4\pi^2\hbar^2/8\mu l^2)\delta_{jk}$, as in Prob. 8.59a. When we switch to reduced (r) units, Eq. (6.139) shows that $Tr_{j,k} = T_{jk}/\mu e'^4\hbar^{-2} = (k^2 4\pi^2\hbar^2/8\mu l^2)\delta_{jk}/\mu e'^4\hbar^{-2} = (k^2\pi^2\hbar^4/2e'^4\mu^2 l^2)\delta_{jk}$. The reduced length is given by (6.139) as $l_r = \mu e'^2 l/\hbar^2$, so
$Tr_{j,k} = (k^2\pi^2\hbar^4\mu^2 e'^4/2e'^4\mu^2 l_r^2\hbar^4)\delta_{jk} = (k^2\pi^2/2l_r^2)\delta_{jk}$.

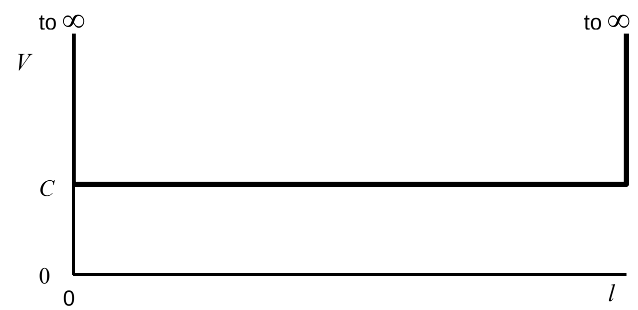
Since the reduced length is taken as 27 in this problem, the $\text{Tr}_{\text{j,k}}$ expression in Prob. 8.59 is modified by replacing the 2 in the denominator with $2(27)^2$. Also fj(j,xr) becomes $(2/27)^{0.5}\cdot\sin(\text{j}\cdot\pi\cdot\text{xr}/27)$ and fk is similarly changed. In $\text{Vr}_{\text{j,k}}$, the integration limits are 0 and 27 and V0 in $\text{Vr}_{\text{j,k}}$ in Prob. 8.59 is changed to (–1/xr). With 28 basis functions, one finds the three lowest eigenvalues are –0.47334, –0.12143, and –0.05396, as compared with the true values $-0.5/n^2$ = –0.50000, –0.12500, and –0.05555… . The accuracy is mediocre. (With 40 basis functions, one finds –0.48852, –0.12351, and –0.05463.)

8.66 **(a)** T; **(b)** T; **(c)** T; (**d)** T; **(e)** T; **(f)** T; **(g)** T; **(h)** F; **(i)** T; **(j)** F; **(k)** F (This is true only if $\mathbf{A}^{-1}$ exists.); **(l)** T; **(m)** T; **(n)** T (This was mentioned in the Sec. 8,6 example.).

Chapter 9

Perturbation Theory

9.1 **(a)**



(b) The perturbation on the particle in a box is $\hat{H}' = C$ for $0 \le x \le l$. So $E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = C\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = C.$

9.2 **(a)** $E_n^{(2)} = \sum_{m \ne n} | H'_{mn} |^2 / (E_n^{(0)} - E_m^{(0)})$. $H'_{mn} = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = C\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = 0,$ since the unperturbed particle-in-a-box (pib) functions are orthogonal. So $E_n^{(2)} = 0.$

(b) We have $\psi_n^{(1)} = \sum_{m \ne n} a_m \psi_m^{(0)}$, where $a_m = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle / [E_n^{(0)} - E_m^{(0)}]$. Since $\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = C\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = 0$, it follows that $a_m = 0$ and $\psi_n^{(1)} = 0.$

(c) From Prob. 4.52, addition of the constant *C* to the pib potential energy leaves the wave functions unchanged and simply adds *C* to the energy eigenvalues. The results $\psi_n^{(1)} = 0$, $E_n^{(1)} = C$, and $E_n^{(2)} = 0$ are thus consistent with Prob. 4.52.

9.3 From (9.22) and (4.57), $E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = (4\alpha^3/\pi)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} (cx^3 + dx^4)\, dx =$ $2(\alpha^3/\pi)^{1/2} [c \int_{-\infty}^{\infty} x^5 e^{-\alpha x^2} dx + d \int_{-\infty}^{\infty} x^6 e^{-\alpha x^2} dx] = 4(\alpha^3/\pi)^{1/2} d \int_0^{\infty} x^6 e^{-\alpha x^2} dx =$ $4(\alpha^3/\pi)^{1/2} d \int_0^{\infty} x^6 e^{-\alpha x^2} dx = 4(\alpha^3/\pi)^{1/2} d\, (3 \cdot 5/2^4)(\pi^{1/2}/\alpha^7)^{1/2} = (15/4)(d/\alpha^2) =$ $15d\hbar^2/16\pi^2\nu^2 m^2$, where (4.53), (4.33), and (A.10) were used.

9.4 **(a)** Since *V* is zero inside the box for the particle in a box, we have $\hat{H}' = V_0$ for $\frac{1}{4}l \le x \le \frac{3}{4}l$ and $\hat{H}' = 0$ elsewhere. So

$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin^2(n\pi x/l)\,dx = (2V_0/l)[\tfrac{1}{2}x - (l/4n\pi)\sin(2n\pi x/l)]\,|_{l/4}^{3l/4}$
$= \tfrac{1}{2}V_0 - (V_0/2n\pi)[\sin(3n\pi/2) - \sin(n\pi/2)]$ with $V_0 = \hbar^2/ml^2$, where (A.2) was used.

(b) $E_n^{(0)} = n^2h^2/8ml^2 = \pi^2 n^2\hbar^2/2ml^2$. For $n = 1$,
$E_1^{(1)} = V_0[\tfrac{1}{2} - (2\pi)^{-1}(\sin 3\pi/2) + (2\pi)^{-1}(\sin \pi/2)] = (\hbar^2/ml^2)(0.5 + \pi^{-1}) = 0.8183099(\hbar^2/ml^2)$
and $E_1^{(0)} + E_1^{(1)} = 5.753112\hbar^2/ml^2$. For $n = 2$,
$E_2^{(1)} = V_0[\tfrac{1}{2} - (4\pi)^{-1}(\sin 3\pi) + (4\pi)^{-1}(\sin \pi)] = \tfrac{1}{2}(\hbar^2/ml^2)$ and
$E_2^{(0)} + E_2^{(1)} = 20.23921\hbar^2/ml^2$. The beginning of Sec. 9.4 explains why these results are the same as the variation results of Probs. 8.2a and 8.17.

9.5 V_0 is a constant and $E_n^{(1)}$ equals V_0 times the area under the ψ_n^2 curve from $l/4$ to $3l/4$. This area in the central region of the box is greatest for the $n = 1$ wave function, which has no interior nodes and has its maximum in ψ^2 at the box center. Other states have interior nodes and have maxima in ψ^2 away from the center, and will have a smaller portion of the area under the ψ^2 curve in the central region.

9.6 From (9.27), $\psi_n^{(1)} = \sum_{m\neq n} a_m\psi_m^{(0)} = (2/l)^{1/2}\sum_{m\neq n} a_m \sin(m\pi x/l)$. To find a_m, which is given by (9.26), we need $\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = H'_{mn}$. We have
$H'_{mn} = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = (2/l)\int_{l/4}^{3l/4} V_0 \sin(m\pi x/l)\sin(n\pi x/l)\,dx =$

$$\frac{2V_0}{l}\left[\frac{l\sin[(m-n)\pi x/l]}{2(m-n)\pi} - \frac{l\sin[(m+n)\pi x/l]}{2(m+n)\pi}\right]\Bigg|_{l/4}^{3l/4} =$$

$$\frac{\hbar^2}{ml^2}\left[\frac{\sin[3(m-n)\pi/4] - \sin[(m-n)\pi/4]}{(m-n)\pi} - \frac{\sin[3(m+n)\pi/4] - \sin[(m+n)\pi/4]}{(m+n)\pi}\right]$$

Then $a_m = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle/[E_n^{(0)} - E_m^{(0)}] = 8ml^2H'_{mn}/(n^2 - m^2)h^2$.

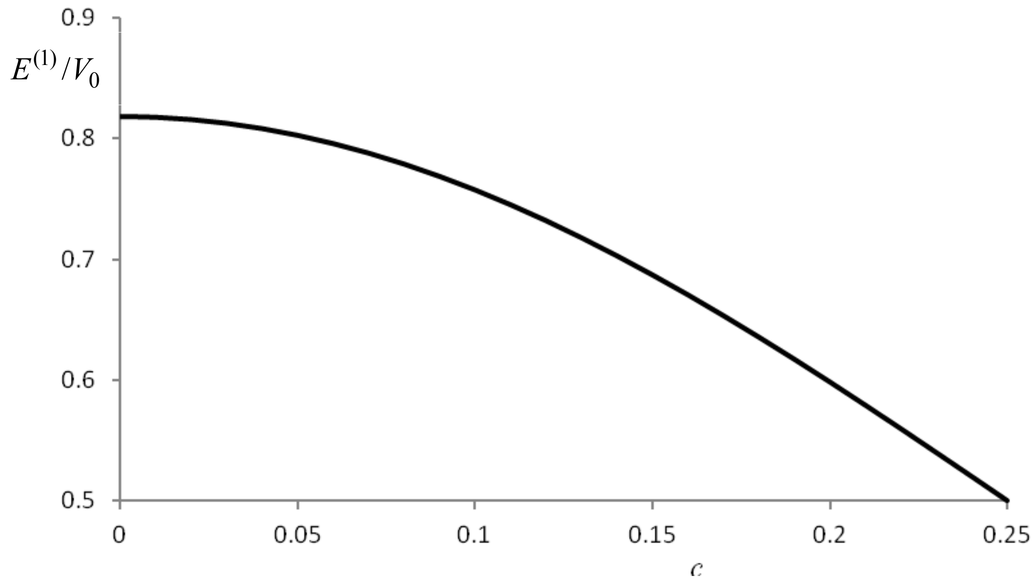
9.7 **(a)** With the origin at the center of the box, the perturbation is an even function (see the figure in Prob. 8.2). The $n = 1$ PIB wave function is an even function. The $m = 2, 4, 6,\ldots$ PIB wave functions are odd functions, and the integrand is an odd function. Hence the integral is zero.

(b) $E_1^{(2)} = \sum_{m\neq 1} |H'_{m1}|^2/(E_1^{(0)} - E_m^{(0)}) = (8ml^2/h^2)\sum_{m=3,5,7\ldots} |H'_{m1}|^2/(1-m^2) =$
$(2ml^2/\hbar^2\pi^2)\sum_{m=3,5,7\ldots} H'_{m1}|^2/(1-m^2)$, where H'_{m1} is given by the expression in the Prob. 9.6 solution with $n = 1$. If one evaluates $E_1^{(2)}$ by summing through $m = 1999$, the last term has the value $-5.15\times 10^{-15}(\hbar^2/ml^2)$ and $E_1^{(2)} = -0.002733825(\hbar^2/ml^2)$. (Because the terms decrease slowly with increasing m, one needs to continue summing until the

terms become extremely small.) Use of $E_1^{(0)} + E_1^{(1)} = 5.753112\hbar^2/ml^2$ from Prob. 9.4b gives $E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = 5.750378\hbar^2/ml^2$, which is much closer to the true value $5.750345\hbar^2/ml^2$ than the $E_1^{(0)} + E_1^{(1)}$ value.

9.8 **(a)** Since V is zero inside the box for the particle in a box, we have $\hat{H}' = V_0$ for $(0.25+c)l \le x \le (0.75+c)l$ and $\hat{H}' = 0$ elsewhere. So $E^{(1)} = \langle\psi^{(0)}|\hat{H}'|\psi^{(0)}\rangle =$ $(2/l)\int_{(0.25+c)l}^{(0.75+c)l} V_0 \sin^2(n\pi x/l)\, dx = (2V_0/l)[\frac{1}{2}x - (l/4n\pi)\sin(2n\pi x/l)]\,|_{(0.25+c)l}^{(0.75+c)l} =$ $\frac{1}{2}V_0 - (V_0/2n\pi)\{\sin[(1.5+2c)n\pi] - \sin[(0.5+2c)n\pi]\}$, where (A.2) was used.

(b) $E^{(1)}/V_0 = 0.5 - (0.5/\pi)\{\sin[(1.5+2c)\pi] - \sin[(0.5+2c)\pi]\}$. The graph is



For $c = 0$, the high potential-energy region is in the central region of the box, where the unperturbed probability density is greatest. As c increases, the high potential-energy region moves to where the unperturbed probability density is lower. $E^{(1)}$ decreases as c increases, because an increase in c decreases the probability that the particle will be found in the high potential-energy region.

9.9 With the assumption that the charge is uniformly distributed in the nucleus, the unpenetrated charge Q equals e times the fraction of nuclear volume occupied by a sphere of radius r. So $Q = \left(\frac{4}{3}\pi r^3 \big/ \frac{4}{3}\pi R_n^{\,3}\right)e = (r/R_n)^3 e$, where $R_n \equiv 10^{-15}$ m. We shall use $E^{(1)}$ to estimate the energy shift. (Evaluation of higher-order corrections is much too hard to be feasible.) The electron's potential energy is affected by the finite nuclear size only when the electron has penetrated the nucleus, so $\hat{H}'$ is nonzero only for $0 \le r \le R_n$. We have $\hat{H}^0 = \hat{T} - e^2/4\pi\varepsilon_0 r$, and $\hat{H} = \hat{T} - eQ/4\pi\varepsilon_0 r$ for $0 \le r \le 10^{-15}$ m. So

$\hat{H}' = \hat{H} - \hat{H}^0 = -\dfrac{eQ}{4\pi\varepsilon_0 r} + \dfrac{e^2}{4\pi\varepsilon_0 r} = \dfrac{e^2}{4\pi\varepsilon_0}\left(\dfrac{1}{r} - \dfrac{r^2}{R_n^3}\right)$ for $0 \le r \le 10^{-15}$ m and

$E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle = \dfrac{1}{\pi a^3}\dfrac{e^2}{4\pi\varepsilon_0}\int_0^{R_n} e^{-2r/a}(r - r^4/R_n^3)\,dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi$. Since $a = 0.5\times 10^{-10}$ m $>> R_n$, $e^{-2r/a}$ differs negligibly from 1 in the integration range. So $E^{(1)} = (1/\pi a^3)(e^2/4\pi\varepsilon_0)(4\pi)(\frac{1}{2}r^2 - r^5/5R_n^3)\,|_0^{R_n} = (e^2/\pi a^3\varepsilon_0)(0.3R_n^2) =$ $(1.602\times 10^{-19}\text{ C})^2(0.3)(10^{-30}\text{ m}^2)/[\pi(0.529\times 10^{-10}\text{ m})^3(8.854\times 10^{-12}\text{ C}^2\text{ N}^{-1}\text{ m}^{-2})] =$ 1.87×10^{-27} J $= 1.17\times 10^{-8}$ eV, which is negligible compared with the –13.6 eV ground-state energy.

9.10 The formula is $E_n^{(2)} = \sum_{m\ne n} |H'_{mn}|^2/(E_n^{(0)} - E_m^{(0)})$ for a nondegenerate level. If *n* is the (nondegenerate) ground state, then $E_n^{(0)} - E_m^{(0)}$ is always negative and $|H'_{mn}|^2$ is never negative, so $E_n^{(2)}$ must be negative or zero. It will be zero if all the H'_{mn} integrals are zero, as in Prob. 9.2.

9.11 **(a)** $E_v^{(1)} = \langle \psi_v^{(0)} | cx^3 | \psi_v^{(0)} \rangle = 0$; the harmonic-oscillator ψ's have definite parity, so $|\psi_v^{(0)}|^2$ is an even function and the integrand is an odd function. Hence the integral from $-\infty$ to ∞ is zero.

(b) From (9.35),

$E_v^{(2)} = \sum_{m\ne v} |\langle \psi_m^{(0)} | \hat{H}' | \psi_v^{(0)} \rangle|^2/(E_v^{(0)} - E_m^{(0)}) = (h\nu)^{-1}\sum_{m\ne v} |\langle \psi_m^{(0)} | cx^3 | \psi_v^{(0)} \rangle|^2/(v - m)$.

To evaluate $|\langle \psi_m^{(0)} | \hat{H}' | \psi_v^{(0)} \rangle|^2$ from the formula given for $\langle \psi_m^{(0)} | \hat{H}' | \psi_v^{(0)} \rangle$, we use $(\delta_{ij})^2 = \delta_{ij}$ and $\delta_{ij}\delta_{ik} = 0$ for $k \ne j$, which follow from the Kronecker-delta definition. So

$E_v^{(2)} =$

$$\frac{c}{8\alpha^3 h\nu}\sum_{m\ne v}\frac{(v+1)(v+2)(v+3)\delta_{m,v+3} + 9(v+1)^3\delta_{m,v+1} + 9v^3\delta_{m,v-1} + v(v-1)(v-2)\delta_{m,v-3}}{v - m}$$

$$E_v^{(2)} = \frac{c}{8\alpha^3 h\nu}[-\tfrac{1}{3}(v+1)(v+2)(v+3) - 9(v+1)^3 + 9v^3 + \tfrac{1}{3}v(v-1)(v-2)]$$

$$E_v^{(2)} = -\frac{c}{8\alpha^3 h\nu}(30v^2 + 30v + 11)$$

(c) From (9.27), $\psi_v^{(1)}$ contains a contribution from the state $\psi_m^{(1)}$ if $\langle \psi_m^{(0)} | cx^3 | \psi_v^{(0)} \rangle \ne 0$. The formula given in the problem shows that this integral is nonzero when *m* is $v+3$, $v+1$, $v-1$, or $v-3$. (The $v-3$ contribution is absent when v is 0, 1, or 2. The $v-1$ contribution is absent when v is 0.)

9.12 The variational integral is given by (9.64) with $Z = 1$, so $\langle \phi \,|\, \hat{H} \,|\, \phi \rangle = -(1 - \frac{5}{16})^2 (e^2/4\pi\varepsilon_0 a_0) = -(11/16)^2 2(13.60 \text{ eV}) = -12.86$ eV, which is higher than the H-atom ground-state energy –13.60 eV, so this trial function predicts H^- is unstable with respect to dissociation to an H atom and an electron.

9.13 The unperturbed Hamiltonian is the sum of two hydrogenlike Hamiltonians, each with nuclear charge $Z - 5/16$. Hence each unperturbed wave function has the form $f(1)g(2)$, where *f* and *g* are hydrogenlike functions with nuclear charge $Z - 5/16$. From (9.48), the ground-state $E^{(0)}$ is $-(2 - 5/16)^2(1+1)(13.60 \text{ eV}) = -77.46 \text{ eV}$. The ground-state unperturbed wave function is 1*s*(1)1*s*(2), where the nuclear charge is 27/16; this is (9.56) with $\zeta = 27/16$. We have $E^{(1)} = (e^2/4\pi\varepsilon_0)\langle 1\text{s}(1)1\text{s}(2) \,|\, 1/r_{12} - 5/16r_1 - 5/16r_2 \,|\, 1\text{s}(1)1\text{s}(2)\rangle$. From (9.61), $\langle 1\text{s}(1)1\text{s}(2) \,|\, 1/r_{12} \,|\, 1\text{s}(1)1\text{s}(2)\rangle = 5\zeta/8a_0$. The equations between (9.60) and (9.61) give $\langle 1\text{s}(1)1\text{s}(2) \,|\, 1/r_1 \,|\, 1\text{s}(1)1\text{s}(2)\rangle = \langle 1\text{s}(1)1\text{s}(2) \,|\, 1/r_2 \,|\, 1\text{s}(1)1\text{s}(2)\rangle = \zeta/a_0$. Hence $E^{(1)} = e'^2[5\zeta/8a_0 - (5/16)(\zeta/a_0) - (5/16)(\zeta/a_0)] = 0$. Note that $E^{(0)} + E^{(1)}$ is more accurate than the perturbation result (9.54) and equals the variation result (9.64).

9.14 Substitution of (9.123) into (9.52) and multiplication by $Y_0^0(Y_0^0)^* 4\pi$ gives

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\int_0^{\infty}\int_0^{\infty} e^{-2Zr_1/a_0}e^{-2Zr_2/a_0}\,\frac{r_<^l}{r_>^{l+1}}\,r_1^2r_2^2\,dr_1\,dr_2$$

$$\times\int_0^{2\pi}\int_0^{\pi}\left[Y_l^m(\theta_1,\phi_1)\right]^* Y_0^0(\theta_1,\phi_1)\sin\theta_1\,d\theta_1\,d\phi_1$$

$$\times\int_0^{2\pi}\int_0^{\pi}\left[Y_0^0(\theta_2,\phi_2)\right]^* Y_l^m(\theta_2,\phi_2)\sin\theta_2\,d\theta_2\,d\phi_2$$

Use of the orthonormality of the spherical harmonics [Eq. (7.27)] gives

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\int_0^{\infty}\int_0^{\infty}(\cdots)\,dr_1\,dr_2\,\delta_{l,0}\delta_{m,0}\delta_{l,0}\delta_{m,0}$$

The Kronecker deltas make all terms vanish except the single term with $m = 0 = l$, so

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^{\infty}\int_0^{\infty} e^{-2Zr_1/a_0}e^{-2Zr_2/a_0}\,\frac{1}{r_>}r_1^2r_2^2\,dr_1\,dr_2$$

If we integrate first over r_1 then in the range $0 \le r_1 \le r_2$, we have $r_> = r_2$; in the range $r_2 \le r_1 \le \infty$, we have $r_> = r_1$. Therefore

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^\infty e^{-2Zr_2/a_0} r_2^2 \left(\int_0^{r_2} e^{-2Zr_1/a_0}\frac{r_1^2}{r_2}dr_1 + \int_{r_2}^\infty e^{-2Zr_1/a_0}\frac{r_1^2}{r_1}dr_1\right)dr_2$$

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^\infty e^{-2Zr_2/a_0} r_2 \left(\int_0^{r_2} e^{-2Zr_1/a_0} r_1^2 dr_1\right)dr_2 + \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^\infty e^{-2Zr_2/a_0} r_2^2 \left(\int_{r_2}^\infty e^{-2Zr_1/a_0} r_1\, dr_1\right)dr_2$$

Using the indefinite integrals (A.6) and (A.7) in the Appendix, we do the r_1 integrals to obtain r_2 integrals that are evaluated using (A.8) The result is

$$E^{(1)} = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right)$$

9.15 From (9.64) and (6.106), the energy is proportional to m_e. The ${}^4_2\text{He}$ nuclear mass m_α is about 4 times the proton mass, which in turn is 1836 times the electron mass, so m_α is about 7350 times m_e. Then $\mu = m_e m_\alpha/(m_e + m_\alpha) = 7350m_e^2/7351m_e = 0.999864$, and use of μ multiplies the energies by 0.999864.

9.16 $\langle 1/r_{12}\rangle = \langle\psi|1/r_{12}|\psi\rangle \approx \langle\psi^{(0)}|1/r_{12}|\psi^{(0)}\rangle = (e^2/4\pi\varepsilon_0)^{-1}\langle\psi^{(0)}|e^2/4\pi\varepsilon_0 r_{12}|\psi^{(0)}\rangle =$ $(e^2/4\pi\varepsilon_0)^{-1}\langle\psi^{(0)}|\hat{H}'|\psi^{(0)}\rangle = (e^2/4\pi\varepsilon_0)^{-1}(34.0\text{ eV})(1.602\times10^{-19}\text{J/eV}) =$ $e^{-2}(4\pi\varepsilon_0)(5.45\times10^{-18}\text{J}) = (1.602\times10^{-19}\text{ C})^{-2}(4\pi\cdot 8.854\times10^{-12}\text{ C}^2/\text{N-m}^2)(5.45\times10^{-18}\text{ J})$ $= 2.36\times10^{10}\text{ m}^{-1}$ and $\langle 1/r_{12}\rangle^{-1} \approx 0.42\times10^{-10}$ m. A more accurate value can be found by replacing Z in (9.53) with $Z - \frac{5}{16} = 1.6875$, Eq. (9.63). This gives $\langle 1/r_{12}\rangle = (1.6875/2)(2.36\times10^{10}\text{ m}^{-1}) = 1.99\times10^{10}\text{ m}^{-1}$ and $\langle 1/r_{12}\rangle^{-1} \approx 0.50\times10^{-10}$ m. The value found from an accurate He ground-state wave function is $\langle 1/r_{12}\rangle^{-1} \approx 0.56\times10^{-10}$ m [Pekeris, *Phys. Rev.*, **115**, 1216 (1959)].

9.17 The trial function (9.56) has the form $\phi = 1s_\zeta(1)1s_\zeta(2)$, where the subscript indicates use of ζ in ϕ. Then $\langle r_1\rangle = \langle 1s_\zeta(1)1s_\zeta(2)|r_1|1s_\zeta(1)1s_\zeta(2)\rangle = \langle 1s_\zeta(1)|r_1|1s_\zeta(1)\rangle$, since $1s_\zeta(2)$ is normalized. The integral $\langle 1s_\zeta(1)|r_1|1s_\zeta(1)\rangle$ is the same as occurs in the calculation of $\langle r\rangle$ for the hydrogenlike atom, except that Z is replaced by ζ. So $\langle r_1\rangle = 3a/2\zeta$.

9.18 **(a)** Since $H'_{21} = (H'_{12})^* = (2b)^* = 2b,$ the secular equation (9.84) is

$$\begin{vmatrix} H'_{11} - E^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E^{(1)} \end{vmatrix} = 0 = \begin{vmatrix} 4b - E^{(1)} & 2b \\ 2b & 6b - E^{(1)} \end{vmatrix} = (E^{(1)})^2 - 10bE^{(1)} + 20b^2$$

$E^{(1)} = 2.7639b,\ 7.2361b$

(b) The equations (9.82) for $E^{(1)} = 2.7639b$ are

$(H'_{11} - E^{(1)})c_1 + H'_{12}c_2 = 0 = (4b - E^{(1)})c_1 + 2bc_2 = 1.2361bc_1 + 2bc_2$

$H'_{21}c_1 + (H'_{22} - E^{(1)})c_2 = 0 = 2bc_1 + (6b - E^{(1)})c_2 = 2bc_1 + 3.2361bc_2$

These equations give $c_1 = -1.6180c_2$. The normalization condition (9.86) is $|c_1^2| + |c_2^2| = 1 = |-1.6180c_2|^2 + |c_2^2| = 3.6179|c_2^2|$ and $c_2 = 0.5257$, $c_1 = -0.8506$.

The equations (9.82) for $E^{(1)} = 7.2361b$ are

$0 = (4b - E^{(1)})c_1 + 2bc_2 = -3.2361bc_1 + 2bc_2$

$0 = 2bc_1 + (6b - E^{(1)})c_2 = 2bc_1 - 1.2361bc_2$

These equations give $c_1 = 0.6180c_2$. The normalization condition (9.86) is $|c_1^2| + |c_2^2| = 1 = |0.6180c_2|^2 + |c_2^2| = 1.3819|c_2^2|$ and $c_2 = 0.8507$, $c_1 = 0.5257$.

The correct zeroth-order functions are $-0.8506\psi_1^{(0)} + 0.5257\psi_2^{(0)}$ for $E^{(1)} = 2.7639b$ and $0.5257\psi_1^{(0)} + 0.8507\psi_2^{(0)}$ for $E^{(1)} = 7.2361b$.

9.19 Solving (9.86) for $E^{(1)}$ amounts to finding the eigenvalues of the matrix with elements H'_{mi}. As noted in the Example in Sec. 8.6,, the sum of the eigenvalues of a matrix equals the sum of the diagonal elements of the matrix. Since $H'_{11} + H'_{22} = 10b$, this must be the sum of the $E^{(1)}$ values.

9.20 $\langle\psi_m^{(0)}|\hat{H}|\psi_i^{(0)}\rangle = \langle\psi_m^{(0)}|\hat{H}^0 + \hat{H}'|\psi_i^{(0)}\rangle = \langle\psi_m^{(0)}|\hat{H}^0|\psi_i^{(0)}\rangle + \langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle =$ $E_n^{(0)}\langle\psi_m^{(0)}|\psi_i^{(0)}\rangle + \langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle = E_n^{(0)}\delta_{mi} + \langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle$, since all the unperturbed wave functions of the degenerate level have the same energy eigenvalue $E_n^{(0)}$. So $\langle\psi_m^{(0)}|\hat{H}|\psi_i^{(0)}\rangle - E_n^{(0)}\delta_{mi} = \langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle$. Substitution of this expression for $\langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle$ into (9.83) converts it to the equation in the problem.

9.21 $1 = \langle\phi_n^{(0)}|\phi_n^{(0)}\rangle = \langle\sum_{i=1}^d c_i\psi_i^{(0)}|\sum_{j=1}^d c_j\psi_j^{(0)}\rangle = \sum_{i=1}^d\sum_{j=1}^d c_i^* c_j\langle\psi_i^{(0)}|\psi_j^{(0)}\rangle = \sum_{i=1}^d\sum_{j=1}^d c_i^* c_j\delta_{ij}$ $= \sum_{i=1}^d |c_i|^2$, where (9.74) and (9.80) were used.

9.22 **(a)** Since $\hat{H} = \hat{H}_x + \hat{H}_y$, the results of Sec. 6.2 give the wave function as the product $(2/l)^{1/2}\sin(n_x\pi x/l)\cdot(2/l)^{1/2}\sin(n_y\pi y/l)$.

(b) $E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle = (2/l)(2/l)\int_{l/4}^{3l/4}\int_{l/4}^{3l/4} b\sin^2(n_x\pi x/l)\sin^2(n_y\pi y/l)\,dx\,dy =$ $(2/l)(2/l)b\int_{l/4}^{3l/4}\sin^2(n_x\pi x/l)\,dx\int_{l/4}^{3l/4}\sin^2(n_y\pi y/l)\,dy$, which is valid for nondegenerate unperturbed levels. In Prob. 9.4, we found that

$(2/l)\int_{l/4}^{3l/4}\sin^2(n\pi x/l)\,dx = \frac{1}{2} - [\sin(3n\pi/2) - \sin(n\pi/2)]/2n\pi$ (Eq. 1) so

$E_n^{(1)} = b\{\frac{1}{2} - [\sin(3n_x\pi/2) - \sin(n_x\pi/2)]/2n_x\pi\}\{\frac{1}{2} - [\sin(3n_y\pi/2) - \sin(n_y\pi/2)]/2n_y\pi\}$.
For the ground state, $n_x = 1$, $n_y = 1$ and $E^{(1)} = b(\frac{1}{2} + 1/\pi)^2 = 0.6696b$.

The unperturbed first excited level is degenerate; the states $n_x = 2$, $n_y = 1$ (state 1) and $n_x = 1$, $n_y = 2$ (state 2) have the same energies for a square box. We have
$H'_{11} = (2/l)(2/l)b\int_{l/4}^{3l/4} \sin^2(2\pi x/l)\,dx \int_{l/4}^{3l/4} \sin^2(\pi y/l)\,dy$. Eq. 1 with *n* = 2 and with *n* = 1 gives $H'_{11} = b(\frac{1}{2})(\frac{1}{2} + 1/\pi) = \frac{1}{4}b(1 + 2/\pi) = 0.4092b$. Similarly
$H'_{22} = (2/l)(2/l)b\int_{l/4}^{3l/4} \sin^2(\pi x/l)\,dx \int_{l/4}^{3l/4} \sin^2(2\pi y/l)\,dy = 0.4092b$. Then
$H'_{12} = (2/l)(2/l)b\int_{l/4}^{3l/4} \sin(2\pi x/l)\sin(\pi x/l)\,dx \int_{l/4}^{3l/4} \sin(\pi y/l)\sin(2\pi y/l)\,dy$. Use of the Prob. 9.6 result $(2/l)\int_{l/4}^{3l/4} \sin(m\pi x/l)\sin(n\pi x/l)\,dx =$

$$\frac{\sin[3(m-n)\pi/4] - \sin[(m-n)\pi/4]}{(m-n)\pi} - \frac{\sin[3(m+n)\pi/4] - \sin[(m+n)\pi/4]}{(m+n)\pi}$$

gives $H'_{12} = 0 = H'_{21}$, since $\sin(3\pi/4) = \sin(\pi/4)$. The secular determinant in (9.84) is diagonal and [Eq. (9.90)] $E_1^{(1)} = H'_{11} = 0.4092b$ and $E_2^{(1)} = H'_{22} = 0.4092b$. As noted in Sec. 9.6, we already have the correct zeroth-order functions, which are given by the expression in part (a) with $n_x = 2$, $n_y = 1$ and with $n_x = 1$, $n_y = 2$.

9.23 To achieve a block-diagonal determinant, we group the *m* = 0 functions together, numbering the functions as follows: $1 = 2s,\ 2 = 2p_0,\ 3 = 2p_1,\ 4 = 2p_{-1}$. By Eq. (7.50), we have $0 = H'_{13} = H'_{31} = H'_{14} = H'_{41} = H'_{23} = H'_{32} = H'_{24} = H'_{42} = H'_{34} = H'_{43}$. The functions 1, 2, 3, 4 are orthonormal. The perturbation H' is an odd function. From Prob. 7.28d, function 1 is even and functions 2, 3, and 4 are odd functions. Therefore $0 = H'_{11} = H'_{22} = H'_{33} = H'_{44}$, since these integrals have odd integrands. The only nonzero H' integrals are $H'_{12} = H'_{21} =$
$e\mathcal{E}\langle 2s\,|\,r\cos\theta\,|\,2p_0\rangle = e\mathcal{E}(32\pi)^{-1}a^{-4}\int_0^\infty (2r^4 - r^5/a)e^{-r/a}\,dr \int_0^\pi \cos^2\theta\sin\theta\,d\theta \int_0^{2\pi} d\phi =$
$e\mathcal{E}(32\pi)^{-1}a^{-4}(2\cdot 4!a^5 - a^{-1}5!a^6)(2/3)(2\pi) = -3e\mathcal{E}a$, where the substitution $w \equiv \cos\theta$ was used. The secular equation (9.84) is

$$\begin{vmatrix} -E^{(1)} & -3e\mathcal{E}a & 0 & 0 \\ -3e\mathcal{E}a & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{vmatrix} = 0 = (E^{(1)})^2[(E^{(1)})^2 - (3e\mathcal{E}a)^2]$$

$E^{(1)} = 0,\ 0,\ 3e\mathcal{E}a,\ -3e\mathcal{E}a$. The third and fourth functions $2p_1$ and $2p_{-1}$ are correct zeroth-order functions. The correct zeroth-order function for $E^{(1)} = -3e\mathcal{E}a$ is found from

$$-E^{(1)}c_1 - 3e\mathcal{E}ac_2 = 0 = 3e\mathcal{E}ac_1 - 3e\mathcal{E}ac_2$$
$$-3e\mathcal{E}ac_1 - E^{(1)}c_2 = 0 = -3e\mathcal{E}ac_1 + 3e\mathcal{E}ac_2$$

which give $c_1 = c_2$. Normalization gives $c_1 = 2^{-1/2}$, so the third zeroth-order function is $2^{-1/2}(2s + 2p_0)$. Similarly, the fourth zeroth-order function is $2^{-1/2}(2s - 2p_0)$.

9.24 By analogy to (9.103), (9.104), and (9.110), the correct zeroth-order functions are

$2^{-1/2}[1s(1)3s(2) - 3s(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3s(2) + 3s(1)1s(2)]$

$2^{-1/2}[1s(1)3p_x(2) - 3p_x(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3p_x(2) + 3p_x(1)1s(2)]$

$2^{-1/2}[1s(1)3p_y(2) - 3p_y(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3p_y(2) + 3p_y(1)1s(2)]$

$2^{-1/2}[1s(1)3p_z(2) - 3p_z(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3p_z(2) + 3p_z(1)1s(2)]$

$2^{-1/2}[1s(1)3d_{z^2}(2) - 3d_{z^2}(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3d_{z^2}(2) + 3d_{z^2}(1)1s(2)]$

$2^{-1/2}[1s(1)3d_{x^2-y^2}(2) - 3d_{x^2-y^2}(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3d_{x^2-y^2}(2) + 3d_{x^2-y^2}(1)1s(2)]$

$2^{-1/2}[1s(1)3d_{xy}(2) - 3d_{xy}(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3d_{xy}(2) + 3d_{xy}(1)1s(2)]$

$2^{-1/2}[1s(1)3d_{xz}(2) - 3d_{xz}(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3d_{xz}(2) + 3d_{xz}(1)1s(2)]$

$2^{-1/2}[1s(1)3d_{yz}(2) - 3d_{yz}(1)1s(2)]$ $\quad$ $2^{-1/2}[1s(1)3d_{yz}(2) + 3d_{yz}(1)1s(2)]$

(The imaginary forms of the *p* or *d* orbitals could also be used.) The two $1s3s$ functions have different energies and give two nondegenerate energy levels. The $1s3p$ functions give two levels, each level being threefold degenerate; $1s3p$ functions with the minus sign belong to a lower level than $1s3p$ functions with the plus sign. The $1s3d$ functions give two levels, each level being fivefold degenerate; $1s3d$ functions with the minus sign belong to a lower level than $1s3d$ functions with the plus sign. The $1s3s$ levels lie lowest. The $1s3d$ levels lie highest.

9.25 From (9.48), $E^{(0)} = -2^2(\frac{1}{4} + \frac{1}{4})(e^2/8\pi\varepsilon_0 a_0) = -2(13.6\text{ eV}) = -27.2\text{ eV}$, as compared with the He^+ ground-state energy [Eq. (6.94)] $-2^2(e^2/8\pi\varepsilon_0 a) = -4(13.6\text{ eV}) = -54.4$ eV. The first-order correction $E^{(1)}$ for He is $\langle 2s(1)2s(2)\,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 2s(1)2s(2)\rangle$. This integral has a positive integrand and is positive, which will make the $2s^2$ He energy larger than –27.2 eV, making even stronger the conclusion that the $2s^2$ He configuration is unstable with respect to loss of an electron.

9.26 $\langle 1s(1)2s(2)\,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(1)2s(2)\rangle = \int\int [1s(1)]^2[2s(2)]^2(e^2/4\pi\varepsilon_0 r_{12})\,d\tau_1\,d\tau_2 = J_{1s2s}$ (Eq. 1). The labeling of the variables in a definite integral does not affect the integral's value. Hence interchange of 1 and 2 in Eq. 1 gives $\langle 1s(2)2s(1)\,|\, e^2/4\pi\varepsilon_0 r_{21} \,|\, 1s(2)2s(1)\rangle = J_{1s2s}$.

Use of (9.104) or (9.103) gives
$\frac{1}{2}\langle 1s(1)2s(2) \pm 1s(2)2s(1) \,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(1)2s(2) \pm 1s(2)2s(1)\rangle =$
$\frac{1}{2}\langle 1s(1)2s(2) \,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(1)2s(2)\rangle \pm \frac{1}{2}\langle 1s(1)2s(2) \,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(2)2s(1)\rangle \pm$
$\frac{1}{2}\langle 1s(2)2s(1) \,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(1)2s(2)\rangle + \frac{1}{2}\langle 1s(2)2s(1) \,|\, e^2/4\pi\varepsilon_0 r_{12} \,|\, 1s(2)2s(1)\rangle =$
$\frac{1}{2}J_{1s2s} \pm \frac{1}{2}K_{1s2s} \pm \frac{1}{2}K_{1s2s} + \frac{1}{2}J_{1s2s} = J_{1s2s} \pm K_{1s2s}$.

9.27 As $s \to 0$, the numerator and denominator both go to zero, so we use l'Hôpital's rule: $\lim_{s\to 0}(e^{as}-1)/s = \lim_{s\to 0}(ae^{as}/1) = a$.

9.28 $\langle \psi_m^0 \,|\, Qx \,|\, \psi_n^0\rangle = Q(2/a)\int_0^l x\sin(m\pi x/l)\sin(n\pi x/l)\,dx =$

$$\frac{2Q}{a}\frac{1}{2}\left[\frac{\cos[(m-n)\pi x/l]}{(m-n)^2\pi^2/l^2} + \frac{x\sin[(m-n)\pi x/l]}{(m-n)\pi/l} - \frac{\cos[(m+n)\pi x/l]}{(m+n)^2\pi^2/l^2} - \frac{x\sin[(m+n)\pi x/l]}{(m+n)\pi/l}\right]\Bigg|_0^l$$

$$= \frac{Q}{a}\left[\frac{(-1)^{m-n}-1}{(m-n)^2\pi^2/l^2} - \frac{(-1)^{m+n}-1}{(m+n)^2\pi^2/l^2}\right]$$

since $\sin k\pi = 0$ and $\cos k\pi = (-1)^k$ where k is an integer. The integral was found from a table or by using integrals.wolfram.com. Since $(-1)^{m-n} = (-1)^{m-n}(-1)^{2n} = (-1)^{m+n}$, we have $\langle \psi_m^0 \,|\, Qx \,|\, \psi_n^0\rangle = \dfrac{Ql^2}{a\pi^2}[(-1)^{m-n}-1]\left[\dfrac{1}{(m-n)^2} - \dfrac{1}{(m+n)^2}\right]$. If $m-n$ is an even number, then $(-1)^{m-n}-1 = 1-1 = 0$ and the particle-in-a-box (PIB) transition is not allowed. So the PIB selection rule is that the change in the quantum number must be odd.

9.29 The transition will be allowed if at least one of the integrals $\langle \psi_m^0 \,|\, Qx \,|\, \psi_n^0\rangle$, $\langle \psi_m^0 \,|\, Qy \,|\, \psi_n^0\rangle$, $\langle \psi_m^0 \,|\, Qz \,|\, \psi_n^0\rangle$ is nonzero. The three-dimensional PIB wave function is the product $f(x)g(y)h(z)$ of three one-dimensional PIB functions. We have $\langle \psi_m^0 \,|\, Qx \,|\, \psi_n^0\rangle = Q\langle f(x)g(y)h(z) \,|\, x \,|\, f(x)g(y)h(z)\rangle = Q\langle f(x) \,|\, x \,|\, f(x)\rangle$, since g and h are normalized. The integral $\langle f(x) \,|\, x \,|\, f(x)\rangle$ was shown in Prob. 9.27 to be nonzero only if the change in quantum number Δn_x is an odd integer. Similarly, $\langle \psi_m^0 \,|\, Qy \,|\, \psi_n^0\rangle$ is nonzero only if Δn_y is odd and $\langle \psi_m^0 \,|\, Qz \,|\, \psi_n^0\rangle$ is nonzero only if Δn_z is odd. Thus three-dimensional PIB transitions involving unpolarized radiation are allowed if and only if one or more of the three quantum numbers changes by an odd integer.

9.30 **(a)** Equation (7.41) becomes $\hat{B}S = \sum_s \langle g_i \,|\, \hat{B}S\rangle g_i$. Operating with $\hat{A}$, we have $\hat{A}\hat{B}S = \hat{A}\sum_s \langle g_i \,|\, \hat{B}S\rangle g_i = \sum_s \langle g_i \,|\, \hat{B}S\rangle \hat{A}g_i$, since $\hat{A}$ is linear. Multiplication by R^* and

integration over all space gives
$\langle R \mid \hat{A}\hat{B} \mid S\rangle = \sum_s \langle g_i \mid \hat{B}S\rangle\langle R \mid \hat{A} \mid g_i\rangle = \sum_s \langle R \mid \hat{A} \mid g_i\rangle\langle g_i \mid \hat{B} \mid S\rangle$.

(b)
$|\langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle|^2 = \langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle^* \langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle = \langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_m^{(0)}\rangle\langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle$
and Eq. (9.35) becomes $E_n^{(2)} \approx (1/\Delta E) \sum_{m\neq n} \langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_m^{(0)}\rangle\langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle =$
$(1/\Delta E)\,[\sum_m \langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_m^{(0)}\rangle\langle \psi_m^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle - \langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle\langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle] =$
$(1/\Delta E)\,[\langle \psi_n^{(0)} \mid (\hat{H}')^2 \mid \psi_n^{(0)}\rangle - \langle \psi_n^{(0)} \mid \hat{H}' \mid \psi_n^{(0)}\rangle^2]$.

9.31 **(a)** T; **(b)** F (This is true only for wave functions with the same energy.);
(c) F; **(d)** F.

Chapter 10

Electron Spin and the Spin–Statistics Theorem

10.1 $|\mathbf{S}| = [s(s+1)]^{1/2}\hbar = (\frac{1}{2}\cdot\frac{3}{2})^{1/2}\hbar = \frac{1}{2}\sqrt{3}(6.62607\times10^{-34}\text{ J s})/2\pi = 9.133\times10^{-35}\text{ J s}.$

10.2 From Fig 10.1, $\cos\theta = m_s\hbar\big/[s(s+1)]^{1/2}\hbar = \frac{1}{2}\big/[\frac{1}{2}(\frac{3}{2})]^{1/2} = 1/3^{1/2} = 0.57735$ and $\theta = 0.95532$ rad = 54.74°.

10.3 **(a)**
$\hat{S}^2(c_1\alpha + c_2\beta) = c_1\hat{S}^2\alpha + c_2\hat{S}^2\beta = c_1 s(s+1)\hbar^2\alpha + c_2 s(s+1)\hbar^2\beta = s(s+1)\hbar^2(c_1\alpha + c_2\beta),$
where $s = \frac{1}{2}$. Also, $\hat{S}_z(c_1\alpha + c_2\beta) = c_1\hat{S}_z\alpha + c_2\hat{S}_z\beta = \frac{1}{2}c_1\hbar\alpha - \frac{1}{2}c_2\hbar\beta.$
$\hat{S}_z^2(c_1\alpha + c_2\beta) = \hat{S}_z[\hat{S}_z(c_1\alpha + c_2\beta)] = \hat{S}_z(\frac{1}{2}c_1\hbar\alpha - \frac{1}{2}c_2\hbar\beta) = \frac{1}{4}\hbar^2(c_1\alpha + c_2\beta).$

(b) $1 = \sum_{m_s=-1/2}^{1/2}[(c_1\alpha + c_2\beta)^*(c_1\alpha + c_2\beta)] = |c_1|^2\sum_{m_s=-1/2}^{1/2}\alpha^*(m_s)\alpha(m_s) +$
$(c_1)^*c_2\sum_{m_s=-1/2}^{1/2}\alpha^*\beta + (c_2)^*c_1\sum_{m_s=-1/2}^{1/2}\beta^*\alpha + |c_2|^2\sum_{m_s=-1/2}^{1/2}\beta^*\beta = |c_1|^2\cdot 1 + 0 + 0 + |c_2|^2\cdot 1$
[where (10.11) and (10.12) were used]; so $|c_1|^2 + |c_2|^2 = 1.$

10.4 **(a)** $-s\hbar,\ -(s+1)\hbar, \ldots, (s-1)\hbar,\ s\hbar$

(b) Since the labels on the directions of space are arbitrary, the answer is the same as in part (a), namely $-s\hbar,\ -(s+1)\hbar, \ldots, (s-1)\hbar,\ s\hbar$.

(c) For $s = \frac{1}{2}$, the only experimentally observable value of S^2 is $\frac{1}{2}\frac{3}{2}\hbar^2 = \frac{3}{4}\hbar^2$. The observable values of each of S_x, S_y, and S_z are $-\frac{1}{2}\hbar$ and $\frac{1}{2}\hbar$, so the only observable value of each of S_x^2, S_y^2, and S_z^2 is $\frac{1}{4}\hbar^2$. The relation $\frac{3}{4}\hbar^2 = \frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2$ shows that $S^2 = S_x^2 + S_y^2 + S_z^2$ is satisfied with observable values.

For $s = 1$, the observable value of S^2 is $2\hbar^2$. The observable values of each of S_x, S_y, and S_z are $-\hbar$, 0, and $\hbar$, and the observable values of S_x^2, S_y^2, and S_z^2 are $\hbar^2$ and 0. The relation $2\hbar^2 = \hbar^2 + \hbar^2 + 0$ shows that $S^2 = S_x^2 + S_y^2 + S_z^2$ can be satisfied with observable values.

For $s = \frac{3}{2}$, the observable value of S^2 is $\frac{3}{2}\frac{5}{2}\hbar^2 = \frac{15}{4}\hbar^2$. The observable values of each of S_x, S_y, and S_z are $-\frac{3}{2}\hbar$, $-\frac{1}{2}\hbar$, $\frac{1}{2}\hbar$, and $\frac{3}{2}\hbar$, and the observable values of S_x^2, S_y^2, and S_z^2 are $\frac{9}{4}\hbar^2$ and $\frac{1}{4}\hbar^2$. The possible observable combinations for $S_x^2 + S_y^2 + S_z^2$ are

$\frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2$, $\frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2 + \frac{9}{4}\hbar^2$, $\frac{1}{4}\hbar^2 + \frac{9}{4}\hbar^2 + \frac{9}{4}\hbar^2$, and $\frac{9}{4}\hbar^2 + \frac{9}{4}\hbar^2 + \frac{9}{4}\hbar^2$, none of which equals $\frac{15}{4}\hbar^2$, so $S^2 = S_x^2 + S_y^2 + S_z^2$ cannot be satisfied with observable values.

10.5 **(a)** Fermion. **(b)** Fermion. **(c)** Fermion. **(d)** Boson.

(e) The ^{12}C nucleus has 12 fermions (6 protons and 6 neutrons); with an even number of fermions, it is a boson.

(f) The ^{13}C nucleus has 13 fermions (6 protons and 7 neutrons); with an odd number of fermions, it is a fermion.

(g) The ^{12}C atom has 18 fermions (6 protons, 6 electrons, and 6 neutrons); with an even number of fermions, it is a boson.

(h) The ^{13}C atom has 19 fermions (6 protons, 6 electrons, and 7 neutrons); with an odd number of fermions, it is a fermion.

(i) The ^{14}N atom has 21 fermions (7 protons, 7 electrons, and 7 neutrons); with an odd number of fermions, it is a fermion.

(j) The ^{15}N atom has 22 fermions (7 protons, 7 electrons, and 8 neutrons); with an even number of fermions, it is a boson.

10.6 **(a)** $[\hat{P}_{12},\ \hat{T}]f(q_1, q_2, q_3) =$

$\hat{P}_{12}(-\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)f(q_1, q_2, q_3) - (-\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)\hat{P}_{12}f(q_1, q_2, q_3) =$

$\hat{P}_{12}(-\hbar^2/2m_e)(\partial^2 f/\partial q_1^2 + \partial^2 f/\partial q_2^2 + \partial^2 f/\partial q_3^2) + (\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)f(q_2, q_1, q_3) =$

$(-\hbar^2/2m_e)[\partial^2 f(q_2, q_1, q_3)/\partial q_2^2 + \partial^2 f(q_2, q_1, q_3)/\partial q_1^2 + \partial^2 f(q_2, q_1, q_3)/\partial q_3^2)] +$

$(\hbar^2/2m_e)[\partial^2 f(q_2, q_1, q_3)/\partial q_1^2 + \partial^2 f(q_2, q_1, q_3)/\partial q_2^2 + \partial^2 f(q_2, q_1, q_3)/\partial q_3^2)] = 0.$

Let $e' \equiv e/(4\pi\varepsilon_0)^{1/2}$. We have $[\hat{P}_{12},\ \hat{V}]f(q_1, q_2, q_3) =$

$\hat{P}_{12}[(-Ze'^2/r_1 - Ze'^2/r_2 - Ze'^2/r_3 + e'^2/r_{12} + e'^2/r_{13} + e'^2/r_{23})f(q_1, q_2, q_3)] -$

$(-Ze'^2/r_1 - Ze'^2/r_2 - Ze'^2/r_3 + e'^2/r_{12} + e'^2/r_{13} + e'^2/r_{23})\hat{P}_{12}f(q_1, q_2, q_3) =$

$(-Ze'^2/r_2 - Ze'^2/r_1 - Ze'^2/r_3 + e'^2/r_{21} + e'^2/r_{23} + e'^2/r_{13})f(q_2, q_1, q_3) -$

$(-Ze'^2/r_1 - Ze'^2/r_2 - Ze'^2/r_3 + e'^2/r_{12} + e'^2/r_{13} + e'^2/r_{23})f(q_2, q_1, q_3) = 0$. It follows from (5.4) that $[\hat{P}_{12},\ \hat{H}] = 0$.

(b) $[\hat{P}_{12},\ \hat{P}_{23}]f(q_1, q_2, q_3) = \hat{P}_{12}\hat{P}_{23}f(q_1, q_2, q_3) - \hat{P}_{23}\hat{P}_{12}f(q_1, q_2, q_3) =$

$\hat{P}_{12}f(q_1, q_3, q_2) - \hat{P}_{23}f(q_2, q_1, q_3) = f(q_2, q_3, q_1) - f(q_3, q_1, q_2) \neq 0$.

(c) If f is antisymmetric, then $\hat{P}_{12}f(q_1, q_2, q_3) = -f(q_1, q_2, q_3)$ and $\hat{P}_{23}f(q_1, q_2, q_3) = -f(q_1, q_2, q_3)$. So

$[\hat{P}_{12},\ \hat{P}_{23}]f(q_1, q_2, q_3) = \hat{P}_{12}\hat{P}_{23}f(q_1, q_2, q_3) - \hat{P}_{23}\hat{P}_{12}f(q_1, q_2, q_3) =$

$(-1)^2 f(q_1, q_2, q_3) - (-1)^2 f(q_1, q_2, q_3) = 0$.

10.7 We must prove that
$\iint [f(q_1,\ q_2)]^* \hat{P}_{12} g(q_1,\ q_2)\, d\tau_1\, d\tau_2 = \iint g(q_1,\ q_2) \hat{P}_{12} [f(q_1,\ q_2)]^* \, d\tau_1\, d\tau_2$, that is, we must show that $\iint [f(q_1,\ q_2)]^* g(q_2,\ q_1)\, d\tau_1\, d\tau_2 = \iint g(q_1,\ q_2)[f(q_2,\ q_1)]^* \, d\tau_1\, d\tau_2$ (Eq. 1). Since the integration variables in definite integrals are dummy variables, we can rename them in any way we please. On the left side of Eq. 1, let q_1 be relabeled as q_2 and let q_2 be relabeled as q_1. Then the left side of Eq. 1 becomes $\iint [f(q_2,\ q_1)]^* g(q_1,\ q_2)\, d\tau_2\, d\tau_1$, which is the same as the right side of Eq. 1.

10.8 **(1)** Neither symmetric nor antisymmetric; **(2)** antisymmetric; **(3)** symmetric; **(4)** neither; **(5)** symmetric; **(6)** symmetric.

10.9 With a spin of zero, electrons would be bosons and would require a symmetric wave function. There would be no exclusion principle to limit the number of electrons in the same orbital. Since the spin is zero, no spin factor is needed in the wave function. The zeroth-order ground-state wave function would be $1s(1)1s(2)1s(3)$, and the first excited state would be $3^{-1/2}[1s(1)1s(2)2s(3) + 1s(1)2s(2)1s(3) + 2s(1)1s(2)1s(3)]$

10.10 This function is antisymmetric, whereas the spatial factor in the He ground-state wave function is symmetric.

10.11 **(a)** $\hat{A}[f(1)g(2)] = 2^{-1/2}[f(1)g(2) - g(1)f(2)] = 2^{-1/2}[f(1)g(2) - \hat{P}_{12} f(1)g(2)] = 2^{-1/2}(1 - \hat{P}_{12}) f(1)g(2)$, so $\hat{A} = 2^{-1/2}(1 - \hat{P}_{12})$.

(b) Use of Eqs. (10.36) and (10.37) gives

$$\hat{A} f(1)g(2)h(3) = (3!)^{-1/2} \begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix} =$$

$$6^{-1/2}[f(1)g(2)h(3) - f(2)g(1)h(3) - f(3)g(2)h(1) - f(1)g(3)h(2) + f(3)g(1)h(2) + f(2)g(3)h(1)] =$$

$$6^{-1/2}(1 - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{12}\hat{P}_{13} + \hat{P}_{13}\hat{P}_{12}) f(1)g(2)h(3)$$

$$\hat{A} = 6^{-1/2}(1 - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{12}\hat{P}_{13} + \hat{P}_{13}\hat{P}_{12})$$

Other answers are possible. For example, $\hat{P}_{13}\hat{P}_{12}$ could be replaced by $\hat{P}_{12}\hat{P}_{23}$.

10.12 Writing the original determinant, we first add $-c_1$ times column 1 to column 3 and then add $-c_2$ times column 2 to column 3:

$$\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)[c_1\alpha(1)+c_2\beta(1)] \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)[c_1\alpha(2)+c_2\beta(2)] \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)[c_1\alpha(3)+c_2\beta(3)] \end{vmatrix} = \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)c_2\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)c_2\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)c_2\beta(3) \end{vmatrix} =$$

$$\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 0 \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 0 \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 0 \end{vmatrix} = 0$$

10.13 To construct wave functions for bosons.

10.14 Since the muon is not identical to an electron, the wave function need not be antisymmetric with respect to interchange of an electron and a muon, and the ground state has both electrons in the 1*s* orbital and the muon in a 1*s* orbital.

10.15 **(a)** Grouping together terms in $\psi^{(0)}$ that have the same spin factor, we have

$$\begin{aligned}\psi^{(0)} &= 6^{-1/2}\left[1s(1)2s(2)1s(3) - 1s(1)1s(2)2s(3)\right]\beta(1)\alpha(2)\alpha(3) \\ &+ 6^{-1/2}\left[1s(1)1s(2)2s(3) - 2s(1)1s(2)1s(3)\right]\alpha(1)\beta(2)\alpha(3) \\ &+ 6^{-1/2}\left[2s(1)1s(2)1s(3) - 1s(1)2s(2)1s(3)\right]\alpha(1)\alpha(2)\beta(3)\end{aligned}$$

$$\psi^{(0)} = a\beta(1)\alpha(2)\alpha(3) + b\alpha(1)\beta(2)\alpha(3) + c\alpha(1)\alpha(2)\beta(3) = A + B + C$$

where the spatial function multiplying the spin function $\beta(1)\alpha(2)\alpha(3)$ is called *a* and where $A = a\beta(1)\alpha(2)\alpha(3)$, with similar definitions for *b*, *c*, *B*, and *C*. We have

$$E^{(1)} = \int |\psi^{(0)}|^2 H'\,d\tau$$

$$\begin{aligned}E^{(1)} &= \int |A|^2 H'\,d\tau + \int |B|^2 H'\,d\tau + \int |C|^2 H'\,d\tau + \int A^*BH'\,d\tau + \int B^*CH'\,d\tau \\ &+ \int A^*CH'\,d\tau + \int AB^*H'\,d\tau + \int BC^*H'\,d\tau + \int AC^*H'\,d\tau\end{aligned}$$

Because of the orthogonality of the different spin functions in *A, B,* and C, the last six integrals in $E^{(1)}$ are zero.

(b) Since the spin functions are normalized, summation over spins in the first three integrals in $E^{(1)}$ gives one. Therefore

$$E^{(1)} = \iiint a^2 H' dv_1\,dv_2\,dv_3 + \iiint b^2 H' dv_1\,dv_2\,dv_3 + \iiint c^2 H' dv_1\,dv_2\,dv_3$$

(c) If we relabel the electrons in the *a* term in $\psi^{(0)}$ as follows: $1 \to 2,\ \ 2 \to 3,\ \ 3 \to 1$, then *a* is converted to *b*. H' is unchanged by this relabeling. Since the value of a definite integral is independent of how we label the integration variables, the first and second integrals in the last equation are equal. If we relabel the electrons in the *a* term as follows:

$1 \to 3,\ \ 2 \to 1,\ \ 3 \to 2,$ then a is converted to c. Therefore the first and third integrals in $E^{(1)}$ are equal. Hence $E^{(1)} = 3\int\int\int a^2 H'\, dv_1\, dv_2\, dv_3$.

(d) We have $3a^2 = \frac{1}{2}[1s(1)2s(2)1s(3)]^2 - [1s(1)]^2 1s(2)2s(2)1s(3)2s(3) + \frac{1}{2}[1s(1)1s(2)2s(3)]^2$ and $H' = e'^2(1/r_{12} + 1/r_{13} + 1/r_{23})$. Because of the orthogonality of 1s(3) and 2s(3), the middle term in $3a^2$ does not contribute to the $1/r_{12}$ integral and

$3\int\int\int a^2(e'^2/r_{12})\, dv_1\, dv_2\, dv_3 =$

$\frac{1}{2}\int\int[1s(1)]^2[2s(2)]^2(e'^2/r_{12})\, dv_1\, dv_2 + \frac{1}{2}\int\int[1s(1)]^2[1s(2)]^2(e'^2/r_{12})\, dv_1\, dv_2 =$

$\frac{1}{2}J_{1s2s} + \frac{1}{2}J_{1s1s}$ Because of the orthogonality of 1s(2) and 2s(2), the middle term in $3a^2$ does not contribute to the $1/r_{13}$ integral and $3\int\int\int a^2(e'^2/r_{13})\, dv_1\, dv_2\, dv_3 =$

$\frac{1}{2}\int\int[1s(1)]^2[1s(3)]^2(e'^2/r_{13})\, dv_1\, dv_2 + \frac{1}{2}\int\int[1s(1)]^2[2s(3)]^2(e'^2/r_{13})\, dv_1\, dv_2 =$

$\frac{1}{2}J_{1s1s} + \frac{1}{2}J_{1s2s}$ Finally, $3\int\int\int a^2(e'^2/r_{23})\, dv_1\, dv_2\, dv_3 =$

$\frac{1}{2}\int\int[2s(2)]^2[1s(3)]^2(e'^2/r_{23})\, dv_1\, dv_2 - \int\int 1s(2)2s(2)1s(3)2s(3)(e'^2/r_{23})\, dv_1\, dv_2 +$

$\frac{1}{2}\int\int[1s(2)]^2[2s(3)]^2(e'^2/r_{23})\, dv_1\, dv_2 = \frac{1}{2}J_{1s2s} - K_{1s2s} + \frac{1}{2}J_{1s2s}$. Adding these three integrals, we get $E^{(1)} = 3\int\int\int a^2 H'\, dv_1\, dv_2\, dv_3 = 2J_{1s2s} + J_{1s1s} - K_{1s2s}$.

10.16 $E^{(1)} = \int\int\int[1s(1)]^2[1s(2)]^2[2s(3)]^2(e'^2/r_{12} + e'^2/r_{13} + e'^2/r_{23})\, d\upsilon_1\, d\upsilon_2\, d\upsilon_3 =$
$\int\int[1s(1)]^2[1s(2)]^2(e'^2/r_{12})\, d\upsilon_1\, d\upsilon_2 + \int\int[1s(1)]^2[2s(3)]^2(e'^2/r_{13})\, d\upsilon_1\, d\upsilon_3 +$
$\int\int[1s(2)]^2[2s(3)]^2(e'^2/r_{23})\, d\upsilon_2\, d\upsilon_3 = J_{1s1s} + 2J_{1s2s}$, since the orbitals are normalized. The exchange integral in the correct result (10.51) is missing.

10.17 $|\mathbf{m}_S| = (g_e e/2m_e)|\mathbf{S}| = (g_e e/2m_e)(\frac{1}{2}\cdot\frac{3}{2}\hbar^2)^{1/2} =$
$\frac{1}{4}3^{1/2}[(2.0023)(1.60218\times10^{-19}\text{ C})(6.6261\times10^{-34}\text{ J s})/[2\pi(9.1094\times10^{-31}\text{ kg})] =$
1.6082×10^{-23} J/T, since 1 T = 1 N C^{-1} m^{-1} s = 1 kg C^{-1} s^{-1}.

10.18 **(a)** $E = -\mathbf{m}_S\cdot\mathbf{B} = -(g_e e/2m_e)\mathbf{S}\cdot\mathbf{B} = -(g_e e/2m_e)|\mathbf{S}||\mathbf{B}|\cos\theta = -(g_e e/2m_e)S_z|\mathbf{B}| =$
$-(g_e e/2m_e)(\pm\frac{1}{2}\hbar)|\mathbf{B}| = \mp(g_e e\hbar/4m_e)|\mathbf{B}|$.

(b) The energy difference between the two levels in part (a) is $(g_e e\hbar/2m_e)|\mathbf{B}|$, so
$\nu = |\Delta E|/h = (g_e e/4\pi m_e)|\mathbf{B}| =$
$[(2.0023)(1.60218\times10^{-19}\text{ C})/[4\pi(9.1094\times10^{-31}\text{ kg})](1.00\text{ T}) = 2.80\times10^{10}\text{ s}^{-1}$, since
1 T = 1 N C^{-1} m^{-1} s = 1 kg C^{-1} s^{-1}.

(c) The proton, like the electron, has a spin quantum number of ½. Replacement of m_e by m_p and g_e by g_N in part (b) gives $\nu = (g_N e/4\pi m_p)|\mathbf{B}| =$ $[(5.5857)(1.60218\times 10^{-19}\text{ C})/[4\pi(1.6726\times 10^{-27}\text{ kg})](1.00\text{ T}) =$ 42.58 MHz.

10.19 **(a)** $|\mathbf{I}| = [I(I+1)]^{1/2}\hbar = (\tfrac{3}{2}\cdot\tfrac{5}{2})^{1/2}\hbar = \tfrac{1}{2}\sqrt{15}(6.62607\times 10^{-34}\text{ J s})/2\pi = 2.042\times 10^{-34}\text{ J s}$.

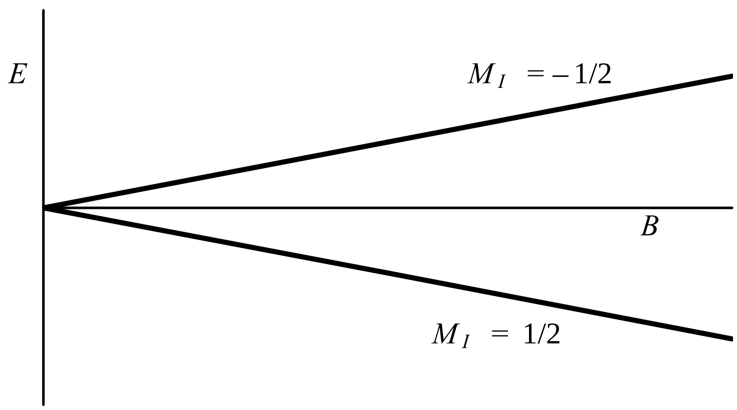
(b) $I_z = M_I\hbar = -\tfrac{3}{2}\hbar,\ -\tfrac{1}{2}\hbar,\ \tfrac{1}{2}\hbar,\ \tfrac{3}{2}\hbar.$

(c) The same as (b).

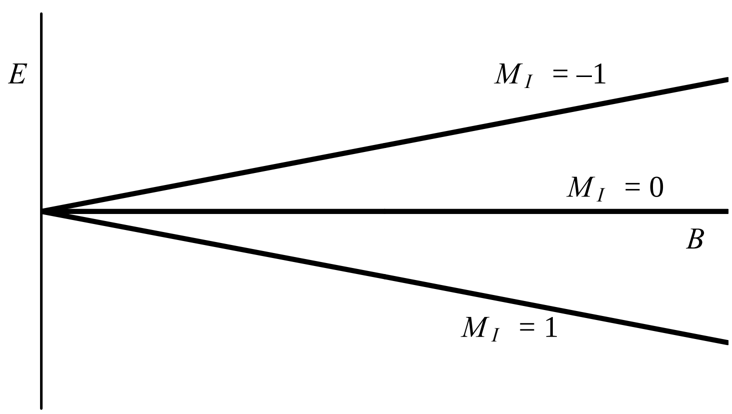
10.20 **(a)** $\gamma = g_N e/2m_p = 5.585695(1.602176\times 10^{-19}\text{ C})\big/2(1.672622\times 10^{-27}\text{ kg}) =$ $2.67522\times 10^{8}\text{ (C/kg)(N C}^{-1}\text{ m}^{-1}\text{ s)/T},$ where the expression for the tesla given in Sec. 6.8 was used. Use of 1 N = 1 kg m/s^2 gives $\gamma = 2.67522\times 10^{8}\text{ s}^{-1}$/T = 267.522 MHz/T.

(b) From (10.60), ν = (267.522 MHz/T)(1.00 T)/2π = 42.5775 Hz.

10.21 **(a)** $E = -\gamma\hbar M_I B$ with $M_I = \tfrac{1}{2}$ and $-\tfrac{1}{2}$. So $|E|$ increases linearly with *B*, and we have



(b) $M_I = 1, 0, -1$. There are three energy levels with $E = 0$ for the middle level:



10.22 ↑↑↑ ↑↑↓ ↑↓↑ ↓↑↑ ↑↓↓ ↓↑↓ ↓↓↑ ↓↓↓

The second, third and fourth arrangements produce the same magnetic field. The fifth, sixth and seventh arrangements, produce the same magnetic field. Thus we have four different possible contributions to the magnetic field: from the first arrangement; from the second, third, or fourth arrangement; from the fifth, sixth, and seventh arrangement; from the eighth arrangement. The CH_2 transition is split into four lines with relative intensities 1:3:3:1.

10.23 **(a)** The methyl peak is a triplet with 1:2:1 relative intensities; the CH_2 peak is split into four lines (of intensities 1:3:3:1) by the methyl protons and each of these lines is split into two lines (of equal intensity) by the CHO proton, so the net result is an octet with relative intensities 1:1:3:3:3:3:1:1; the CHO peak is split into three lines of relative intensities 1:2:1. The total relative intensities of the CH_3, CH_2, and CHO proton peaks are 3:2:1.

(b) The methyl protons give a triplet (intensities 1:2:1) and the CH_2 protons give a quartet (intensities 1:3:3:1). The total relative intensities of the CH_3 and CH_2 proton peaks are 6:4 (that is, 3:2).

(c) One peak that is not split.

(d) One peak that is not split.

(e) The proton on the 2 position gives an unsplit peak; the protons at the 4 and 6 positions give a peak that is a doublet (1:1 intensity ratio); the peak of the proton at the 5 position is split into two peaks by the proton at the 6 position, and each of these two peaks is split into two peaks by the proton at the 4 position—because the spin–spin coupling constant between the 5 and 6 protons is the same as the spin–spin coupling constant between the 5 and 4 protons, two of the lines resulting from the splitting coincide with each other, and the net result for the 5-position proton is a triplet with 1:2:1 relative intensities. The total relative intensities of the 2-position proton, the 4- and 6-position protons, and the 5-position proton peaks are 1:2:1. (Actually, because the NMR frequency differences between nonequivalent protons in this molecule are very small, the first-order analysis is not valid for this molecule and the spectrum is complicated.)

10.24 Similar to (10.66), we have $\hat{S}_{-}\alpha = k\beta$ (Eq. 1), where k is a constant. Normalization gives $1 = \sum_{m_s}[\beta(m_s)]^*\beta(m_s) = \sum_{m_s}(\hat{S}_{-}\alpha/k)^*\hat{S}_{-}\alpha/k$ so $|k|^2 = \sum_{m_s}(\hat{S}_{-}\alpha)^*\hat{S}_{-}\alpha =$ $\sum_{m_s}(\hat{S}_{-}\alpha)^*(\hat{S}_x - i\hat{S}_y)\alpha = \sum_{m_s}(\hat{S}_{-}\alpha)^*\hat{S}_x\alpha - i\sum_{m_s}(\hat{S}_{-}\alpha)^*\hat{S}_y\alpha$. Use of the Hermitian property (10.68) for $\hat{S}_x$ and $\hat{S}_y$ gives $k^*k = \sum_{m_s}\alpha(\hat{S}_x\hat{S}_{-}\alpha)^* - i\sum_{m_s}\alpha(\hat{S}_y\hat{S}_{-}\alpha)^*$. Taking the complex conjugate of the last equation and using (10.63) and (10.64), we have $kk^* = \sum_{m_s}\alpha^*\hat{S}_x\hat{S}_{-}\alpha + i\sum_{m_s}\alpha^*\hat{S}_y\hat{S}_{-}\alpha = \sum_{m_s}\alpha^*(\hat{S}_x + i\hat{S}_y)\hat{S}_{-}\alpha = \sum_{m_s}\alpha^*\hat{S}_{+}\hat{S}_{-}\alpha =$ $\sum_{m_s}\alpha^*(\hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z)\alpha = \sum_{m_s}\alpha^*(\frac{3}{4}\hbar^2 - \frac{1}{4}\hbar^2 + \frac{1}{2}\hbar^2)\alpha = \hbar^2\sum_{m_s}\alpha^*\alpha = \hbar^2$. So

$|k| = |\hbar|$, and we can take $k = \hbar$, and Eq. 1 becomes $\hat{S}_-\alpha = \hbar\beta$, which is (10.70). From (10.70) and the equation that follows it, we have $\hat{S}_-\alpha = \hbar\beta$ and $\hat{S}_+\alpha = 0$. Combining these two equations we have $(\hat{S}_+ + \hat{S}_-)\alpha = \hbar\beta$ and $(\hat{S}_+ - \hat{S}_-)\alpha = -\hbar\beta$. But (10.63) gives $\hat{S}_+ + \hat{S}_- = 2\hat{S}_x$ and $\hat{S}_+ - \hat{S}_- = 2i\hat{S}_y$, so $\hat{S}_x\alpha = \frac{1}{2}\hbar\beta$ and $\hat{S}_y\alpha = \frac{1}{2}i\hbar\beta$.

10.25 Use of (10.73) and (10.72) gives $\hat{S}_x^2\alpha = \hat{S}_x\hat{S}_x\alpha = \hat{S}_x(\frac{1}{2}\hbar\beta) = \frac{1}{4}\hbar^2\alpha$. As noted in Prob. 10.26a, the possible results of a measurement of S_x are $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, so it makes sense that a measurement of S_x^2 must give $\frac{1}{4}\hbar^2$.

10.26 **(a)** Since the labels on directions in space are arbitrary, the answer must be the same as for S_z, namely, $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.

(b) From $\hat{S}_x\alpha = \frac{1}{2}\hbar\beta$ and $\hat{S}_x\beta = \frac{1}{2}\hbar\alpha$, we have $\hat{S}_x(\alpha+\beta) = \frac{1}{2}\hbar\beta + \frac{1}{2}\hbar\alpha = \frac{1}{2}\hbar(\alpha+\beta)$, so $\alpha+\beta$ is an eigenfunction of $\hat{S}_x$ with eigenvalue $\frac{1}{2}\hbar$. To normalize it, we multiply by $2^{-1/2}$ to get $2^{-1/2}(\alpha+\beta)$, since α and β are orthonormal. Also $\hat{S}_x(\alpha-\beta) = \frac{1}{2}\hbar\beta - \frac{1}{2}\hbar\alpha = \frac{1}{2}\hbar(\beta-\alpha) = -\frac{1}{2}\hbar(\alpha-\beta)$, and $2^{-1/2}(\alpha-\beta)$ is a normalized eigenfunction of $\hat{S}_x$ with eigenvalue $-\frac{1}{2}\hbar$.

(c) Immediately after the measurement, the spin state function is $\Psi = \alpha$. From part (b), the $\hat{S}_x$ eigenfunctions are $f_1 \equiv 2^{-1/2}(\alpha+\beta)$ with eigenvalue $\frac{1}{2}\hbar$ and $f_2 \equiv 2^{-1/2}(\alpha-\beta)$ with eigenvalue $-\frac{1}{2}\hbar$. Note that $f_1 + f_2 = 2^{1/2}\alpha$. Hence if we expand the state function in terms of the $\hat{S}_x$ eigenfunctions, we have $\Psi = \alpha = 2^{-1/2}f_1 + 2^{-1/2}f_2$. The probabilities are given by the absolute squares of the coefficients, so there is 50% probability to get $\frac{1}{2}\hbar$ and 50% probability to get $-\frac{1}{2}\hbar$ when S_x is measured.

(d) From $\hat{S}_y\alpha = \frac{1}{2}i\hbar\beta$ and $\hat{S}_y\beta = -\frac{1}{2}i\hbar\alpha$, we have $\hat{S}_y(\alpha+i\beta) = \frac{1}{2}i\hbar\beta - \frac{1}{2}\hbar i^2\alpha = \frac{1}{2}\hbar(\alpha+i\beta)$, so $\alpha+i\beta$ is an eigenfunction of $\hat{S}_y$ with eigenvalue $\frac{1}{2}\hbar$. To normalize it, we multiply by $2^{-1/2}$ to get $2^{-1/2}(\alpha+i\beta)$, since α and β are orthonormal. Also $\hat{S}_y(\alpha-i\beta) = \frac{1}{2}i\hbar\beta + \frac{1}{2}i^2\hbar\alpha = \frac{1}{2}\hbar(i\beta-\alpha) = -\frac{1}{2}\hbar(\alpha-i\beta)$, and $2^{-1/2}(\alpha-i\beta)$ is a normalized eigenfunction of $\hat{S}_y$ with eigenvalue $-\frac{1}{2}\hbar$.

10.27 **(a)** $\hat{M}_+Y_{jm} = AY_{j,m+1}$ Normalization gives $1 = \langle Y_{j,m+1} | Y_{j,m+1}\rangle = (1/A^*A)\langle \hat{M}_+Y_{jm} | \hat{M}_+Y_{jm}\rangle$ so $|A|^2 = \langle \hat{M}_+Y_{jm} | \hat{M}_+Y_{jm}\rangle = \langle \hat{M}_+Y_{jm} | (\hat{M}_x + i\hat{M}_y)Y_{jm}\rangle =$ $\langle \hat{M}_+Y_{jm} | \hat{M}_x | Y_{jm}\rangle + i\langle \hat{M}_+Y_{jm} | \hat{M}_y | Y_{jm}\rangle$. Use of the Hermitian property for $\hat{M}_x$ and $\hat{M}_y$ gives $A^*A = \langle Y_{jm} | \hat{M}_x | \hat{M}_+Y_{jm}\rangle^* + i\langle Y_{jm} | \hat{M}_y | \hat{M}_+Y_{jm}\rangle^*$. Taking the complex conjugate of the last equation and using (5.113) and (5.143) and (5.144), we have

$AA^* = \langle Y_{jm} \,|\, \hat{M}_x \,|\, \hat{M}_+ Y_{jm}\rangle - i\langle Y_{jm} \,|\, \hat{M}_y \,|\, \hat{M}_+ Y_{jm}\rangle = \langle Y_{jm} \,|\, \hat{M}_x - i\hat{M}_y \,|\, \hat{M}_+ Y_{jm}\rangle =$
$\langle Y_{jm} \,|\, \hat{M}_- \hat{M}_+ Y_{jm}\rangle = \langle Y_{jm} \,|\, (\hat{M}^2 - \hat{M}_z^2 - \hbar\hat{M}_z) Y_{jm}\rangle = [j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2]\langle Y_{jm} \,|\, Y_{jm}\rangle =$
$[j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2]$. So $|A| = [j(j+1) - m(m+1)]^{1/2}\hbar$, in agreement with (10.74).
Also, $\hat{M}_- Y_{jm} = BY_{j,m-1}$. Normalization gives
$1 = \langle Y_{j,m-1} \,|\, Y_{j,m-1}\rangle = (1/B^*B)\langle \hat{M}_- Y_{jm} \,|\, \hat{M}_- Y_{jm}\rangle$ so $|B|^2 = \langle \hat{M}_- Y_{jm} \,|\, \hat{M}_- Y_{jm}\rangle$
$= \langle \hat{M}_- Y_{jm} \,|\, (\hat{M}_x - i\hat{M}_y) Y_{jm}\rangle = \langle \hat{M}_- Y_{jm} \,|\, \hat{M}_x \,|\, Y_{jm}\rangle - i\langle \hat{M}_- Y_{jm} \,|\, \hat{M}_y \,|\, Y_{jm}\rangle$. Use of the Hermitian property for $\hat{M}_x$ and $\hat{M}_y$ gives
$B^*B = \langle Y_{jm} \,|\, \hat{M}_x \,|\, \hat{M}_- Y_{jm}\rangle^* - i\langle Y_{jm} \,|\, \hat{M}_y \,|\, \hat{M}_- Y_{jm}\rangle^*$. Taking the complex conjugate of the last equation and using (5.112) and (5.143) and (5.144), we have
$BB^* = \langle Y_{jm} \,|\, \hat{M}_x \,|\, \hat{M}_- Y_{jm}\rangle + i\langle Y_{jm} \,|\, \hat{M}_y \,|\, \hat{M}_- Y_{jm}\rangle = \langle Y_{jm} \,|\, \hat{M}_x + i\hat{M}_y \,|\, \hat{M}_- Y_{jm}\rangle =$
$\langle Y_{jm} \,|\, \hat{M}_+ \hat{M}_- Y_{jm}\rangle = \langle Y_{jm} \,|\, (\hat{M}^2 - \hat{M}_z^2 + \hbar\hat{M}_z) Y_{jm}\rangle = [j(j+1)\hbar^2 - m^2\hbar^2 + m\hbar^2]\langle Y_{jm} \,|\, Y_{jm}\rangle =$
$[j(j+1)\hbar^2 - m^2\hbar^2 + m\hbar^2]$. So $|B| = [j(j+1) - m(m-1)]^{1/2}\hbar$, in agreement with (10.75).

(b) With $\hat{M}_+ = \hat{S}_+$, $Y_{jm} = \beta$, $j = s = \frac{1}{2}$, and $m = m_s = -\frac{1}{2}$, Eq. (10.74) becomes $\hat{S}_+\beta = [\frac{3}{4} - (-\frac{1}{4})]^{1/2}\hbar\alpha = \hbar\alpha$. With $\hat{M}_- = \hat{S}_-$, $Y_{jm} = \alpha$, $j = s = \frac{1}{2}$, and $m = m_s = \frac{1}{2}$, Eq. (10.75) becomes $\hat{S}_-\alpha = [\frac{3}{4} - (-\frac{1}{4})]^{1/2}\hbar\beta = \hbar\beta$.

(c) With $j = l = 2$, Eq. (10.74) becomes $\hat{L}_+ Y_2^{-1} = 6^{1/2}\hbar Y_2^0$ (Eq. 1). From (5.65) and (5.66), $\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y = i\hbar[(\sin\phi - i\cos\phi)(\partial/\partial\theta) + \cot\theta(\cos\phi + i\sin\phi)(\partial/\partial\phi)] =$
$i\hbar[-ie^{i\phi}(\partial/\partial\theta) + \cot\theta\, e^{i\phi}(\partial/\partial\phi)] = \hbar e^{i\phi}[(\partial/\partial\theta) + i\cot\theta(\partial/\partial\phi)]$. From (5.99) and Table 5.1, $Y_2^{-1} = (2\pi)^{-1/2}\frac{1}{2}(15)^{1/2}\sin\theta\cos\theta\, e^{-i\phi}$. So
$\hat{L}_+ Y_2^{-1} = \hbar e^{i\phi}[(\partial/\partial\theta) + i\cot\theta(\partial/\partial\phi)](15/8\pi)^{1/2}\sin\theta\cos\theta\, e^{-i\phi} =$
$\hbar e^{i\phi}(15/8\pi)^{1/2}[(\cos^2\theta - \sin^2\theta)e^{-i\phi} - i\cdot i(\cos\theta/\sin\theta)\sin\theta\cos\theta\, e^{-i\phi}] =$
$\hbar(15/8\pi)^{1/2}(\cos^2\theta - \sin^2\theta + \cos^2\theta) = \hbar(15/4)^{1/2}(2\pi)^{-1/2}(3\cos^2\theta - 1) =$
$6^{1/2}\hbar[(15/4\cdot 6)^{1/2}(2\pi)^{-1/2}(3\cos^2\theta - 1)] = 6^{1/2}\hbar Y_2^0$, since (5.99) and Table 5.1 give
$Y_2^0 = (2\pi)^{-1/2}(10/16)^{1/2}(3\cos^2\theta - 1) = (2\pi)^{-1/2}(15/24)^{1/2}(3\cos^2\theta - 1)$.

10.28 **(a)** The α, β, and $c_1\alpha + c_2\beta$ column vectors are

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

(b) $(\mathbf{S}_x)_{11} = \langle \alpha \,|\, \hat{S}_x \,|\, \alpha\rangle = \frac{1}{2}\hbar\langle \alpha \,|\, \beta\rangle = 0$, $(\mathbf{S}_x)_{12} = \langle \alpha \,|\, \hat{S}_x \,|\, \beta\rangle = \frac{1}{2}\hbar\langle \alpha \,|\, \alpha\rangle = \frac{1}{2}\hbar$,
$(\mathbf{S}_x)_{21} = [(\mathbf{S}_x)_{12}]^* = \frac{1}{2}\hbar$, $(\mathbf{S}_x)_{22} = \langle \beta \,|\, \hat{S}_x \,|\, \beta\rangle = \frac{1}{2}\hbar\langle \beta \,|\, \alpha\rangle = 0$, where (10.72), (10.73), and orthonormality were used. So

$$\mathbf{S}_x = \begin{pmatrix} 0 & \frac{1}{2}\hbar \\ \frac{1}{2}\hbar & 0 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$(\mathbf{S}_y)_{11} = \langle \alpha | \hat{S}_y | \alpha \rangle = \frac{1}{2} i\hbar \langle \alpha | \beta \rangle = 0$, $\quad (\mathbf{S}_y)_{12} = \langle \alpha | \hat{S}_y | \beta \rangle = -\frac{1}{2} i\hbar \langle \alpha | \alpha \rangle = -\frac{1}{2} i\hbar$,
$(\mathbf{S}_y)_{21} = [(\mathbf{S}_y)_{12}]^* = \frac{1}{2} i\hbar$, $\quad (\mathbf{S}_y)_{22} = \langle \beta | \hat{S}_y | \beta \rangle = -\frac{1}{2} i\hbar \langle \beta | \alpha \rangle = 0$, so

$$\mathbf{S}_y = \begin{pmatrix} 0 & -\frac{1}{2} i\hbar \\ \frac{1}{2} i\hbar & 0 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$(\mathbf{S}_z)_{11} = \langle \alpha | \hat{S}_z | \alpha \rangle = \frac{1}{2}\hbar \langle \alpha | \alpha \rangle = \frac{1}{2}\hbar$, $\quad (\mathbf{S}_z)_{12} = \langle \alpha | \hat{S}_z | \beta \rangle = -\frac{1}{2}\hbar \langle \alpha | \beta \rangle = 0$,
$(\mathbf{S}_z)_{21} = [(\mathbf{S}_z)_{12}]^* = 0$, $\quad (\mathbf{S}_z)_{22} = \langle \beta | \hat{S}_z | \beta \rangle = -\frac{1}{2}\hbar \langle \beta | \beta \rangle = -\frac{1}{2}\hbar$, so

$$\mathbf{S}_z = \begin{pmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$(\mathbf{S}^2)_{11} = \langle \alpha | \hat{S}^2 | \alpha \rangle = \frac{1}{2}\frac{3}{2}\hbar^2 \langle \alpha | \alpha \rangle = \frac{3}{4}\hbar^2$, $\quad (\mathbf{S}^2)_{12} = \langle \alpha | \hat{S}^2 | \beta \rangle = \frac{1}{2}\frac{3}{2}\hbar^2 \langle \alpha | \beta \rangle = 0$,
$(\mathbf{S}^2)_{21} = [(\mathbf{S}^2)_{12}]^* = 0$, $\quad (\mathbf{S}^2)_{22} = \langle \beta | \hat{S}^2 | \beta \rangle = \frac{1}{2}\frac{3}{2}\hbar^2 \langle \beta | \beta \rangle = \frac{3}{4}\hbar^2$. So

$$\mathbf{S}^2 = \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix} = \frac{1}{4}\hbar^2 \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$$

(c)

$$\mathbf{S}_x\mathbf{S}_y - \mathbf{S}_y\mathbf{S}_x = \frac{1}{4}\hbar^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \frac{1}{4}\hbar^2 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} =$$

$$\frac{1}{4}\hbar^2 \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \frac{1}{4}\hbar^2 \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = \frac{1}{4}\hbar^2 \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} = i\hbar \begin{pmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{pmatrix} = i\hbar\mathbf{S}_z$$

(d) Equation (8.82) is

$$\begin{vmatrix} -\lambda & \frac{1}{2}\hbar \\ \frac{1}{2}\hbar & -\lambda \end{vmatrix} = 0 = \lambda^2 - (\tfrac{1}{2}\hbar)^2 \quad \text{and} \quad \lambda = \pm\tfrac{1}{2}\hbar$$

The eigenvectors for $\lambda = \pm\frac{1}{2}\hbar$ are found from

$-\lambda c_1 + \frac{1}{2}\hbar c_2 = 0 = \mp\frac{1}{2}\hbar c_1 + \frac{1}{2}\hbar c_2$

$\frac{1}{2}\hbar c_1 - \lambda c_2 = 0 = \frac{1}{2}\hbar c_1 \mp \frac{1}{2}\hbar c_2$

which gives $c_1 = \pm c_2$. Since the two basis functions are orthonormal, normalization gives $|c_1| = |c_2| = 2^{-1/2}$ and the eigenfunctions are $2^{-1/2}(\alpha \pm \beta)$, where the upper sign is for the positive eigenvalue. These results agree with Prob. 10.26b.

10.29 **(a)** F. **(b)** T. **(c)** F. (The complete wave function must be antisymmetric.) **(d)** F. (This is true only if the fermions are identical.) **(e)** T. An atom of ${}^{79}_{35}\mathrm{Br}$ has 35 electrons and 79 nucleons, for a total of 114 fermions, which is an even number, so this atom is a boson. **(f)** T. **(g)** T, since the nuclear and electron magnetic moments have m_p and m_e, respectively, in the denominator. **(h)** T [since γ in the equation after (10.59) is positive for a proton].

Chapter 11

Many-Electron Atoms

11.1 **(a)** It was noted near the end of Sec. 6.5 that n^2 states belong to an H-atom energy level with quantum number *n*. This is the number of orbitals belonging to a given *n*. Since each orbital holds two electrons, a shell with quantum number *n* holds up to $2n^2$ electrons.

(b) For a given *l*, there are $2l+1$ values of *m*. Since each orbital holds two electrons, the capacity of a given subshell is $2(2l+1) = 4l+2$.

(c) 2 electrons.

(d) 1 electron.

11.2 $$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}\right)$$

11.3 As noted after (11.19), the radial equation for $R(r_1)$ has the form (6.17), namely,
$-(\hbar^2/2m_e)(R_1'' + 2r_1^{-1}R_1') + [l(l+1)\hbar^2/2m_e r_1^2]R_1 + V_1(r_1)R_1 = \varepsilon_1 R_1$,
where V_1 is given by (11.8).

11.4 The STOs (11.14) have r^{n-1} in place of $r^l \sum_{j=0}^{n-l-1} b_j r^j$ in the hydrogenlike radial function (6.100). Only if $n-l-1=0$ will the sum have a single term, as does the STO. When $n-l-1=0$, the $r^l \sum_{j=0}^{n-l-1} b_j r^j$ factor becomes $r^l b_0 = b_0 r^{n-1}$, which is the STO form. Hence only when $l = n-1$ (1*s*, 2*p*, 3*d*…), do STO and hydrogenlike AOs have the same form.

11.5 By analogy to the hydrogenlike formula (6.94), we can estimate an orbital energy as $E \approx -(Z_{\text{eff}}^2/n^2)(e^2/8\pi\varepsilon_0 a_0)$. The 1*s* AO is the innermost orbital and 1*s* electrons screen each other only slightly. So the effective nuclear charge Z_{eff} for a 1*s* electron is slightly less than the atomic number of 18. If we use the helium-atom variation result $Z - \frac{5}{16}$ (Eq. 9.65), then $Z_{\text{eff}} \approx 17.7$ and $E_{1s} \approx -(17.7^2/1)(13.6\text{ eV}) = -4260\text{ eV}$. Figure 11.2 (with allowance for the logarithmic scales) gives $(E_{1s}/E_{\text{H}})^{1/2} = 14._9$ and $E_{1s} = -(14._9)^2(13.6\text{ eV}) = -3020\text{ eV}$.

11.6 The crossing occurs at the point that is 0.36 of the way from $Z = 20$ to 30. Since $10^{0.36} = 2.3$, the crossing occurs between $Z = 22$ and 23.

11.7 **(a)** $E_{\text{corr}} \approx -(0.01702)2^{1.31}(27.2 \text{ eV}) = -1.15 \text{ eV},$ as compared with the true value -1.14 eV.

(b) $E_{\text{corr}} \approx -(0.01702)7^{1.31}(27.2 \text{ eV}) = -5.92 \text{ eV}.$
$E = -(14.534 + 29.601 + 47.448 + 77.472 + 97.888 + 552.057 + 667.029) \text{ eV} = -1486.03 \text{ eV}.$
E_{corr} is 0.40% of E.

11.8 **(a)** From (11.39), the possible J values go from $\frac{3}{2} + 4$ to $|\frac{3}{2} - 4|$ by integral steps and so are $\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}$.

(b) Addition of $j_1 = 2$ and $j_2 = 3$, gives J values of 5, 4, 3, 2, 1. Addition of $j_3 = \frac{1}{2}$ to each of these five J values gives total J values of $\frac{11}{2}, \frac{9}{2}, \frac{9}{2}, \frac{7}{2}, \frac{7}{2}, \frac{5}{2}, \frac{5}{2}, \frac{3}{2}, \frac{3}{2}, \frac{1}{2}$.

11.9 True. Suppose that $j_2 \le j_1$. Then the J values are
$j_1 + j_2,\ j_1 + j_2 - 1,\ j_1 + j_2 - 2, \ldots,\ j_1 + j_2 - (j_2 - 1),\ \boxed{j_1 + j_2 - j_2},\ j_1 + j_2 - (j_2 + 1),$
$j_1 + j_2 - (j_2 + 2), \ldots\ j_1 + j_2 - (j_2 + j_2) = j_1 - j_2$. There are j_2 values that precede the value in the box and j_2 values that follow the value in the box, so the total number of values is $2j_2 + 1,$ where j_2 is not larger than j_1.

11.10 $[\hat{M}_x,\ \hat{M}_1^2] = [\hat{M}_{1x} + \hat{M}_{2x},\ \hat{M}_1^2] = [\hat{M}_{1x},\ \hat{M}_1^2] + [\hat{M}_{2x},\ \hat{M}_1^2] = 0 + 0 = 0$, where we used (11.22), (5.4), (5.109) for $\mathbf{M}_1$, and the sentence after Eq. (11.24).

11.11 $\hat{M}_z \,|\, j_1 j_2 J M_J\rangle = (\hat{M}_{1z} + \hat{M}_{2z})\sum C(j_1 \ldots m_2)\,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle =$
$\sum C(j_1 \ldots m_2)\hat{M}_{1z} \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle + \sum C(j_1 \ldots m_2)\hat{M}_{2z} \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle$ (Eq. 1), where operator linearity was used and the sums go over m_1 and m_2. We have
$\hat{M}_z \,|\, j_1 j_2 J M_J\rangle = M_J \hbar \,|\, j_1 j_2 J M_J\rangle$, $\hat{M}_{1z} \,|\, j_1 m_1\rangle = m_1 \hbar \,|\, j_1 m_1\rangle$, and
$\hat{M}_{2z} \,|\, j_2 m_2\rangle = m_2 \hbar \,|\, j_2 m_2\rangle$ [see the tables between Eqs. (11.33) and (11.34)]. Also, as far as $\hat{M}_{1z}$ is concerned , $|\, j_2 m_2\rangle$ is a constant and as far as $\hat{M}_{2z}$ is concerned , $|\, j_1 m_1\rangle$ is a constant. Hence Eq. 1 becomes
$M_J \hbar \,|\, j_1 j_2 J M_J\rangle = \sum C(j_1 \ldots m_2) m_1 \hbar \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle + \sum C(j_1 \ldots m_2) m_2 \hbar \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle =$
$\sum C(j_1 \ldots m_2)(m_1 + m_2)\hbar \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle$ (Eq. 2). Use of (11.33) in Eq. 2 gives
$M_J \sum C(j_1 \ldots m_2) \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle = \sum C(j_1 \ldots m_2)(m_1 + m_2) \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle$ so
$\sum C(j_1 \ldots m_2)(m_1 + m_2 - M_J) \,|\, j_1 m_1\rangle \,|\, j_2 m_2\rangle = 0$ (Eq. 3). Since the product functions

$|j_1m_1\rangle|j_2m_2\rangle$ are a linearly independent set, no one of them can be expressed as a linear combination of the others and the coefficients of $|j_1m_1\rangle|j_2m_2\rangle$ in the sum in Eq. 3 must vanish: $C(j_1\ldots m_2)(m_1+m_2-M_J)=0$. Hence $C(j_1\ldots m_2)=0$ whenever $m_1+m_2-M_J\neq 0$. The Clebsch–Gordan coefficient is nonzero only when $m_1+m_2=M_J$.

11.12 Use of (11.26) gives
$[\hat{M}^2,\ \hat{M}_{1z}]=[\hat{M}_1^2+\hat{M}_2^2+2(\hat{M}_{1x}\hat{M}_{2x}+\hat{M}_{1y}\hat{M}_{2y}+\hat{M}_{1z}\hat{M}_{2z}),\ \hat{M}_{1z}]=$
$[\hat{M}_1^2,\ \hat{M}_{1z}]+[\hat{M}_2^2,\ \hat{M}_{1z}]+[2\hat{M}_{1x}\hat{M}_{2x},\ \hat{M}_{1z}]+[2\hat{M}_{1y}\hat{M}_{2y},\ \hat{M}_{1z}]+[2\hat{M}_{1z}\hat{M}_{2z},\ \hat{M}_{1z}]=$
$0+0+2\hat{M}_{2x}[\hat{M}_{1x},\ \hat{M}_{1z}]+2\hat{M}_{2y}[\hat{M}_{1y},\ \hat{M}_{1z}]+2\hat{M}_{2z}[\hat{M}_{1z},\ \hat{M}_{1z}]=$
$-2i\hbar\hat{M}_{2x}\hat{M}_{1y}+2i\hbar\hat{M}_{2y}\hat{M}_{1x}+0=2i\hbar(\hat{M}_{2y}\hat{M}_{1x}-\hat{M}_{2x}\hat{M}_{1y})$**,** where (5.4), (5.109) for $\mathbf{M}_1$ and for $\mathbf{M}_2$, and (5.107) were used.

11.13 **(a)** False. **(b)** True.

11.14 For the *ss* case, $l_1=0$ and $l_2=0$, so $L=0$. Also $s_1=\frac{1}{2}$ and $s_2=\frac{1}{2}$, so (11.39) gives $S=1,\ 0$ and $2S+1=3,\ 1$. These spin multiplicities also apply to all other cases of two nonequivalent electrons. The terms are ${}^3S$ and ${}^1S$.
For the *sp* case, $l_1=0$ and $l_2=1$, so $L=1$. The terms are ${}^3P$ and ${}^1P$.
For the *sd* case, $l_1=0$ and $l_2=2$, so $L=2$. The terms are ${}^3D$ and ${}^1D$.
For the *pp* case, $l_1=1$ and $l_2=1$, so $L=2,\ 1,\ 0$. The terms are ${}^3D$, ${}^1D$, ${}^3P$, ${}^1P$, ${}^3S$, ${}^1S$.

11.15 **(a)** The electrons in closed subshells contribute nothing to the orbital or spin angular momentum and are ignored. For $3p5g$, we have $l_1=1$ and $l_2=4$, so the possible L values are 5, 4, 3 (*H*, *G*, and *F* terms). Also $s_1=\frac{1}{2}$ and $s_2=\frac{1}{2}$, so (11.39) gives $S=1,\ 0$ and $2S+1=3,\ 1$. The terms are ${}^1F,\ {}^3F,\ {}^1G,\ {}^3G,\ {}^1H,\ {}^3H$.

(b) For the $2p3p3d$ configuration, we have $l_1=1$, $l_2=1$, and $l_3=2$. Addition of l_2 and l_3 gives 3, 2, 1, and addition of l_1 to these values then gives L values of 4, 3, 2, 3, 2, 1, 2, 1, 0. Addition of $s_1=\frac{1}{2}$ and $s_2=\frac{1}{2}$ gives $S=1,\ 0$, and addition of $s_3=\frac{1}{2}$ gives the total S quantum number possibilities as $\frac{3}{2},\ \frac{1}{2},\ \frac{1}{2}$, with $2S+1=4,\ 2,\ 2$. The terms are
${}^2S,\ {}^2S,\ {}^4S,\ {}^2P,\ {}^2P,\ {}^4P,\ {}^2P,\ {}^2P,\ {}^4P,\ {}^2D,\ {}^2D,\ {}^4D,\ {}^2D,\ {}^2D,\ {}^4D,\ {}^2D,\ {}^2D,\ {}^4D,\ {}^2F,\ {}^2F,\ {}^4F,$
${}^2F,\ {}^2F,\ {}^4F,\ {}^2G,\ {}^2G,\ {}^4G$.

(c) From Table 11.2a, the terms for the $2p^4$ configuration are ${}^3P$ ($L=1$, $S=1$), ${}^1D$ ($L=2$, $S=0$), and ${}^1S$ ($L=0$, $S=0$). Addition of $l=2$ and $s=\frac{1}{2}$ of the 4*d* electron to

the L and the S of each of the $2p^4$ terms gives the terms
${}^2P,\ {}^4P,\ {}^2D,\ {}^4D,\ {}^2F,\ {}^4F,\ {}^2S,\ {}^2P,\ {}^2D,\ {}^2F,\ {}^2G,\ {}^2D$.

11.16 The He ground state is a ${}^1S$ term with $L = 0$ and $S = 0$.

(a) The $1s2s$ configuration will give rise to a ${}^1S$ term and will contribute.

(b) The $1s2p$ configuration produces only P terms and does not contribute.

(c) $2s^2$ gives a ${}^1S$ term and contributes.

(d) $2s2p$ gives only P terms and does not contribute.

(e) $2p^2$ gives rise to a ${}^1S$ term and contributes.

(f) $3d^2$ gives rise to a ${}^1S$ term and contributes.

11.17 $\hat{S}_z\beta(1)\beta(2) = (\hat{S}_{1z} + \hat{S}_{2z})\beta(1)\beta(2) = \hat{S}_{1z}\beta(1)\beta(2) + \hat{S}_{2z}\beta(1)\beta(2) =$
$\beta(2)\hat{S}_{1z}\beta(1) + \beta(1)\hat{S}_{2z}\beta(2) = -\frac{1}{2}\hbar\beta(2)\beta(1) - \frac{1}{2}\hbar\beta(1)\beta(2) = -\hbar\beta(1)\beta(2)$.

$\hat{S}_z[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] = (\hat{S}_{1z} + \hat{S}_{2z})[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] =$
$\hat{S}_{1z}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] + \hat{S}_{2z}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] =$
$\hat{S}_{1z}\alpha(1)\beta(2) \pm \hat{S}_{1z}\beta(1)\alpha(2) + \alpha(1)\hat{S}_{2z}\beta(2) \pm \beta(1)\hat{S}_{2z}\alpha(2) =$
$\frac{1}{2}\hbar\alpha(1)\beta(2) \mp \frac{1}{2}\hbar\beta(1)\alpha(2) - \frac{1}{2}\hbar\alpha(1)\beta(2) \pm \frac{1}{2}\hbar\beta(1)\alpha(2) = 0.$

$\hat{S}^2\alpha(1)\alpha(2) =$
$\hat{S}_1^2\alpha(1)\alpha(2) + \alpha(1)\hat{S}_2^2\alpha(2) + 2\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\alpha(2) + 2\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\alpha(2) + 2\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\alpha(2) =$
$\frac{1}{2}\frac{3}{2}\hbar^2\alpha(1)\alpha(2) + \frac{1}{2}\frac{3}{2}\hbar^2\alpha(1)\alpha(2) + 2\cdot\frac{1}{2}\hbar\beta(1)\frac{1}{2}\hbar\beta(2) + 2\cdot\frac{1}{2}i\hbar\beta(1)\frac{1}{2}i\hbar\beta(2) +$
$2\cdot\frac{1}{2}\hbar\alpha(1)\frac{1}{2}\hbar\alpha(2) = 2\hbar^2\alpha(1)\alpha(2)$.

$\hat{S}^2\beta(1)\beta(2) =$
$\hat{S}_1^2\beta(1)\beta(2) + \beta(1)\hat{S}_2^2\beta(2) + 2\hat{S}_{1x}\beta(1)\hat{S}_{2x}\beta(2) + 2\hat{S}_{1y}\beta(1)\hat{S}_{2y}\beta(2) + 2\hat{S}_{1z}\beta(1)\hat{S}_{2z}\beta(2) =$
$\frac{1}{2}\frac{3}{2}\hbar^2\beta(1)\beta(2) + \frac{1}{2}\frac{3}{2}\hbar^2\beta(1)\beta(2) + 2\cdot\frac{1}{2}\hbar\alpha(1)\frac{1}{2}\hbar\alpha(2) + 2(-\frac{1}{2}i\hbar)\alpha(1)(-\frac{1}{2}i\hbar)\alpha(2) +$
$2(-\frac{1}{2}\hbar)\beta(1)(-\frac{1}{2}\hbar)\beta(2) = 2\hbar^2\beta(1)\beta(2)$.

$\hat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = \hat{S}_1^2\alpha(1)\beta(2) + \hat{S}_1^2\beta(1)\alpha(2) + \hat{S}_2^2\alpha(1)\beta(2) + \hat{S}_2^2\beta(1)\alpha(2) +$
$2\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2) + 2\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2) + 2\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2) + 2\hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2) +$
$2\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2) + 2\hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2) =$
$\frac{3}{4}\hbar^2\alpha(1)\beta(2) + \frac{3}{4}\hbar^2\beta(1)\alpha(2) + \frac{3}{4}\hbar^2\alpha(1)\beta(2) + \frac{3}{4}\hbar^2\beta(1)\alpha(2) +$
$2\cdot\frac{1}{2}\hbar\beta(1)\frac{1}{2}\hbar\alpha(2) + 2\cdot\frac{1}{2}\hbar\alpha(1)\frac{1}{2}\hbar\beta(2) + 2\cdot\frac{1}{2}i\hbar\beta(1)(-\frac{1}{2}i\hbar)\alpha(2) + 2(-\frac{1}{2}i\hbar)\alpha(1)\frac{1}{2}i\hbar\beta(2) +$
$2\cdot\frac{1}{2}\hbar\alpha(1)(-\frac{1}{2}\hbar)\beta(2) + 2(-\frac{1}{2}\hbar)\beta(1)\frac{1}{2}\hbar\alpha(2) = 2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$.

$\hat{S}^2[\alpha(1)\beta(2)-\beta(1)\alpha(2)] = \hat{S}_1^2\alpha(1)\beta(2)-\hat{S}_1^2\beta(1)\alpha(2)+\hat{S}_2^2\alpha(1)\beta(2)-\hat{S}_2^2\beta(1)\alpha(2)+$
$2\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2)-2\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2)+2\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2)-2\hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2)+$
$2\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2)-2\hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2)=$
$\frac{3}{4}\hbar^2\alpha(1)\beta(2)-\frac{3}{4}\hbar^2\beta(1)\alpha(2)+\frac{3}{4}\hbar^2\alpha(1)\beta(2)-\frac{3}{4}\hbar^2\beta(1)\alpha(2)+$
$2\cdot\frac{1}{2}\hbar\beta(1)\frac{1}{2}\hbar\alpha(2)-2\cdot\frac{1}{2}\hbar\alpha(1)\frac{1}{2}\hbar\beta(2)\ +2\cdot\frac{1}{2}i\hbar\beta(1)(-\frac{1}{2}i\hbar)\alpha(2)-2(-\frac{1}{2}i\hbar)\alpha(1)\frac{1}{2}i\hbar\beta(2)+$
$2\cdot\frac{1}{2}\hbar\alpha(1)(-\frac{1}{2}\hbar)\beta(2)-2(-\frac{1}{2}\hbar)\beta(1)\frac{1}{2}\hbar\alpha(2)=0$.

11.18 **(a)** Similar to Figs. 5.6 and 10.1, $\cos\theta = S_z/|\mathbf{S}| = \hbar/[1(2)]^{1/2}\hbar = 0.70711$ and $\theta = 0.78540$ rad = 45° [see Eqs. (11.51), (11.56), and (11.57)].

(b) $|\mathbf{S}|^2 = \mathbf{S}\cdot\mathbf{S} = (\mathbf{S}_1+\mathbf{S}_2)\cdot(\mathbf{S}_1+\mathbf{S}_2) = |\mathbf{S}_1|^2+|\mathbf{S}_2|^2+2\mathbf{S}_1\cdot\mathbf{S}_2 = 2|\mathbf{S}_1|^2+2|\mathbf{S}_1||\mathbf{S}_2|\cos\theta$ and $\cos\theta = (|\mathbf{S}|^2-2|\mathbf{S}_1|^2)/2|\mathbf{S}_1|^2$. Since $|\mathbf{S}_1|^2 = \frac{1}{2}\frac{3}{2}\hbar^2 = \frac{3}{4}\hbar^2$, we have $\cos\theta = (|\mathbf{S}|^2-\frac{3}{2}\hbar^2)/\frac{3}{2}\hbar^2 = \frac{2}{3}|\mathbf{S}|^2/\hbar^2-1$.

For (11.57), (11.58), and (11.59), $\cos\theta = \frac{2}{3}(1)(2)\hbar^2/\hbar^2-1=\frac{1}{3}$ and $\theta = 1.23096$ rad = 70.53°. For (11.60), Fig. 11.3 (or the preceding formula for $\cos\theta$) gives θ = 180°.

(c) From Fig. 5.2, the components are A_x and A_y. Let $\mathbf{S}_{1p}$ and $\mathbf{S}_{2p}$ be the projections of $\mathbf{S}_1$ and $\mathbf{S}_2$ in the *xy* plane. The components of $\mathbf{S}_{1p}$ and $\mathbf{S}_{2p}$ equal the *x* and *y* components of $\mathbf{S}_1$ and $\mathbf{S}_2$, so $\mathbf{S}_{1p}\cdot\mathbf{S}_{2p} = |\mathbf{S}_{1p}||\mathbf{S}_{2p}|\cos\omega = S_{1x}S_{2x}+S_{1y}S_{2y}$ where ω is the angle between $\mathbf{S}_{1p}$ and $\mathbf{S}_{2p}$. Then $S_{1x}S_{2x}+S_{1y}S_{2y} = S_{1x}S_{2x}+S_{1y}S_{2y}+S_{1z}S_{2z}-S_{1z}S_{2z} =$ $\mathbf{S}_1\cdot\mathbf{S}_2-S_{1z}S_{2z} = |\mathbf{S}_1||\mathbf{S}_2|\cos\theta-S_{1z}S_{2z} = |\mathbf{S}_1|^2\cos\theta-S_{1z}S_{2z} = \frac{3}{4}\hbar^2\cdot\frac{1}{3}-\frac{1}{2}\hbar\cdot\frac{1}{2}\hbar = 0$, so $\cos\omega = 0$ and $\omega = 90°$.

11.19 $[\hat{S}^2, \hat{P}_{12}]f(q_1,q_2,q_3,\ldots) = (\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)\cdot(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)\hat{P}_{12}f(q_1,q_2,q_3,\ldots)-$
$\hat{P}_{12}[(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)\cdot(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)f(q_1,q_2,q_3,\ldots)]=$
$(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)\cdot(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_3+\cdots)f(q_2,q_1,q_3,\ldots)-$
$(\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_3+\cdots)\cdot(\hat{\mathbf{S}}_2+\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_3+\cdots)f(q_2,q_1,q_3,\ldots)=0$, since $\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2 = \hat{\mathbf{S}}_2+\hat{\mathbf{S}}_1$ (Prob. 3.6). A similar proof shows that $[\hat{S}^2, \hat{P}_{ij}]=0$. Replacement of **S** with **L** in the proof gives $[\hat{L}^2, \hat{P}_{12}]=0$.

11.20 As noted in Sec. 11.5, the atomic wave function is odd if $\sum_i l_i$ is odd. For the H, He, Li, and Be ground states, all the electrons are *s* electrons and $\sum_i l_i = 0$. The ground-state configurations $1s^22s^22p$ of B, $1s^22s^22p^3$ of N, and $1s^22s^22p^5$ of F have $\sum_i l_i$ equal to 1, 3, and 5, respectively, and these atoms have odd-parity ground states.

11.21 **(a)** As noted in the Atomic Terms subsection of Sec. 11.5, the number of states belonging to a term is $(2L+1)(2S+1)$.

For ^4F, $(2L+1)(2S+1) = (2\cdot 3+1)4 = 28$.

(b) $(2L+1)(2S+1) = 1\cdot 1 = 1$.

(c) $(2L+1)(2S+1) = (2+1)3 = 9$.

(d) $(2L+1)(2S+1) = (4+1)2 = 10$.

11.22 **(a)** From Table 11.2, the $2p^2$ configuration gives rise to these terms: ^3P with $(2L+1)(2S+1) = 3(3) = 9$ states, ^1D with $(2L+1)(2S+1) = 5(1) = 5$ states, and ^1S with $(2L+1)(2S+1) = 1(1) = 1$ state. The total number of states is 15.

(b) The $2p3p$ configuration gives these terms: ^3D with $(2L+1)(2S+1) = 5(3) = 15$ states, ^1D with $(2L+1)(2S+1) = 5(1) = 5$ states, ^3P with $(2L+1)(2S+1) = 3(3) = 9$ states, ^1P with $(2L+1)(2S+1) = 3(1) = 3$ states, ^3S with $(2L+1)(2S+1) = 1(3) = 3$ states, and ^1S with $(2L+1)(2S+1) = 1(1) = 1$ state. The total number of states is 36 states.

11.23 **(a)** A single electron has $s = \frac{1}{2}$, so $S = \frac{1}{2}$ and $2S+1 = 2$.

(b) Addition of $s_1 = \frac{1}{2}$ to $s_2 = \frac{1}{2}$ gives $S = 0,\ 1$ and $2S+1 = 1,\ 3$.

(c) Addition of $s_3 = \frac{1}{2}$ to $S = 0,\ 1$ (the possibilities for two electrons) gives $S = \frac{1}{2}$ and $S = \frac{3}{2}$ as the possible different *S* values for three electrons, with the possible spin multiplicities being $2S+1 = 2$ and 4.

(d) Addition of $s_4 = \frac{1}{2}$ to $S = \frac{1}{2},\ \frac{3}{2}$ (the possibilities for three electrons) gives $S = 0, 1, 2$ as the possible different *S* values for four electrons. Addition of $s_5 = \frac{1}{2}$ to $S = 0, 1, 2$ gives $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ as the possible different *S* values for five electrons. Addition of $s_6 = \frac{1}{2}$ to $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ gives $S = 0, 1, 2, 3$ as the possible different *S* values for six electrons. Addition of $s_7 = \frac{1}{2}$ to $S = 0, 1, 2, 3$ gives $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ as the possible different *S* values for seven electrons, and the possible spin multiplicities are 2, 4, 6, 8.

(e) f^{12} has the same terms as f^2 and the spin multiplicities are 1 and 3.

(f) The same as *f*, namely 2.

11.24 **(a)** For ^1S, $L = 0$ and $S = 0$. Hence (11.62) gives $J = 0$. The only level is $^1S_0$, with degeneracy $2J+1 = 1$.

(b) For ^2S, $L = 0$ and $S = \frac{1}{2}$, so $J = \frac{1}{2}$ and the only level is $^2S_{1/2}$ with degeneracy $2J+1 = 2$.

(c) For ^3F, $L = 3$ and $S = 1$, so $J = 4, 3, 2$. The levels are $^3F_4,\ ^3F_3,\ ^3F_2$ with degeneracies 9, 7, and 5, respectively.

(d) For ^4D, $L = 2$ and $S = \frac{3}{2}$, so $J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. The levels are $^4D_{7/2},\ ^4D_{5/2},\ ^4D_{3/2},\ ^4D_{1/2}$ with degeneracies 8, 6, 4, 2, respectively.

11.25 For a $^3D_3$ level, $L = 2$, $S = 1$, and $J = 3$.

(a) $[L(L+1)]^{1/2}\hbar = 6^{1/2}\hbar$.

(b) $[S(S+1)]^{1/2}\hbar = 2^{1/2}\hbar$.

(c) $[J(J+1)]^{1/2}\hbar = 12^{1/2}\hbar$.

11.26 For the $1s$ configuration of H and for the $1s^2 2s$ configuration of Li, the ground level is $^2S_{1/2}$. For the closed-subshell $1s^2$ configuration of He, the $1s^2 2s^2$ configuration of Be and the $1s^2 2s^2 2p^6$ configuration of Ne, the ground level is $^1S_0$. For the $1s^2 2s^2 2p$ configuration of B, $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$; by the rule near the end of Sec. 11.6, the lowest level is $^2P_{1/2}$. For the $1s^2 2s^2 2p^2$ configuration of C, the terms are given by Table 11.2 as ^3P, ^1D, and ^1S. By Hund's rule ^3P lies lowest. For ^3P the *J* values are 2, 1, 0 and the lowest level is $^3P_0$. For the $1s^2 2s^2 2p^3$ configuration of N, the terms are given by Table 11.2 as ^2P, ^2D, and ^4S. By Hund's rule ^4S lies lowest. For ^4S the only level is $^4S_{3/2}$. For the $1s^2 2s^2 2p^4$ configuration of O, the terms are given by Table 11.2 as ^3P, ^1D, and ^1S. By Hund's rule ^3P lies lowest. For ^3P the *J* values are 2, 1, 0 and the lowest level is $^3P_2$. For the $1s^2 2s^2 2p^5$ configuration of F, the terms are given by Table 11.2 as ^2P. For ^2P, the levels are $^2P_{3/2}$ and $^2P_{1/2}$. By the rule near the end of Sec. 11.6, $^2P_{3/2}$ is lowest.

11.27 For the $_{21}\text{Sc}$ configuration $[\text{Ar}]3d4s^2$, the rule near the end of Sec. 11.6 gives the ground level as $^2D_{3/2}$.

For the $_{22}\text{Ti}$ configuration $[\text{Ar}]3d^2 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^3F with $L = 3$ and $S = 1$; the *J* values are 4, 3, 2 and the ground level is $^3F_2$.

For the V configuration $[\text{Ar}]3d^3 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^4F; the *J* values are $9/2, 7/2, 5/2, 3/2$ and the ground level is $^4F_{3/2}$.

For the Cr configuration $[\text{Ar}]3d^5 4s^1$, Table 11.2 gives the highest-multiplicity term of d^5 as ^6S with $S = 5/2$ and $L = 0$. When the contribution of the 4*s* electron is included, the highest-multiplicity term will have $S = 3$ and $L = 0$, a ^7S term with the single level $^7S_3$.

For the Mn configuration [Ar]$3d^5 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^6S with the single level $^6S_{5/2}$.

For the Fe configuration [Ar]$3d^6 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^5D; the *J* values are 4, 3, 2, 1, 0 and the ground level is $^5D_4$.

For the Co configuration [Ar]$3d^7 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^4F; the *J* values are $9/2, 7/2, 5/2, 3/2$ and the ground level is $^4F_{9/2}$.

For the Ni configuration [Ar]$3d^8 4s^2$, Table 11.2 and Hund's rule give the lowest term as ^3F; the *J* values are 4, 3, 2 and the ground level is $^3F_4$.

For the Cu configuration [Ar]$3d^{10} 4s^1$, the only term is ^2S with the single level $^2S_{1/2}$.

For Zn with [Ar]$3d^{10} 4s^2$, the ground level is $^1S_0$.

The most degenerate level has the highest *J*, namely $^4F_{9/2}$ of Co.

11.28 **(a)** The *m* values go from $-l$ to *l*, and we have

$$\begin{array}{cccccc} & \underline{\uparrow} & \underline{\uparrow} & \cdots & \underline{\uparrow} & \underline{\uparrow} \\ m: & l & l-1 & \cdots & -l+1 & -l \end{array}$$

The only value of M_L for this arrangement is zero, since positive and negative *m* values cancel. With only $M_L = 0$ allowed for the ground term, this term must have $L = 0$.

(b) If $L = 0$, we get only a single level that has $J = S$. Hence no rule is needed to decide which is the lowest level of the term.

11.29 $E/hc = (1\text{ eV})[(1.602177 \times 10^{-19}\text{ J})/(1\text{ eV})]/[(6.62607 \times 10^{-34}\text{ J s})(2.997925 \times 10^8\text{ m/s})] = 806554\text{ m}^{-1}(1\text{ m})/(100\text{ cm}) = 8065.54\text{ cm}^{-1}$.

11.30 For the $2s^2 2p3p$ electron configuration, Hund's rule predicts ^3D as the lowest term, but the ^1P term lies slightly below ^3D. For $2s^2 2p3d$, Hund's rule is violated. The atomic energy-level tables at physics.nist.gov/asd show at least 13 other configurations of C where Hund's rule is violated.

11.31 The $\Delta L = 0, \pm 1$ rule means that *S* levels can go to *S* and *P* levels, *P* levels go to *S*, *P*, and *D* levels, and *D* levels go to *P*, *D*, and *F* levels. The $\Delta S = 0$ rule means levels of singlet terms go to singlet levels and triplet levels go to triplet levels. The $\Delta(\sum_i l_i) = \pm 1$ rule prevents transitions between two levels that arise from the same electron configuration.

The $\Delta l = \pm 1$ rule is obeyed for $2s^2 2p^2$ going to $2s2p^3$. The allowed-transition wavenumbers in cm^{-1} are:

${}^3P_0 \to {}^3D_1$ 64089.8, ${}^3P_0 \to {}^3P_1$ 75254.0, ${}^3P_0 \to {}^3S_1$ 105798.7,

${}^3P_1 \to {}^3D_1$ 64073.4, ${}^3P_1 \to {}^3D_2$ 64074.5, ${}^3P_1 \to {}^3P_1$ 75237.6, ${}^3P_1 \to {}^3P_2$ 75238.9, ${}^3P_1 \to {}^3P_0$ 75239.7, ${}^3P_1 \to {}^3S_1$ 105782.3,

${}^3P_2 \to {}^3D_3$ 64043.5, ${}^3P_2 \to {}^3D_1$ 64046.4, ${}^3P_2 \to {}^3D_2$ 64047.5, ${}^3P_2 \to {}^3P_1$ 75210.6, ${}^3P_2 \to {}^3P_2$ 75211.9, ${}^3P_2 \to {}^3S_1$ 105755.3,

${}^1D_2 \to {}^1D_2$ 87685, ${}^1D_2 \to {}^1P_1$ 109685,

and ${}^1S_0 \to {}^1P_1$ 98230,

where the first level in each pair arises from the $2s^2 2p^2$ configuration.

11.32 The $2s^2 2p3s$ levels are listed as:

Level	${}^3P_0$	${}^3P_1$	${}^3P_2$	${}^1P_1$
$(E/hc)/\text{cm}^{-1}$	60333.43	60352.63	60393.14	61981.82

The discussion at the beginning of Prob. 11.31 gives the following allowed transition wavenumbers in cm^{-1} (the first number listed for each transition) and wavelengths in nm (the second number listed), where the first level in each pair arises from the $2s^2 2p3s$ configuration:

${}^3P_0 \to {}^3P_1$ 60317.0, 165.791;

${}^3P_1 \to {}^3P_2$ 60309.2, 165.812; ${}^3P_1 \to {}^3P_1$ 60336.2, 165.738; ${}^3P_1 \to {}^3P_0$ 60352.6, 165.693;

${}^3P_2 \to {}^3P_2$ 60349.7, 165.701; ${}^3P_2 \to {}^3P_1$ 60376.7, 165.627;

${}^1P_1 \to {}^1D_2$ 51789.2, 193.090; ${}^1P_1 \to {}^1S_0$ 40333.8, 247.931.

The calculated wavelengths agree with the ones listed in the NIST database except for the wavelength of the last line, which NIST gives as 247.856 nm. This is because NIST lists wavelengths that are between 200 nm and 2000 nm as wavelengths in air (rather than in vacuum), so the index of refraction of air affects the NIST value.

11.33 For ${}^2P_{3/2}$, Eq. (11.66) gives $E_{\text{S.O.}} = \frac{1}{2}\langle\xi\rangle\hbar^2[\frac{3}{2}\cdot\frac{5}{2} - 1(2) - \frac{1}{2}\cdot\frac{3}{2}] = \frac{1}{2}\langle\xi\rangle\hbar^2$.

For ${}^2P_{1/2}$, $E_{\text{S.O.}} = \frac{1}{2}\langle\xi\rangle\hbar^2[\frac{1}{2}\cdot\frac{3}{2} - 1(2) - \frac{1}{2}\cdot\frac{3}{2}] = -\langle\xi\rangle\hbar^2$. So $\Delta E_{\text{S.O.}} = \frac{3}{2}\langle\xi\rangle\hbar^2$. From (11.64),

$$\xi = \frac{1}{2m_e^2c^2r}\frac{dV}{dr} = -\frac{1}{2m_e^2c^2r}\frac{d}{dr}\frac{Ze^2}{4\pi\varepsilon_0 r} = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2c^2r^3} \text{ and}$$

$$\langle \xi \rangle = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2}\int_0^\infty (R_{2p})^2 r^{-3} r^2 dr =$$

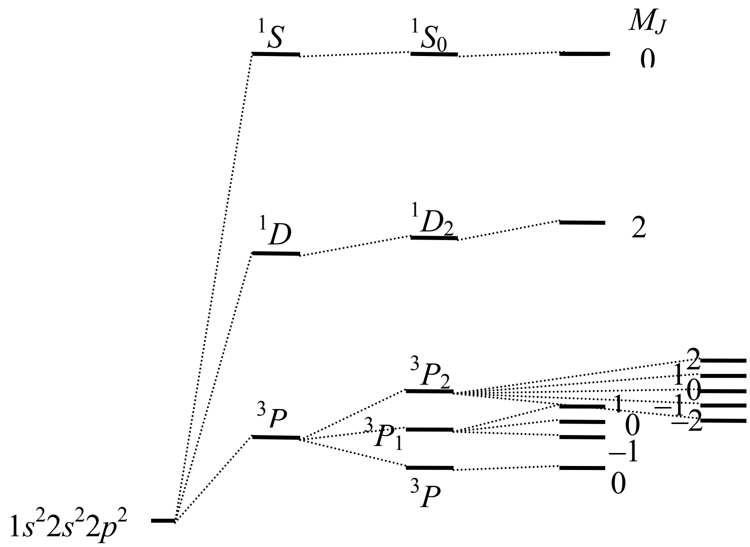
$$\frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2}\frac{Z^5}{24a^5}\int_0^\infty re^{-Zr/a}dr = \frac{Z^6e^2}{192\pi\varepsilon_0 m_e^2 c^2 a^5}\frac{a^2}{Z^2} = \frac{Z^4e^2}{192\pi\varepsilon_0 m_e^2 c^2 a^3}$$, since the spherical harmonics are normalized. So $\Delta E_{\text{S.O.}} = (Z^4h^2e^2/512\varepsilon_0\pi^3 m_e^2 c^2 a^3) =$

$$\frac{(6.626\times 10^{-34}\ \text{J s})^2(1.6022\times 10^{-19}\ \text{C})^2}{512(8.854\times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})\pi^3(9.109\times 10^{-31}\ \text{kg})^2(2.998\times 10^8\ \text{m/s})^2(0.5295\times 10^{-10}\ \text{m})^3}$$

$= 7.242 \times 10^{-24}$ J = 0.00004520 eV.

11.34 No. The $1s2p$ configuration has *two* partly filled subshells.

11.35



11.36 $\Delta E_B = \mu_B gB\,\Delta M_J = \mu_B gB$. From (11.75), $g = 1+[(0.75-2+0.75)/1.5] = 2/3$. From Table A.1, $|\Delta E_B| = (9.274\times 10^{-24}\ \text{J/T})(0.200\ \text{T})(2/3) = 1.24\times 10^{-24}\ \text{J} = 0.00000772\ \text{eV}$.

11.37 $\langle D|\sum_{i=1}^n \hat{f}_i|D\rangle = \sum_{i=1}^n \langle D|\hat{f}_i|D\rangle$. In D in (11.76), rows 1, 2, 3,… contain entries with electrons 1, 2, 3…. The Prob. 8.22 expression with *ijk* replaced by *pqr* and by *stw* gives $\langle D|\sum_{i=1}^n \hat{f}_i|D\rangle = (1/n!)\sum_{i=1}^n \langle \sum(\pm 1)u_p(1)u_q(2)u_r(3)\cdots|\hat{f}_i|\sum(\pm 1)u_s(1)u_t(2)u_w(3)\cdots\rangle =$ $(1/n!)\sum_{i=1}^n \sum\sum\langle(\pm 1)u_p(1)u_q(2)u_r(3)\cdots|\hat{f}_i|(\pm 1)u_s(1)u_t(2)u_w(3)\cdots\rangle$ (Eq. 1). Consider the integral $I \equiv \langle u_p(1)u_q(2)u_r(3)\cdots|\hat{f}_1|u_s(1)u_t(2)u_w(3)\cdots\rangle =$ $\langle u_p(1)|\hat{f}_1|u_s(1)\rangle\langle u_q(2)|u_t(2)\rangle\langle u_r(3)|u_w(3)\rangle\cdots = \langle u_p(1)|\hat{f}_1|u_s(1)\rangle\delta_{qt}\delta_{rw}\cdots$, since the spin-orbitals are orthonormal. Unless each of electrons 2, 3, …, n, is in the same spin-orbital on the left and on the right of $\hat{f}_1$, the integral I will be zero. When each of electrons 2, 3, …, n, is in the same spin-orbital on the left and on the right of $\hat{f}_1$, then electron 1 is also in the same spin-orbital on the left and on the right of $\hat{f}_1$. Thus, each integral in Eq. 1 is zero unless the permutation $stw\cdots$ is the same as the permutation $pqr\cdots$. The rightmost sum in Eq. 1 is over the various possible permutations $stw\cdots$. Thus we drop the rightmost summation and change $s, t, w,\ldots,$ to $p, q, r,\ldots,$ respectively. Also, since the permutations on the left and right of $\hat{f}_i$ are now the same, we will get either a factor of $(+1)^2$ or $(-1)^2$. Hence Eq. 1 becomes

$\langle D\,|\sum_{i=1}^{n}\hat{f}_i\,|\,D\rangle = (1/n!)\sum_{i=1}^{n}\sum\langle u_p(1)u_q(2)u_r(3)\cdots|\,\hat{f}_i\,|\,u_p(1)u_q(2)u_r(3)\cdots\rangle$ (Eq. 2).

Because $\hat{f}_i$ refers only to electron i and the spin-orbitals are normalized, we have $\langle u_p(1)u_q(2)u_r(3)\cdots|\,\hat{f}_i\,|\,u_p(1)u_q(2)u_r(3)\cdots\rangle = \langle u_w(i)\,|\,\hat{f}_i\,|\,u_w(i)\rangle$ (Eq. 3), where u_w is the spin-orbital in $u_p(1)u_q(2)u_r(3)\cdots$ that involves electron i. Also, note that $\langle u_w(i)\,|\,\hat{f}_i\,|\,u_w(i)\rangle = \langle u_w(1)\,|\,\hat{f}_1\,|\,u_w(1)\rangle$ (Eq. 4), since whether we label the electron as 1 or as i does not affect the value of this definite integral. The second $\sum$ in Eq. 2 is a summation over the n! permutations of $p, q, r,\ldots.$ One-nth of these permutations have electron i in spin-orbital u_p, one-nth have electron i in u_q, etc. Since $(1/n)n! = (n-1)!$, Eqs. 3 and 4 show that $\sum\langle u_p(1)u_q(2)u_r(3)\cdots|\,\hat{f}_i\,|\,u_p(1)u_q(2)u_r(3)\cdots\rangle =$ $(n-1)![\langle u_p(1)\,|\,\hat{f}_1\,|\,u_p(1)\rangle + \langle u_q(1)\,|\,\hat{f}_1\,|\,u_q(1)\rangle + \langle u_r(1)\,|\,\hat{f}_1\,|\,u_r(1)\rangle + \cdots]$ and Eq. 2 becomes

$\langle D\,|\sum_{i=1}^{n}\hat{f}_i\,|\,D\rangle = (1/n)\sum_{i=1}^{n}[\langle u_p(1)\,|\,\hat{f}_1\,|\,u_p(1)\rangle + \langle u_q(1)\,|\,\hat{f}_1\,|\,u_q(1)\rangle + \langle u_r(1)\,|\,\hat{f}_1\,|\,u_r(1)\rangle + \cdots] =$
$\langle u_p(1)\,|\,\hat{f}_1\,|\,u_p(1)\rangle + \langle u_q(1)\,|\,\hat{f}_1\,|\,u_q(1)\rangle + \langle u_r(1)\,|\,\hat{f}_1\,|\,u_r(1)\rangle + \cdots = \sum_{j=1}^{n}\langle u_j(1)\,|\,\hat{f}_1\,|\,u_j(1)\rangle$,

since the quantity in brackets has the same value for each value of i. Use of $\langle u_j(1)\,|\,\hat{f}_1\,|\,u_j(1)\rangle = \langle\theta_j(1)\,|\,\hat{f}_1\,|\,\theta_j(1)\rangle$ [the displayed equation after (11.77)] gives $\langle D\,|\sum_{i=1}^{n}\hat{f}_i\,|\,D\rangle = \sum_{j=1}^{n}\langle\theta_j(1)\,|\,\hat{f}_1\,|\,\theta_j(1)\rangle$, which is (11.78).

Proceeding similarly with the $\hat{g}_{ij}$ integrals, we have $\langle D|\sum_{i=1}^{n-1}\sum_{j>i}\hat{g}_{ij}\,|D\rangle = \sum_{i=1}^{n-1}\sum_{j>i}\langle D|\,\hat{g}_{ij}\,|D\rangle$. Use of Prob. 8.22 gives

$\langle D|\sum_{i=1}^{n-1}\sum_{j>i}\hat{g}_{ij}\,|D\rangle =$
$(1/n!)\sum_{i=1}^{n-1}\sum_{j>i}\langle\sum(\pm 1)u_p(1)u_q(2)u_r(3)\cdots|\,\hat{g}_{ij}\,|\sum(\pm 1)u_s(1)u_t(2)u_w(3)\cdots\rangle =$
$(1/n!)\sum_{i=1}^{n-1}\sum_{j>i}\sum\sum\langle(\pm 1)u_p(1)u_q(2)u_r(3)\cdots|\,\hat{g}_{ij}\,|\,(\pm 1)u_s(1)u_t(2)u_w(3)\cdots\rangle$ (Eq. 5).

Consider the integral $G \equiv \langle u_p(1)u_q(2)u_r(3)\cdots|\,\hat{g}_{12}\,|\,u_s(1)u_t(2)u_w(3)\cdots\rangle =$ $\langle u_p(1)u_q(2)\,|\,\hat{g}_{12}\,|\,u_s(1)u_t(2)\rangle\langle u_r(3)\,|\,u_w(3)\rangle\cdots = \langle u_p(1)u_q(2)\,|\,\hat{g}_{12}\,|\,u_s(1)u_t(2)\rangle\delta_{rw}\cdots$, since the spin-orbitals are orthonormal. Unless each of electrons 3, …, n, is in the same spin-orbital on the left and on the right of $\hat{g}_{12}$, the integral G will be zero. The rightmost sum in Eq. 5 is over the various possible permutations $stw\cdots$, and the nonzero terms in this sum have each of electrons 3,…, n in the same spin-orbital on the right of $\hat{g}_{12}$ as on the left. Hence, for $\hat{g}_{ij} = \hat{g}_{12}$, the only nonzero terms in the rightmost sum in Eq. 5 are $\langle u_p(1)u_q(2) | \hat{g}_{12} | u_p(1)u_q(2)\rangle$ and $-\langle u_p(1)u_q(2) | \hat{g}_{12} | u_q(1)u_p(2)\rangle$; the first of these integrals involves the same permutation on the left and right, so the ± 1's disappear. In the second integral, the permutation on the right is gotten from the one on the left by one interchange, so in this integral, the spin-orbitals are multiplied by $(+1)(-1) = -1$. Thus, the integral $\langle(\pm 1)u_p(1)u_q(2)u_r(3)\cdots | \hat{g}_{ij} | (\pm 1)u_s(1)u_t(2)u_w(3)\cdots\rangle$ in Eq. 5 is zero unless the permutation $stw\cdots$ is either the same as the permutation $pqr\cdots$ or differs from $pqr\cdots$ in having the two spin-orbitals for electrons *i* and *j* interchanged. The rightmost sum in Eq. 1 is over the various permutations $stw\cdots$. Thus when we do the rightmost summation, Eq. 5 gives $\langle D | \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} | D\rangle =$

$$(1/n!)\sum_{i=1}^{n-1} \sum_{j>i}\sum[\langle u_p(1)u_q(2)\cdots u_w(i)\cdots u_y(j)\cdots | \hat{g}_{ij} | u_p(1)u_q(2)\cdots u_w(i)\cdots u_y(j)\cdots\rangle -$$
$$\langle u_p(1)u_q(2)\cdots u_w(i)\cdots u_y(j)\cdots | \hat{g}_{ij} | u_p(1)u_q(2)\cdots u_y(i)\cdots u_w(j)\cdots\rangle] \text{ (Eq. 6)}$$

The rightmost $\sum$ in Eq. 6 is a summation over the *n*! permutations of *p*, *q*, *r*,…. One-*n*th of these *n*! permutations [that is, $(n-1)!$ permutations] have electron *i* in spin-orbital u_w; of these $(n-1)!$ permutations with electron *i* in u_w, a fraction $[1/(n-1)]$ have electron *j* in u_y. Thus $(n-2)!$ of the $n!$ permutations have electron *i* in u_w and electron *j* in u_y. Also $(n-2)!$ of the $n!$ permutations have electron *i* in u_y and electron *j* in u_w. Equation 6 therefore becomes $\langle D | \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} | D\rangle =$

$$\{2/[n(n-1)]\}\sum_{i=1}^{n-1} \sum_{j>i} [\langle u_p(1)u_q(2) | \hat{g}_{12} | u_p(1)u_q(2)\rangle + \langle u_p(1)u_r(2) | \hat{g}_{12} | u_p(1)u_r(2)\rangle + \cdots$$
$$- \langle u_p(1)u_q(2) | \hat{g}_{12} | u_q(1)u_p(2)\rangle - \langle u_p(1)u_r(2) | \hat{g}_{12} | u_r(1)u_p(2)\rangle - \cdots] \text{ (Eq. 7),}$$

where the dots indicate that terms with all pairs of spin-orbitals are included, with each pair appearing once; that is, the term $\langle u_q(1)u_p(2) | \hat{g}_{12} | u_q(1)u_p(2)\rangle$ does not appear in addition to $\langle u_p(1)u_q(2) | \hat{g}_{12} | u_p(1)u_q(2)\rangle$, since $\langle u_q(1)u_p(2) | \hat{g}_{12} | u_q(1)u_p(2)\rangle$ has been allowed for by the factor 2 in Eq. 7. In writing down Eq. 7, we used the relations
$\langle u_p(1)u_q(2)\cdots u_w(i)\cdots u_y(j)\cdots | \hat{g}_{ij} | u_p(1)u_q(2)\cdots u_w(i)\cdots u_y(j)\cdots\rangle =$
$\langle u_w(i)u_y(j) | \hat{g}_{ij} | u_w(i)u_y(j)\rangle$ and
$\langle u_w(i)u_y(j) | \hat{g}_{ij} | u_w(i)u_y(j)\rangle = \langle u_w(1)u_y(2) | \hat{g}_{12} | u_w(1)u_y(2)\rangle$. The quantity in brackets in Eq. 7 has the same value for each term in the double summation over *i* and *j*, and there are $\frac{1}{2}n(n-1)$ terms in the double sum. Hence Eq. 7 becomes $\langle D | \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} |D\rangle =$
$\langle u_p(1)u_q(2) | \hat{g}_{12} | u_p(1)u_q(2)\rangle + \langle u_p(1)u_r(2) | \hat{g}_{12} | u_p(1)u_r(2)\rangle + \cdots$
$- \langle u_p(1)u_q(2) | \hat{g}_{12} | u_q(1)u_p(2)\rangle - \langle u_p(1)u_r(2) | \hat{g}_{12} | u_r(1)u_p(2)\rangle - \cdots$ (Eq. 8), where the dots indicate that terms with all pairs of spin-orbitals are included. Instead of the dots, we can use a double sum over the spin-orbitals to include each pair of spin-orbitals, and Eq. 8 is $\langle D | \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} | D\rangle =$

$$\sum_{k=1}^{n-1} \sum_{m>k}[\langle u_k(1)u_m(2) | \hat{g}_{12} | u_k(1)u_m(2)\rangle - \langle u_k(1)u_m(2) | \hat{g}_{12} | u_m(1)u_k(2)\rangle] \text{ (Eq. 9).}$$

Each spin-orbital is the product of a spatial and a spin factor: $u_k = \theta_k \sigma_k$. Since the spin functions α and β are orthonormal, we have
$\langle u_k(1)u_m(2) \,|\, \hat{g}_{12} \,|\, u_k(1)u_m(2)\rangle = \langle \theta_k(1)\theta_m(2) \,|\, \hat{g}_{12} \,|\, \theta_k(1)\theta_m(2)\rangle$ and
$\langle u_k(1)u_m(2) \,|\, \hat{g}_{12} \,|\, u_m(1)u_k(2)\rangle = \delta_{m_{s,k}m_{s,m}} \langle \theta_k(1)\theta_m(2) \,|\, \hat{g}_{12} \,|\, \theta_m(1)\theta_k(2)\rangle$ and Eq. 9 becomes
$\langle D \,|\, \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \,|\, D\rangle =$
$\sum_{k=1}^{n-1} \sum_{m>k} [\langle \theta_k(1)\theta_m(2) \,|\, \hat{g}_{12} \,|\, \theta_k(1)\theta_m(2)\rangle - \delta_{m_{s,k}m_{s,m}} \langle \theta_k(1)\theta_m(2) \,|\, \hat{g}_{12} \,|\, \theta_m(1)\theta_k(2)\rangle]$,
which is (11.79).

11.38 **(a)** For a closed-subshell configuration, $\theta_1 = \theta_2 = \phi_1$, $\theta_3 = \theta_4 = \phi_2, \ldots, \theta_{n-1} = \theta_n = \phi_{n/2}$. Consider the Coulomb integrals in (11.80) that involve $\theta_1, \theta_2, \theta_3, \theta_4$. The contribution of these integrals to (11.80) is $J_{12} + J_{13} + J_{14} + J_{23} + J_{24} + J_{34}$, where the subscripts refer to the θ functions. Let J_{ij}^{ϕ} denote a Coulomb integral involving ϕ_i and ϕ_j. From the relations between the θ's and the ϕ's, we have $J_{12} = J_{11}^{\phi}$, $J_{13} = J_{12}^{\phi}$, $J_{14} = J_{12}^{\phi}$, $J_{23} = J_{12}^{\phi}$, $J_{24} = J_{12}^{\phi}$, $J_{34} = J_{22}^{\phi}$. So $J_{12} + J_{13} + J_{14} + J_{23} + J_{24} + J_{34} = 4J_{12}^{\phi} + J_{11}^{\phi} + J_{22}^{\phi}$, whose form agrees with that of the Coulomb integrals in the expression to be proved. A similar result holds for the Coulomb integrals involving the four orbitals $\theta_i, \theta_{i+1}, \theta_j, \theta_{j+1}$ having $\theta_i = \theta_{i+1}$ and $\theta_j = \theta_{j+1}$, so the Coulomb-integral part of the expression in Prob. 11.38a is correct. The orbitals $\theta_1, \theta_2, \theta_3, \theta_4$ have spin functions $\alpha, \beta, \alpha, \beta$, respectively, so the contribution of the exchange integrals in (11.80) that involve $\theta_1, \theta_2, \theta_3, \theta_4$ is $-K_{13} - K_{24}$. The integrals K_{12}, K_{14}, K_{23}, and K_{34} do not appear because of the Kronecker delta in (11.80). We have $K_{13} = K_{12}^{\phi}$ and $K_{24} = K_{12}^{\phi}$, so $-K_{13} - K_{24} = -2K_{12}^{\phi}$, whose form agrees with that of the exchange integrals in the expression to be proved. A similar result holds for the exchange integrals involving the four orbitals $\theta_i, \theta_{i+1}, \theta_j, \theta_{j+1}$ having $\theta_i = \theta_{i+1}$ and $\theta_j = \theta_{j+1}$, so the exchange-integral part of the expression in Prob. 11.38a is correct.

(b) First consider integrals where $i \neq j$. In the double sum in (11.83), the terms $2J_{ij} - K_{ij}$ and $2J_{ji} - K_{ji}$ occur, whereas the restriction $j > i$ means that in the Prob. 11.38 double sum, we get $4J_{ij} - 2K_{ij}$ instead of $2J_{ij} - K_{ij} + 2J_{ji} - K_{ji}$. Because $J_{ij} = J_{ji}$ and $K_{ij} = K_{ji}$, these two expressions are equal. The contribution of integrals with $i = j$ to the double sum in (11.80) is $\sum_{i=1}^{n/2}(2J_{ii} - K_{ii}) = \sum_{i=1}^{n/2}(2J_{ii} - J_{ii}) = \sum_{i=1}^{n/2} J_{ii}$.

11.39 If we take the special case that $\hat{f}_i = 1$, then Table 11.3 gives
$\langle D \,|\, n \,|\, D\rangle = n\langle D \,|\, D\rangle = \sum_{i=1}^{n} \langle u_i(1) \,|\, u_i(1)\rangle = n$ (since the spin-orbitals are normalized) and $\langle D \,|\, D\rangle = 1$. If D and D' differ by one spin-orbital $u_n \neq u_n'$, then
$n\langle D' \,|\, D\rangle = \langle u_n'(1) \,|\, u_n(1)\rangle = 0$, since the spin-orbitals are orthogonal. If D and D' differ by more than one spin-orbital, Table 11.3 gives $\langle D' \,|\, D\rangle = 0$.

11.40 The zero level of energy is taken with the electrons and the nucleus infinitely far from one another. Therefore the ground-state energy is minus the energy change for the process $Li \rightarrow Li^{3+} + 3e^{-}$, which is minus the total energy change for the processes $Li \rightarrow Li^{+} + e^{-}$, $Li^{+} \rightarrow Li^{2+} + e^{-}$, $Li^{2+} \rightarrow Li^{3+} + e^{-}$. In the second and third steps, the 1*s* electron is being removed from Li^{2+} and from Li^{3+}, respectively, whereas the 1*s* ionization energy of Li refers to removal of a 1*s* electron from Li. Hence the procedure mentioned in the problem does not give the correct Li ground-state energy.

11.41 **(a)** Because the proton mass occurs in the denominator of $\mathbf{m}_I$, whereas the electron mass occurs in the denominators of $\mathbf{m}_L$ and $\mathbf{m}_S$, the magnitude of $\mathbf{m}_I$ is much smaller than that of $\mathbf{m}_L$ and $\mathbf{m}_S$.

(b) The inner-shell electrons are in closed subshells and do not contribute to the orbital or spin angular momenta. The valence electron is in an *s* orbital and has no orbital angular momentum. Hence $\mathbf{L}$ is zero and $\mathbf{m}_L$ is zero. (The nuclear spin is nonzero since the nucleus has an odd number of protons.)

11.42 **(a)** T. With an odd number of electrons, there must be an odd number of unpaired electrons. Since each electron has $s = \frac{1}{2}$, the total-electron-spin quantum number *S* must be half-integral $(\frac{1}{2}$ or $\frac{3}{2}$ or $\frac{5}{2}$ or $\cdots)$ with an odd number of unpaired electrons. Hence $2S$ is odd and the spin multiplicity $2S + 1$ is even.

(b) T. With an even number of electrons, there must be an even number of unpaired electrons. The quantum number *S* must be an integer (0 or 1 or 2 or $\cdots$). Hence $2S$ is even and the spin multiplicity $2S + 1$ is odd.

(c) F. For example, a ^3S term has only one level.

(d) F. [See (11.10).]

(e) F.

Chapter 12

Molecular Symmetry

12.1 **(a)** F. **(b)** F. **(c)** T.

12.2 **(a)** A C_2 axis bisecting the bond angle; two planes of symmetry—one containing the plane of the nuclei and one perpendicular to the nuclear plane and containing the C_2 axis.

(b) A C_3 axis and three vertical planes of symmetry; each plane contains the C_3 axis and an N–H bond.

(c) A C_3 axis through the H–C bond and three planes of symmetry; each plane contains the C_3 axis and a C–F bond.

(d) A plane of symmetry containing the nuclei.

(e) A C_3 axis perpendicular to the molecular plane and passing through the center of the benzene ring; the C_3 axis is also an S_3 axis; three vertical planes of symmetry, each of which contains the C_3 axis and a C–Cl bond; a horizontal plane of symmetry containing all the nuclei; three C_2 axes, each containing a C–Cl bond.

(f) A C_2 axis that bisects the HCH bond; two vertical planes of symmetry, one containing the H, C, H nuclei and one containing the F, C, F nuclei.

(g) No symmetry elements.

12.3 **(a)** $\hat{E}, \hat{C}_2, \hat{\sigma}_a, \hat{\sigma}_b$.

(b) $\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c$.

(c) $\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c$

(d) $\hat{E}, \hat{\sigma}$.

(e) $\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{S}_3, \hat{S}_3^5, \hat{\sigma}_a, \hat{\sigma}_b\ \hat{\sigma}_c, \hat{\sigma}_d, \hat{C}_{2a}, \hat{C}_{2b}, \hat{C}_{2c}$.

(f) $\hat{E}, \hat{C}_2, \hat{\sigma}_a, \hat{\sigma}_b$.

(g) $\hat{E}$.

12.4 This does not meet the definition of a symmetry operation since it does not preserve the distances between all pairs of points in the body. For example, the distance between one of the Cl atoms that is moved and one of the Cl atoms that is not moved is changed.

12.5 **(a)** $\hat{E}$;

(b) $\hat{\sigma}$;

(c) $\hat{C}_2$;

(d) $\hat{C}_2$;

(e) $\hat{C}_2$;

(f) $\hat{S}_2 = \hat{i}$;

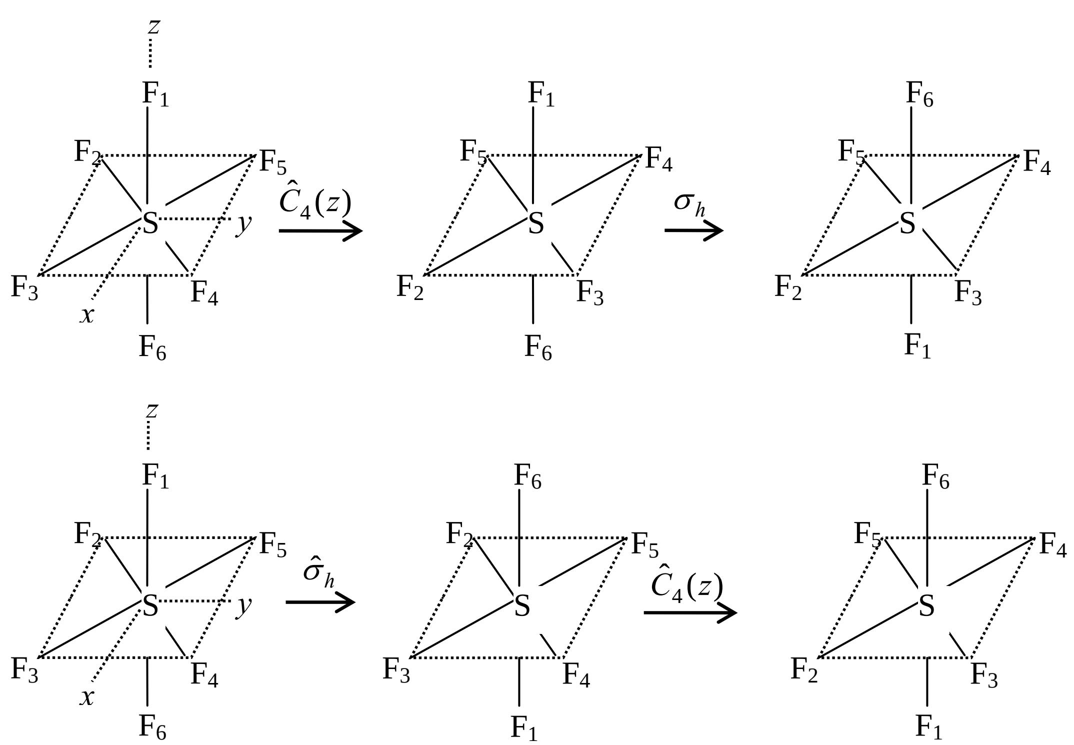
(g) $\hat{C}_4$;

(h) $\hat{i}$.

12.6 **(a)** The top drawing in Fig. 12.7 shows that $\hat{C}_2(x)\hat{C}_4(z)$ leaves the locations of F_3 and F_5 unchanged, interchanges F_1 and F_6, and interchanges F_4 and F_2. This is a $\hat{C}_2$ rotation about the F_3SF_5 axis.

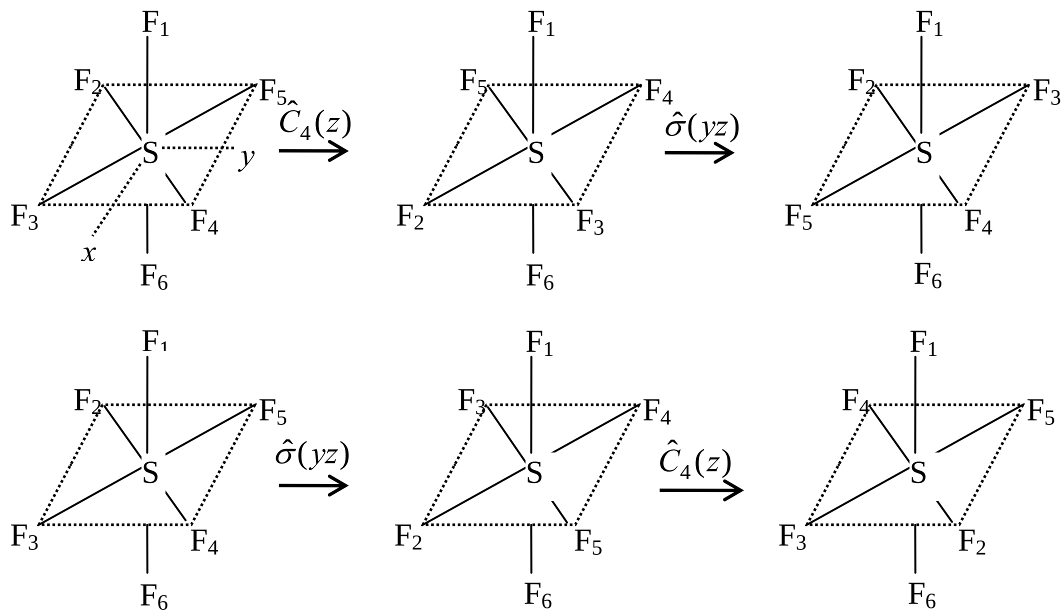
(b) The bottom drawing in Fig. 12.7 shows that $\hat{C}_4(z)\hat{C}_2(x)$ leaves the locations of F_2 and F_4 unchanged, interchanges F_1 and F_6, and interchanges F_3 and F_5. This is a $\hat{C}_2$ rotation about the F_2SF_4 axis.

12.7 **(a)**



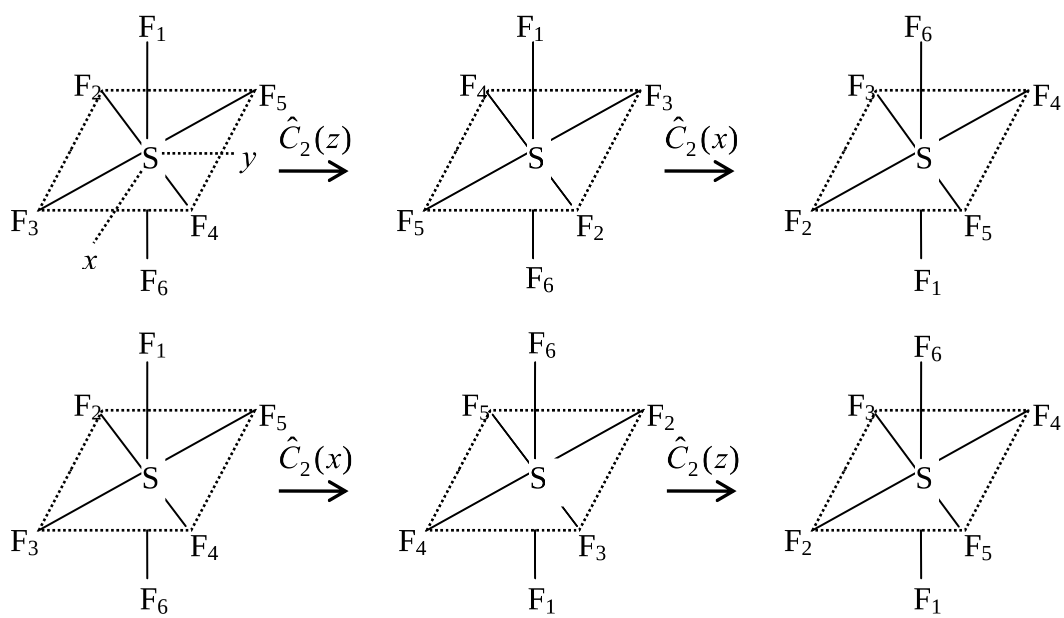
The top and bottom rightmost figures are the same, and these two operators commute.

(b)



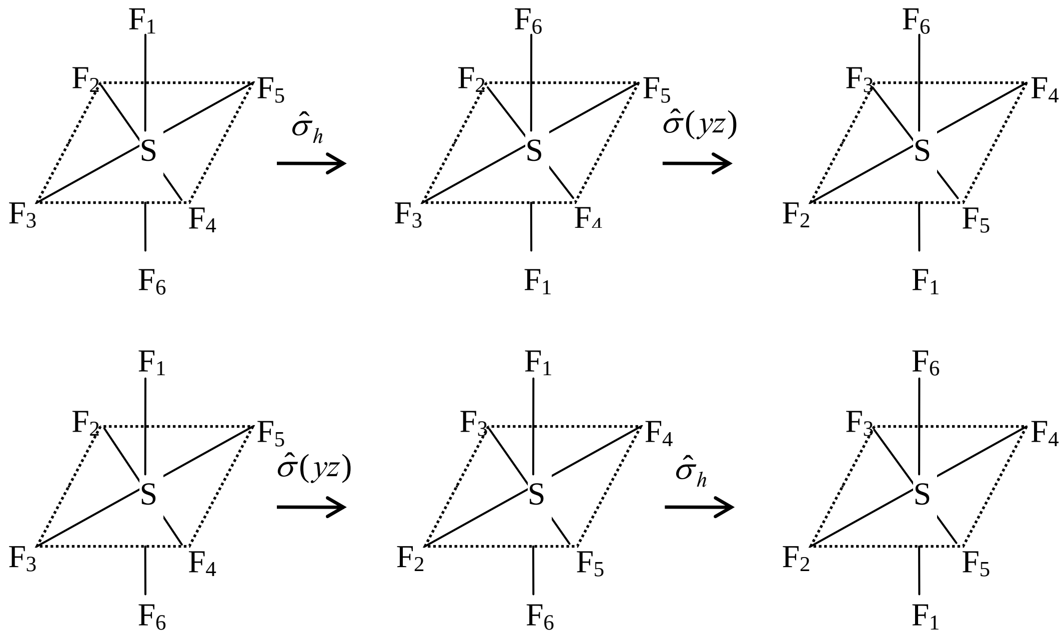
These two operators do not commute.

(c)



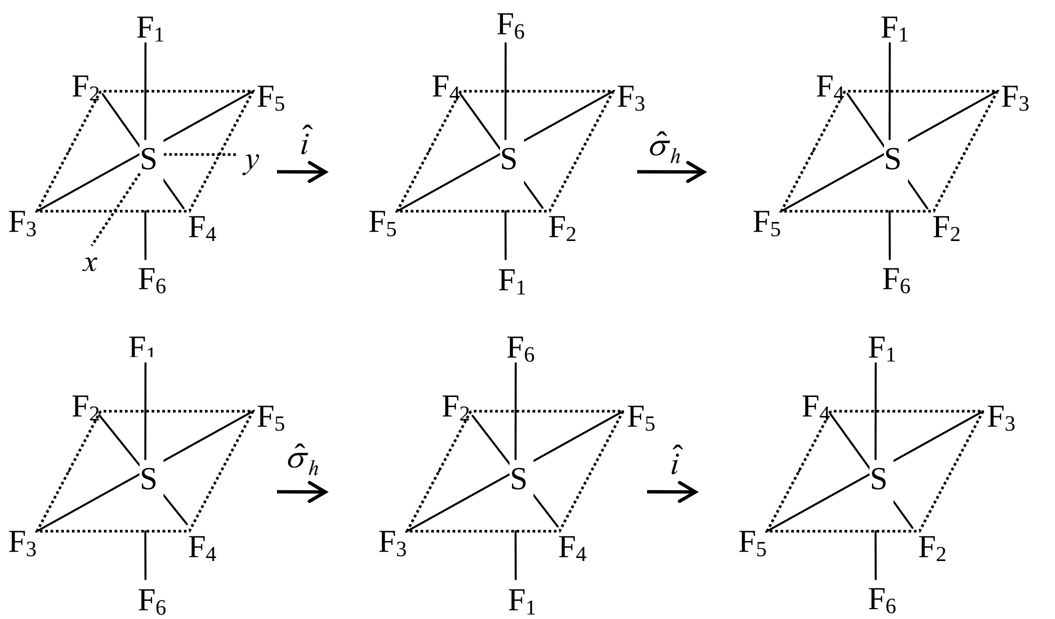
These operators commute.

(d)



These operators commute.

(e)



The operators commute.

12.8 **(a)** It lies along the C_2 axis bisecting the bond angle.

(b) It lies on the C_3 axis.

(c) It lies on the C_3 axis coinciding with the C–H bond.

(d) It lies in the molecular plane.

(e) No dipole moment, since we have noncoincident C_2 and C_3 axes.

(f) It lies on the C_2 axis bisecting the HCH bond angle.

(g) No information.

12.9 **(a)** No.

(b) Because of the absence of an S_n axis, the molecule is not superimposable on its mirror image. However, the mirror image differs from the original molecule by rotation about the O–O bond, and there is a low barrier to rotation about this single bond. Hence, the molecule is not optically active.

12.10 **(a)** $\hat{E}$ has no effect on the coordinates, so its matrix representative is

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(b) $\hat{\sigma}(xy)$ converts z to $-z$ while leaving the x and y coordinates unchanged, so its matrix representative is

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

(c) $\hat{\sigma}(yz)$ converts x to $-x$ and leaves the y and z coordinates unchanged. Its matrix representative is

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

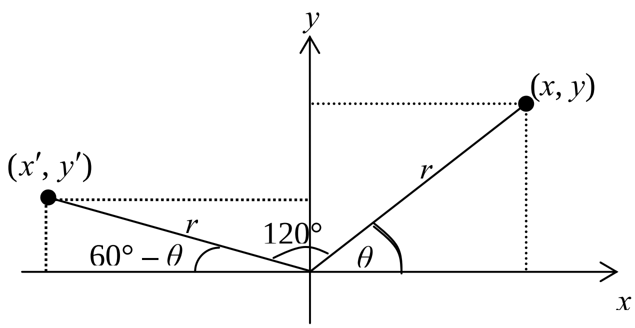
(d) $\hat{C}_2(x)$ converts y to $-y$ and z to $-z$, while leaving x unchanged. Hence, we have

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

(e) The $\hat{S}_4(z)$ operation combines the effects of $\hat{C}_4(z)$ and $\hat{\sigma}(xy)$. As shown in Fig. 12.9, a $\hat{C}_4(z)$ rotation gives $x' = -y$ and $y' = x$. The operation $\hat{\sigma}(xy)$ converts z to $-z$. Therefore the $\hat{S}_4(z)$ matrix representative is [see also the $\hat{C}_4(z)$ representative near the end of Sec. 12.1.]

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

(f) The following figure shows the effect of $\hat{C}_3(z)$:



From the figure, we have

$x = r\cos\theta,\ \ y = r\sin\theta$ and

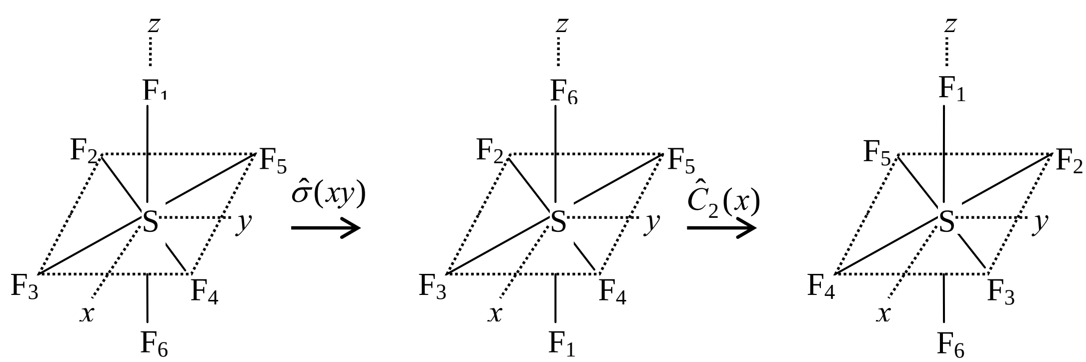
$x' = -r\cos(60° - \theta) = -r(\cos 60° \cos\theta + \sin 60° \sin\theta) = -\frac{1}{2} r\cos\theta - \frac{1}{2}\sqrt{3} r\sin\theta$

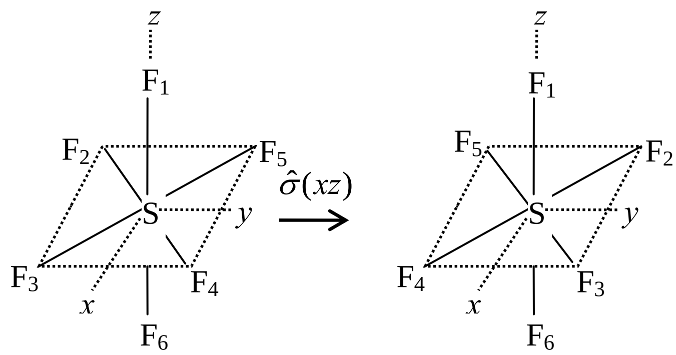
$x' = -\frac{1}{2}x - \frac{1}{2}\sqrt{3}y$

$y' = r\sin(60° - \theta) = r(\sin 60° \cos\theta - \cos 60° \sin\theta) = \frac{1}{2}\sqrt{3}x - \frac{1}{2}y$, where trigonometric identities were used. Hence the matrix representative is

$$\begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

12.11 (a)





(b)

$$\mathbf{C_2}(x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \boldsymbol{\sigma}(xy) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \boldsymbol{\sigma}(xz) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{C_2}(x)\boldsymbol{\sigma}(xy) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \boldsymbol{\sigma}(xz)$$

12.12 **(a)** Since $(\hat{O}_{C_4})^4 = 1$, the result of Prob. 7.25 shows the eigenvalues to be 1, i, –1, i.

(b) Since some eigenvalues are not real this operator cannot be Hermitian. Note also that the $\hat{C}_4(z)$ matrix representative near the end of Sec. 12.1 is not Hermitian.

12.13 **(a)** Since $(\hat{O}_{C_2})^2 = 1$, the result of Prob. 7.25 shows the eigenvalues to be 1 and –1.

(b) To prove this operator is Hermitian, we must show that
$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} [f(x, y, z)]^* \hat{O}_{C_2(z)} g(x, y, z)\,dx\,dy\,dz =$
$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g(x, y, z)[\hat{O}_{C_2(z)} f(x, y, z)]^*\,dx\,dy\,dz$ (Eq. 1). The left side (ls) of Eq. 1 is
ls = $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} [f(x, y, z)]^* g(-x, -y, z)\,dx\,dy\,dz$. Let $s \equiv -x,\ t \equiv -y$. Then
ls = $\int_{-\infty}^{\infty}\int_{\infty}^{-\infty}\int_{\infty}^{-\infty} [f(-s, -t, z)]^* g(s, t, z)\,ds\,dt\,dz =$
$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} [f(-x, -y, z)]^* g(x, y, z)\,dx\,dy\,dz$, where the dummy variables s and t were changed to x and y. The right side of Eq. 1 is
rs = $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g(x, y, z)[f(-x, -y, z)]^*\,dx\,dy\,dz$. Since rs = ls, the operator is Hermitian. (Note also that the matrix in Prob. 12.10d is Hermitian.)

12.14 **(a)** A rotation around the z axis leaves $2p_z$ unchanged.

(b) A 90° counterclockwise rotation about the y axis moves the positive lobe of $2p_z$ onto the positive half of the x axis and the negative lobe onto the negative x axis, and so converts $2p_z$ to $2p_x$.

12.15 Figure 12.6 shows that $\hat{i} = \hat{\sigma}(xy)\hat{C}_2(z)$. Also, $\hat{S}_n = \hat{\sigma}(xy)\hat{C}_n(z)$. Since two rotations about the z axis clearly commute with each other, we have $\hat{i}\hat{C}_n(z)\hat{C}_2(z) = \hat{i}\hat{C}_2(z)\hat{C}_n(z) = \hat{\sigma}(xy)\hat{C}_2(z)\hat{C}_2(z)\hat{C}_n(z) = \hat{\sigma}(xy)\hat{E}\hat{C}_n(z) = \hat{\sigma}(xy)\hat{C}_n(z) = \hat{S}_n$. For $n = 1$, the relation $\hat{S}_n(z) = \hat{i}[\hat{C}_n(z)\hat{C}_2(z)]$ (Eq. 1) becomes $\hat{S}_1(z) = \hat{i}\hat{C}_2(z)$, so an S_1 axis is a $\overline{2}$ axis. For $n = 2$, Eq. 1 becomes $\hat{S}_2(z) = \hat{i}\hat{C}_2(z)\hat{C}_2(z) = \hat{i}\hat{E} = \hat{i}\hat{C}_1(z)$, so an S_2 axis is a $\overline{1}$ axis. For $n = 3$, Eq. 1 becomes $\hat{S}_3(z) = \hat{i}\hat{C}_3(z)\hat{C}_2(z) = \hat{i}[\hat{C}_6(z)]^5 = \hat{i}[\hat{C}_6(z)]^{-1}$, so an S_3 axis is a $\overline{6}$ axis. For $n = 4$, Eq. 1 becomes $\hat{S}_4(z) = \hat{i}\hat{C}_4(z)\hat{C}_2(z) = \hat{i}[\hat{C}_4(z)]^3 = \hat{i}[\hat{C}_4(z)]^{-1}$, so an S_4 axis is a $\overline{4}$ axis. For $n = 5$, $\hat{S}_5 = \hat{i}\hat{C}_5(z)\hat{C}_2(z) = \hat{i}[\hat{C}_{10}(z)]^7$ and $\hat{S}_5^3 = \hat{i}^3(\hat{C}_{10})^{21} = \hat{i}\hat{C}_{10}$, so an S_5 axis is a $\overline{10}$ axis. For $n = 6$, $\hat{S}_6 = \hat{i}\hat{C}_6(z)\hat{C}_2(z) = \hat{i}(\hat{C}_3)^2 = \hat{i}(\hat{C}_3)^{-1}$ and an S_6 axis is a $\overline{3}$ axis. For $n = 7$, $\hat{S}_7 = \hat{i}\hat{C}_7\hat{C}_2 = \hat{i}(\hat{C}_{14})^9$ and $(\hat{S}_7)^3 = \hat{i}^3(\hat{C}_{14})^{27} = \hat{i}(\hat{C}_{14})^{-1}$ and an S_7 axis is a $\overline{14}$ axis.

12.16 **(a)** Since the sum of two real numbers is a real number, closure is satisfied. The identity element is 0. The inverse is the negative of the real number. (0 is its own inverse.) Addition is associative. Hence this is a group.

(b) The identity element is 1. The inverse of 2 is $\frac{1}{2}$, which is not an element in the proposed group, so this is not a group.

(c) Multiplication is associative. The identity element is 1. The inverse is the reciprocal of the number, and every member has an inverse. The product of two real nonzero numbers is a real nonzero number, so closure is satisfied. This is a group.

12.17 The sum of two square matrices of order 4 is a square matrix of order 4, so closure is satisfied. The identity element is the square order-4 null matrix (all elements equal to zero). Matrix addition is associative. The inverse of a matrix with elements a_{ij} is the matrix with elements $-a_{ij}$. So these matrices do form a group.

12.18 We have $e^{i2\pi k/n}e^{i2\pi j/n} = e^{i2\pi(k+j)/n}$ (where k and j are integers) and $[e^{i2\pi(k+j)/n}]^n = 1$, so closure is satisfied. The identity element is 1. The inverse is $e^{-i2\pi k/n}$ (which is an nth root of unity). Multiplication is associative. So this is a group.

12.19 **(a)** $\mathcal{T}_d$; **(b)** $\mathcal{C}_{3v}$; **(c)** $\mathcal{C}_{2v}$; **(d)** $\mathcal{C}_{3v}$; **(e)** $\mathcal{O}_h$; **(f)** $\mathcal{C}_{4v}$; **(g)** $\mathcal{D}_{4h}$; **(h)** $\mathcal{C}_{3v}$.

12.20 **(a)** $\mathcal{D}_{2h}$; **(b)** $\mathcal{C}_s$; **(c)** $\mathcal{C}_{2v}$; **(d)** $\mathcal{C}_{2v}$; **(e)** $\mathcal{C}_{2h}$.

12.21 **(a)** $\mathcal{D}_{6h}$; **(b)** $\mathcal{C}_{2v}$; **(c)** $\mathcal{C}_{2v}$; **(d)** $\mathcal{C}_{2v}$; **(e)** $\mathcal{D}_{2h}$; **(f)** $\mathcal{D}_{3h}$; **(g)** $\mathcal{C}_{2h}$; **(h)** $\mathcal{D}_{2h}$; **(i)** $\mathcal{C}_s$.

12.22 **(a)** $\mathcal{C}_{\infty v}$; **(b)** $\mathcal{C}_{2v}$; **(c)** $\mathcal{D}_{\infty h}$; **(d)** $\mathcal{C}_{\infty v}$; **(e)** $\mathcal{D}_{\infty h}$; **(f)** $\mathcal{C}_s$ (The OH hydrogen is staggered between two methyl hydrogens.); **(g)** $\mathcal{C}_{3v}$; **(h)** $\mathcal{C}_{\infty v}$; **(i)** $\mathcal{T}_d$; **(j)** $\mathcal{C}_{3v}$; **(k)** $\mathcal{D}_{3h}$; **(l)** $\mathcal{I}_h$; **(m)** $\mathcal{O}_h$; **(n)** $\mathcal{K}_h$.

12.23 **(a)** $\mathcal{O}_h$; **(b)** $\mathcal{C}_{4v}$; **(c)** $\mathcal{D}_{2d}$; **(d)** $\mathcal{O}_h$; **(e)** $\mathcal{C}_{3v}$; **(f)** $\mathcal{D}_{2h}$; **(g)** $\mathcal{D}_{4h}$; **(h)** $\mathcal{C}_{2v}$; **(i)** $\mathcal{D}_{2d}$.

12.24 **(a)** From Prob. 12.3b, there are 6 symmetry operations and the order is 6.

(b) From Prob. 12.3d, the order is 2.

(c) The order is infinity, since there are an infinite number of rotations.

(d) From Prob. 12.3e, the order is 12.

12.25 **(a)** $\hat{E},\ \hat{C}_2(z),\ \hat{\sigma}_\text{v}(xz),\ \hat{\sigma}_\text{v}(yz)$.

(b) The product of $\hat{E}$ with a symmetry operation $\hat{B}$ is equal to $\hat{B}$. The product of each of the four operations in (a) with itself is equal to $\hat{E}$. The $\hat{C}_2(z)$ operation converts the *x* coordinate to –*x* and the *y* coordinate to –*y* and does not affect *z*. The $\hat{\sigma}_\text{v}(xz)$ operation converts *y* to –*y* and leaves *x* and *z* unchanged. The $\hat{\sigma}_\text{v}(yz)$ operation converts *x* to –*x* and leaves *y* and *z* unchanged. Thus $(x, y, z)\xrightarrow{\hat{C}_2(z)}(-x, -y, z)\xrightarrow{\hat{\sigma}_\text{v}(xz)}(-x, y, z)$, so $\hat{\sigma}_\text{v}(xz)\,\hat{C}_2(z) = \hat{\sigma}_\text{v}(yz)$. Similarly, $\hat{C}_2(z)\,\hat{\sigma}_\text{v}(xz) = \hat{\sigma}_\text{v}(yz)$. Also $(x, y, z)\xrightarrow{\hat{C}_2(z)}(-x, -y, z)\xrightarrow{\hat{\sigma}_\text{v}(yz)}(x, -y, z)$, so $\hat{\sigma}_\text{v}(yz)\,\hat{C}_2(z) = \hat{\sigma}_\text{v}(xz)$. Similarly, $\hat{C}_2(z)\,\hat{\sigma}_\text{v}(yz) = \hat{\sigma}_\text{v}(xz)$. Also, $(x, y, z)\xrightarrow{\hat{\sigma}_\text{v}(xz)}(x, -y, z)\xrightarrow{\hat{\sigma}_\text{v}(yz)}(-x, -y, z)$, so $\hat{\sigma}_\text{v}(yz)\,\hat{\sigma}_\text{v}(xz) = \hat{C}_2(z)$. Similarly, $\hat{\sigma}_\text{v}(xz)\,\hat{\sigma}_\text{v}(yz) = \hat{C}_2(z)$.

(c) The results of part (b) give the following multiplication table

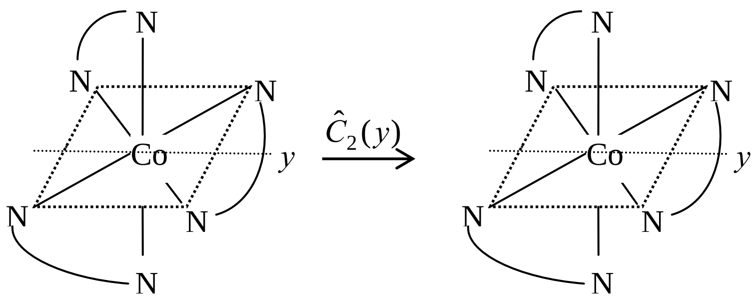
	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_\text{v}(xz)$	$\hat{\sigma}_\text{v}(yz)$
$\hat{E}$	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_\text{v}(xz)$	$\hat{\sigma}_\text{v}(yz)$
$\hat{C}_2(z)$	$\hat{C}_2(z)$	$\hat{E}$	$\hat{\sigma}_\text{v}(yz)$	$\hat{\sigma}_\text{v}(xz)$
$\hat{\sigma}_\text{v}(xz)$	$\hat{\sigma}_\text{v}(xz)$	$\hat{\sigma}_\text{v}(yz)$	$\hat{E}$	$\hat{C}_2(z)$
$\hat{\sigma}_\text{v}(yz)$	$\hat{\sigma}_\text{v}(yz)$	$\hat{\sigma}_\text{v}(xz)$	$\hat{C}_2(z)$	$\hat{E}$

12.26 **(a)** Since $\hat{E}$, $\hat{C}_3$, and $\hat{C}_3^2$ all commute with one another, this group is Abelian.

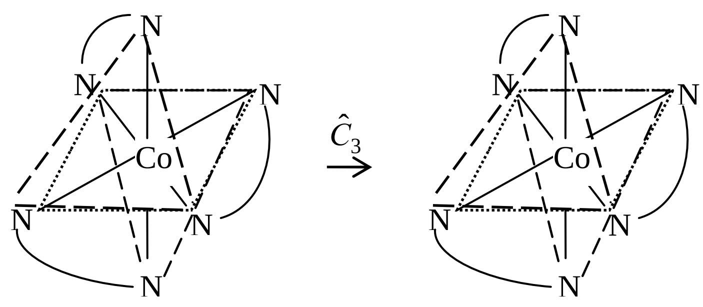
(b) Let the z axis go through the N atom and be perpendicular to the plane of the three hydrogens. Drawing the projections of the atoms into the xy plane, we find that $\hat{C}_3$ and $\hat{\sigma}(xz)$ do not commute, so the group is non-Abelian.

12.27 **(a)** $\mathcal{D}_{5h}$; **(b)** $\mathcal{D}_{5d}$.

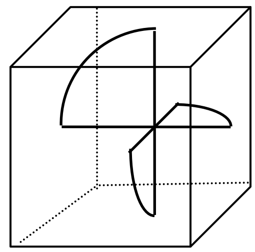
12.28 There are three C_2 axes, one through each $NH_2CH_2CH_2NH_2$ group:



The point group $\mathcal{D}_2$ has three C_2 axes, but in $\mathcal{D}_2$ these axes are mutually perpendicular, which is not true here. The three C_2 axes in this complex ion actually lie in the same plane; this plane contains the y axis and is tilted away from the viewer above the equatorial square and toward the viewer below the equatorial square. These three coplanar C_2 axes indicate a C_3 axis perpendicular to the plane of the C_2 axes. (This C_3 axis is one of the diagonals of the cube in which one can inscribe the octahedral ion; recall from the description of the group $\mathcal{O}_h$ the presence of C_3 axes in a cube.) The following figure shows two of the triangular faces of the octahedron. The C_3 axis is perpendicular to these two parallel planes, and a $\hat{C}_3$ rotation sends an atom at one corner of a triangle to another corner of the same triangle.



This complex ion, whose point group is $\mathcal{D}_3$, can be viewed as a three-bladed propeller:



12.29 We have $(x, y, z) \xrightarrow{\hat{C}_2(x)} (x, -y, -z) \xrightarrow{\hat{\sigma}(xy)} (x, -y, z)$.

12.30 **(a)** $\mathcal{C}_{4v}$; **(b)** $\mathcal{C}_{\infty v}$; **(c)** $\mathcal{D}_{4h}$; **(d)** $\mathcal{C}_{4v}$; **(e)** $\mathcal{D}_{\infty h}$; **(f)** $\mathcal{C}_{\infty v}$; **(g)** $\mathcal{C}_{2v}$; **(h)** $\mathcal{D}_{6h}$; **(i)** $\mathcal{D}_{\infty h}$; **(j)** $\mathcal{D}_{2d}$; **(k)** $\mathcal{D}_{\infty h}$ if the opposite signs of the wave function on the two lobes are ignored or $\mathcal{C}_{\infty v}$ if these signs are not ignored; **(l)** $\mathcal{C}_s$.

12.31 **(a)** A regular tetrahedron.

(b) The regular pentagonal dodecahedron is dual to the icosahedron, which has 20 faces (Fig. 12.14). Hence the pentagonal dodecahedron has 20 vertices. (For drawings, see mathworld.wolfram.com/Dodecahedron.html.)

12.32 **(a)** 1, 3, 5,… (as noted in the description of the group $\mathcal{S}_n$).

(b) 2, 6, 10, …, since $(\hat{S}_{2n})^n = \hat{\sigma}_h \hat{C}_2 = \hat{S}_2$ for $n =$ 1, 3, 5,….

(c) $2n = 2, 6, 10, \ldots$, so $n =$ 1, 3, 5,….

12.33 To have a dipole moment, the molecular point group must not have noncoincident symmetry axes, must not have a center of symmetry, must not have a symmetry plane perpendicular to a symmetry axis (since the dipole moment vector cannot simultaneously lie both on the axis and in the plane), and cannot contain an S_n axis with $n \geq 2$, since the $\hat{S}_n$ operation reverses the direction of a vector. The following groups satisfy these conditions: $\mathcal{C}_1$, $\mathcal{C}_s$, $\mathcal{C}_{nv}$, $\mathcal{C}_n$.

12.34 For optical activity, the molecule must have no S_n axis, including the cases of a plane of symmetry and a center of symmetry. The following point groups satisfy this condition: $\mathcal{C}_1$, $\mathcal{D}_n$, $\mathcal{C}_n$, $\mathcal{T}$, $\mathcal{O}$, $\mathcal{I}$.

12.35 The first player will win. As a hint, consider what chapter this problem is in. (The problem did not specify whether or not pennies are allowed to overlap the edge of the board, and the winning strategy is the same whether or not pennies are allowed to overlap the edge of the board.)

Chapter 13

Electronic Structure of Diatomic Molecules

13.1 **(a)** F. **(b)** T. **(c)** F. (The total energy is E in the nuclear Schrödinger equation.)

13.2 At 0 K, the enthalpy change of a gas-phase reaction equals the internal-energy change.

$$\frac{4.4781 \text{ eV}}{\text{molecule}}\ \frac{1.60218\times 10^{-19}\text{ J}}{1\text{ eV}}\ \frac{6.02214\times 10^{23}\text{ molecules}}{1\text{ mol}} = 432.07\text{ kJ/mol}$$

13.3 Consider the following processes, where all species are in their ground electronic (and vibrational) states:

$$\begin{tikzcd}
\mathrm{H_2} \arrow[r, "1"] \arrow[d, "3"] & \mathrm{H_2^+} + \mathrm{e^-} \arrow[r, "2"] & \mathrm{H} + \mathrm{H^+} + \mathrm{e^-} \\
2\mathrm{H} \arrow[urr, "4"'] & &
\end{tikzcd}$$

The energy change for step 1 is $I(\mathrm{H_2})$, the ionization energy of $\mathrm{H_2}$. The energy changes for steps 2 and 3 are $D_0(\mathrm{H_2^+})$ and $D_0(\mathrm{H_2})$, respectively. We have $\Delta E_1 + \Delta E_2 = \Delta E_3 + \Delta E_4$, so $I(\mathrm{H_2}) + D_0(\mathrm{H_2^+}) = D_0(\mathrm{H_2}) + I(\mathrm{H})$, and $I(\mathrm{H_2}) = 4.478$ eV + 13.598 eV – 2.651 eV = 15.425 eV.

13.4 **(a)** From Sec. 4.3, the frequency of the strongest infrared band equals the vibrational frequency of the diatomic molecule if the vibration is approximated as that of a harmonic oscillator. The zero-point energy is $\frac{1}{2}h\nu = \frac{1}{2}(6.626\times 10^{-34}\text{ J s})(8.65\times 10^{13}\text{ s}^{-1}) =$ $2.866\times 10^{-20}\text{ J}(1\text{ eV}/1.6022\times 10^{-19}\text{ J}) = 0.18\text{ eV}$. So $D_e = 4.43\text{ eV} + 0.18\text{ eV} = 4.61$ eV.

(b) The electronic energy function $U(R)$ is the same for $^2\mathrm{H}^{35}\mathrm{Cl}$ and $^1\mathrm{H}^{35}\mathrm{Cl}$ [since a change in the mass of a nucleus does not change anything in the electronic Schrödinger equation (13.4)–(13.6)], so the force constant $k_e \equiv U''(R_e)$ is the same for these species and D_e in Fig. 13.1 is the same for the two species. Equation (13.27) gives

$$\frac{\nu_e(^2\mathrm{H}^{35}\mathrm{Cl})}{\nu_e(^1\mathrm{H}^{35}\mathrm{Cl})} = \left[\frac{\mu(^1\mathrm{H}^{35}\mathrm{Cl})}{\mu(^2\mathrm{H}^{35}\mathrm{Cl})}\right]^{1/2} = \left[\frac{1.008(34.97)}{35.98}\frac{36.98}{2.014(34.97)}\right]^{1/2} = 0.717$$

Then $\nu_e(^2\mathrm{H}^{35}\mathrm{Cl}) = 0.717(8.65\times 10^{13}\text{ s}^{-1}) = 6.20\times 10^{13}\text{ s}^{-1}$ and $\frac{1}{2}h\nu = 0.128\text{ eV}$. So $D_e = 4.61\text{ eV} = D_0 + 0.13\text{ eV}$ and $D_0 = 4.48\text{ eV}$.

13.5 **(a)** Setting $\text{v} = 0$ in (4.60), we get the zero-point energy as $\frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$, so $D_e = D_0 + \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$.

(b) $\frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e =$
$(6.6261\times10^{-34}\text{ J s})(2.9979\times10^{10}\text{ cm/s})[0.5(1405.65\text{ cm}^{-1}) - 0.25(23.20\text{ cm}^{-1})] =$
$(1.3846\times10^{-20}\text{ J})(1\text{ eV}/1.6022\times10^{-19}\text{ J}) = 0.08642\text{ eV}$.
So $D_e = 2.4287\text{ eV} + 0.0864\text{ eV} = 2.5151\text{ eV}$.

13.6 The complete nonrelativistic $\hat{H}$ is Eq. (13.2). The purely electronic Hamiltonian is

$$\hat{H}_{\text{el}} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{1\alpha}} - \frac{e^2}{4\pi\varepsilon_0 r_{1\beta}} - \frac{e^2}{4\pi\varepsilon_0 r_{2\alpha}} - \frac{e^2}{4\pi\varepsilon_0 r_{2\beta}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

13.7 Let $f(z) \equiv (1+z)^{-2}$. Then $f' = -2(1+z)^{-3},\ f'' = 6(1+z)^{-4},\ f''' = -24(1+z)^{-5},\ldots$ and $f(0) = 1,\ f'(0) = -2,\ f''(0) = 6,\ f'''(0) = -24,\ldots$. The Taylor series (4.85) with $a = 0$ gives $(1+z)^{-2} = 1 - 2z + 3z^2 - 4z^3 + \cdots$ and replacing *z* by x/R_e, we get the series in (13.24).

13.8 **(a)** Since $a(R - R_e)$ in $e^{-a(R-R_e)}$ is dimensionless, *a* has dimensions of L^{-1}. Let $A = \mu^b a^c \hbar^d$ and $B = \mu^e a^f \hbar^g$. From Eqs. (4.71) and (4.70), $[A] = \text{ML}^2\text{T}^{-2} = [\mu]^b[a]^c[\hbar]^d = \text{M}^b\text{L}^{-c}\text{M}^d\text{L}^{2d}\text{T}^{-d} = \text{M}^{b+d}\text{L}^{2d-c}\text{T}^{-d}$. We have $b + d = 1,\ \ 2d - c = 2,\ \ -d = -2$. Hence $d = 2,\ c = 2,\ b = -1$ and $A = \mu^{-1}a^2\hbar^2$. The same procedure can be used to find *e*, *f*, and *g*, but it is simplest to note that since *a* has dimensions of L^{-1} and *B* has dimensions of L, we must have $B = a^{-1}$.

(b) The result of Prob. 4.29 gives $a = (k_e/2D_e)^{1/2}$ and Eq. 13.27 gives $k_e^{1/2} = 2\pi\nu_e\mu^{1/2}$, so $a = 2\pi\nu_e(\mu/2D_e)^{1/2}$. Then
$A = \mu^{-1}a^2\hbar^2 = 2\pi^2\nu_e^2\hbar^2/D_e = \nu_e^2 h^2/2D_e = (4403.2\text{ cm}^{-1})^2 c^2 h^2/2hc(38297\text{ cm}^{-1}) =$
$(253.12_9\text{ cm}^{-1})hc = (253.12_9\text{ cm}^{-1})(6.6261\times10^{-34}\text{ J s})(2.9979\times10^{10}\text{ cm/s}) = 5.0283\times10^{-21}\text{ J}$
$B = a^{-1} = (2D_e/\mu)^{1/2}/2\pi\nu_e$.
$\mu = m_1 m_1/(m_1 + m_1) = m_1/2 = 0.5(1.007825\text{ g})/(6.02214\times10^{23}) = 8.36766\times10^{-25}\text{ g}$.
$B = [2(38297\text{ cm}^{-1})hc/\mu]^{1/2}/2\pi(4403.2\text{ cm}^{-1})c = 0.010003_4(h/\mu c)^{1/2}\text{cm}^{1/2} =$
$0.010003_4[(6.6261\times10^{-34}\text{ J s})/(8.36766\times10^{-28}\text{ kg})(2.99792\times10^{10}\text{ cm/s})]^{1/2}\text{cm}^{1/2} =$
$5.1412\times10^{-11}\text{ m}$.
$D_{e,r} = D_e/A = (38297\text{ cm}^{-1})hc/(253.12_9\text{ cm}^{-1})hc = 151.29$.

13.9 **(a)** We set up the spreadsheet similar to Fig. 4.9 but with the $D_{e,r}$ value 151,29$_4$ (from the Sec. 13.2 example) put in cell D2. x_r goes from –1.44 to 2.8 in steps of 0.02. Since $G_r = 2D_{e,r}(1-e^{-x_r})^2 - 2E_{\text{vib},r}$, the formula in B7 is =2*D2*(1-EXP(-A7))^2-2*B3. You may well find that the Solver has trouble converging. Instead of taking the unnormalized vibrational wave function value in C219 as the target cell, it is better to calculate the normalized $S_r(x_r)$ wave function values [where $S_r(x_r)$ is defined in the Sec. 13.2 example] in column E (using the procedure given near the end of Sec. 4.4; see also part b of this problem) and use E219 as the target cell. Add the constraint $E_r \geq 0$. Increase the number of Solver iterations to 5000. Also, graph the normalized wave function. You may still find the Solver does not converge (especially for the lowest levels), and using E209 instead of E219 as the target cell may increase the chances of convergence. You can also temporarily decrease the precision to, say, 0.01 to get an initial estimate of E_r, which can then be found more accurately by increasing the precision. Even so, for some levels you may have to adjust the energy value by hand (after finding an initial estimate by running the Solver a few times in succession), being guided by the number of nodes. One finds the six lowest $E_{\text{vib},r}$ values as 8.57252518603940, 24.9675657754079, 40.3625822603903, 54.7575697506298, 68.1525305970211, and 80.5474722505875. (A ridiculously large number of significant figures were found to ensure that the wave function stays very close to zero at the right end, so that the answers to (b) will be accurate.) Use of the A value in Prob. 13.8b gives $E_{\text{vib}}/hc = (A/hc)E_{\text{vib},r} =$ $(253.12_9 \text{ cm}^{-1})E_{\text{vib},r}$ and we find the six lowest Morse-function vibrational levels as 2169.95, 6320.01, 10216.94, 13860.73, 17251.38, and 20388.90 cm^{-1}.

(b) We calculate the normalized S_r values in column E. For example, cell E7 contains the formula =C7/H2^0.5, where cell H2 has the formula =SUMSQ(C8:C219)*D3, where D3 contains the interval value. In column F, we calculate the $x_r S_r^2 s_r$ values. For example, cell F7 has the formula =A7*E7^2*D3. Then $\langle x_r \rangle$ is found from the formula =SUM(F7:F209). The $\langle x_r \rangle$ values found for the six lowest vibrational levels are 0.0440, 0.1365, 0.2360, 0.3435, 0.4605, and 0.5884. Use of
$x_r = x/B = (R - R_e)/B = (R - 0.741 \text{ Å})/(0.5141 \text{ Å})$ gives $\langle R \rangle = 0.741 \text{ Å} + (0.5141 \text{ Å})\langle x_r \rangle$ and we find the following $\langle R \rangle$ values for the six lowest levels: 0.764, 0.811, 0.862, 0.918, 0.978, 1.043 Å.

(c) The x_r limits in the Sec. 13.2 example are appropriate for energies below $E_r = 95.7$. The energy spacing between the highest two levels in part (a) is 12. The spacing between adjacent levels will continue to decrease as we go to higher levels, and we want to calculate four more levels. We shall therefore add 4(12) = 48 to the highest energy value of 80 in part (a) to get 128. For $E_r = 128$, we find the classically allowed region as in the Sec. 13.2 example: $128 = D_{e,r}(1-e^{-x_r})^2 = 151(1-e^{-x_r})^2$, which gives $x_r = 2.53$ as the right limit of the classically allowed region. Adding 1.2 to this, we get 3.7 as the right limit for x_r. We shall keep 0.02 as the interval. For these higher levels, the Solver more readily converges and the target cell should be E264. Continuing the process in (a), we find $E_{\text{vib},r}$ for the next four levels to be 91.9424054, 102.337342, 111.732295, 120.127274. Use of $E_{\text{vib}}/hc = (253.12_9 \text{ cm}^{-1})E_{\text{vib},r}$ gives the E_{vib}/hc values as 23273.3, 25904.5, 28282.7, and 30407.7 cm^{-1}.

13.10 From Prob. 13.8b, $A = \nu_e^2 h^2/2D_e = (214.5 \text{ cm}^{-1})^2 c^2 h^2/2hc(12550 \text{ cm}^{-1}) =$
$(1.83308 \text{ cm}^{-1})hc$. $D_{e,r} = D_e/A = (12550 \text{ cm}^{-1})hc/(1.83308 \text{ cm}^{-1})hc = 6846.4$.
$\mu = m_1 m_1/(m_1 + m_1) = m_1/2 = 0.5(126.904 \text{ g})/(6.02214\times 10^{23}) = 1.05365\times 10^{-22}$ g.
$B = (2D_e/\mu)^{1/2}/2\pi\nu_e =$
$[2(12550 \text{ cm}^{-1})hc/\mu]^{1/2}/2\pi(214.5 \text{ cm}^{-1})c = 0.11755(h/\mu c)^{1/2}\text{cm}^{1/2} =$
$0.11755[(6.6261\times 10^{-34} \text{ J s})/(1.05365\times 10^{-25} \text{ kg})(2.99792\times 10^{10} \text{ cm/s})]^{1/2} \text{ cm}^{1/2} =$
5.384×10^{-11} m $= 0.5384$ Å. $R_{e,r} = 2.666/0.5384 = 4.952$.
The sixth-lowest vibrational level will have an energy that is less than $5.5h\nu_e = 5.5h(214.5 \text{ cm}^{-1})c = (1180 \text{ cm}^{-1})hc$, which division by A gives as a reduced energy of 1180/1.833 = 644. To find the limits of the classically allowed region for this energy, we have $644 = D_{e,r}(1 - e^{-x_r})^2 = 6846(1 - e^{-x_r})^2$ and $1 - e^{-x_r} = \pm 0.307$. We get $x_r = -0.27$ and $x_r = 0.37$. We shall extend this region by 0.43 at each end and take the range from –0.70 to 0.80 with $s_r = 0.01$. (Note that the minimum possible x_r is $(0 - 2.67)/0.539 = -4.95$, so –0.70 is OK.) Because the classically allowed region is much narrower here than in Prob. 13.9, it is appropriate to use a shorter extension here into the classically forbidden region. For the lowest levels, the Solver has trouble converging; see Prob. 13.9a for how to deal with this. We find the following values:
$E_{\text{vib},r} =$ 58.383056671139, 174.398929144567, 289.414096609111, 403.428129942721, 516.440634357965, 628.451248394192.
Then $E_{\text{vib}}/hc = (A/hc)E_{\text{vib},r} = (1.83308 \text{ cm}^{-1})E_{\text{vib},r}$ and we find the lowest E_{vib}/hc values as 107.02, 319.69, 530.52, 739.52, 946.68, 1152.00 cm^{-1}.

13.11 **(a)** $E_{\text{vib}}/hc = (\text{v} + \frac{1}{2})(\nu_e/c) - (\text{v} + \frac{1}{2})^2(\nu_e/c)^2/4(D_e/hc)$. Substitution of D_e and ν_e values from the Sec. 13.2 example gives for $\text{v} = 0$:
$E_{\text{vib}}/hc = [\frac{1}{2}(4403.2) - \frac{1}{4}(4403.2)^2/4(38297)] \text{ cm}^{-1} = 2169.96 \text{ cm}^{-1}$. For the next five levels, the formula gives 6320.03, 10216.97, 13860.78, 17251.47, 20389.02 cm^{-1}.
(b) To find the predicted $\text{v}_{\max}$, we set $D_e/hc = E_{\text{vib}}/hc$ to get
$38297 \text{ cm}^{-1} = E_{\text{vib}}/hc = [(\text{v}_{\max} + \frac{1}{2})(4403.2) - (\text{v}_{\max} + \frac{1}{2})^2(4403.2)^2/4(38297)] \text{ cm}^{-1}$.

Setting $z \equiv \mathrm{v}_{\max} + \frac{1}{2}$, we have $126.564z^2 - 4403.2z + 38297 = 0$ and $z = 17.43,\ 17.36$, which corresponds to $\mathrm{v}_{\max} = 16.93,\ 16.86$, so the Morse function predicts $\mathrm{v}_{\max} = 16$.

13.12 We have from Eq. (13.16) $\langle R - R_e \rangle = \int |\psi_{N,\text{int}}|^2 (R - R_e)\, d\tau =$ $\int_0^\infty |P(r)|^2 (R - R_e) R^2\, dR \int_0^{2\pi} \int_0^\pi |Y_J^M(\theta_N, \phi_N)|^2 \sin\theta\, d\theta\, d\phi = \int_0^\infty |P(r)|^2 (R - R_e) R^2\, dR =$ $\int_0^\infty |F(r)|^2 (R - R_e)\, dR$, since the spherical harmonics are normalized and $F = RP$ [Eq. (13.18)]. Use of $x \equiv R - R_e$ and $S(x) = F(R)$ gives $\langle R - R_e \rangle = \int_{-R_e}^\infty |S(x)|^2 x\, dx$.

13.13 **(a)** Coulomb's law $F = Q_1 Q_2 / 4\pi\varepsilon_0 r_{12}^2$ gives $[4\pi\varepsilon_0] = [Q]^2/[F]\mathrm{L}^2 = \mathrm{Q}^2/\mathrm{MLT}^{-2}\mathrm{L}^2 = \mathrm{Q}^2\mathrm{M}^{-1}\mathrm{L}^{-3}\mathrm{T}^2$.

(b) Let $A = \hbar^a m_e^b e^c (4\pi\varepsilon_0)^d$. Then $[A] = [E] = \mathrm{ML}^2\mathrm{T}^{-2} = [\hbar]^a [m_e]^b [e]^c [4\pi\varepsilon_0]^d = (\mathrm{ML}^2\mathrm{T}^{-1})^a \mathrm{M}^b \mathrm{Q}^c (\mathrm{Q}^2\mathrm{M}^{-1}\mathrm{L}^{-3}\mathrm{T}^2)^d$, so $a + b - d = 1,\ 2a - 3d = 2,\ c + 2d = 0,\ -a + 2d = -2$. Adding twice the last equation to the second equation, we get $d = -2$. Then $a = -2$, $c = 4$, and $b = 1$, so $A = \hbar^{-2} m_e e^4 (4\pi\varepsilon_0)^{-2} = e^2/4\pi\varepsilon_0 a_0$.

Let $B = \hbar^s m_e^f e^g (4\pi\varepsilon_0)^r$. Then $[B] = \mathrm{L} = [\hbar]^s [m_e]^f [e]^g [4\pi\varepsilon_0]^r =$ $(\mathrm{ML}^2\mathrm{T}^{-1})^s \mathrm{M}^f \mathrm{Q}^g (\mathrm{Q}^2\mathrm{M}^{-1}\mathrm{L}^{-3}\mathrm{T}^2)^r$ so $s + f - r = 0,\ 2s - 3r = 1$, $g + 2r = 0$, $-s + 2r = 0$. Then $r = 1$, $s = 2$, $g = -2$, $f = -1$ and $B = \hbar^2 m_e^{-1} e^{-2} (4\pi\varepsilon_0) = a_0$.

(c) From $\psi_r = \psi B^{3/2}$ and $r_r = r/B$, we have $\partial\psi_r/\partial r_r = B^{3/2}(\partial\psi/\partial r)(\partial r/\partial r_r) = B^{3/2}(\partial\psi/\partial r)B = B^{3/2}(\partial\psi/\partial r)a_0$. Also, as shown in Sec. 13.3, $\partial^2\psi_r/\partial r_r^2 = B^{3/2}(\partial^2\psi/\partial r^2)a_0^2$. Substitution into the H-atom infinite-nuclear mass Schrödinger equation $-\dfrac{\hbar^2}{2m_e}\left(\dfrac{\partial^2\psi}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial\psi}{\partial r}\right) + \dfrac{1}{2m_e r^2}\hat{L}^2\psi - \dfrac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi$ gives

$$-\frac{\hbar^2}{2m_e}\left(\frac{B^{-3/2}}{a_0^2}\frac{\partial^2\psi_r}{\partial r_r^2} + \frac{2}{Br_r}\frac{B^{-3/2}}{a_0}\frac{\partial\psi_r}{\partial r_r}\right) + \frac{\hbar^2}{2m_e B^2 r_r^2} B^{-3/2}(\hbar^{-2}\hat{L}^2)\psi_r - \frac{e^2}{4\pi\varepsilon_0 B r_r} B^{-3/2}\psi_r =$$
$$AE_r B^{-3/2}\psi_r = (e^2/4\pi\varepsilon_0 a_0)E_r B^{-3/2}\psi_r$$

Multiplying by $a_0 B^{3/2}$ and using $B = a_0$ and $(\hbar^2/m_e a_0) = (\hbar^2/m_e)(m_e e^2/\hbar^2 4\pi\varepsilon_0) = e^2/4\pi\varepsilon_0$, we see that all terms have the factor $e^2/4\pi\varepsilon_0$, which cancels. So we get $-\dfrac{1}{2}\left(\dfrac{\partial^2\psi_r}{\partial r_r^2} + \dfrac{2}{r_r}\dfrac{\partial\psi_r}{\partial r_r}\right) + \dfrac{1}{2r_r^2}(\hbar^{-2}\hat{L}^2)\psi_r - \dfrac{1}{r_r}\psi_r = E_r\psi_r$.

Use of (5.68) gives

$$-\frac{1}{2}\left(\frac{\partial^2\psi_r}{\partial r_r^2}+\frac{2}{r_r}\frac{\partial\psi_r}{\partial r_r}\right)-\frac{1}{2r_r^2}\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi_r-\frac{1}{r_r}\psi_r=E_r\psi_r$$

which is the desired result.

13.14 **(a)** Let $\hbar^a m_e^b e^c (4\pi\varepsilon_0)^d$ be the desired atomic unit of time. We thus have (see Prob. 13.13a) $\mathrm{T} = [\hbar]^a[m_e]^b[e]^c[4\pi\varepsilon_0]^d = (\mathrm{ML^2T^{-1}})^a \mathrm{M}^b\mathrm{Q}^c(\mathrm{Q^2M^{-1}L^{-3}T^2})^d$. So $a+b-d=0,\ 2a-3d=0,\ c+2d=0,\ -a+2d=1$. Adding twice the last equation to the second equation, we get $d=2$. Then $a=3,\ c=-4,\ b=-1$ and the atomic unit of time is $\hbar^3 m_e^{-1}e^{-4}(4\pi\varepsilon_0)^2$. Noting that E_h in (13.29) is $E_\mathrm{h} = e^2/4\pi\varepsilon_0 a_0 = (e^2/4\pi\varepsilon_0)(m_e e^2/4\pi\varepsilon_0\hbar^2) = m_e e^4/(4\pi\varepsilon_0)^2\hbar^2$, we get $\hbar/E_\mathrm{h}$ as the atomic unit of time.

The dimensions of electric dipole moment are charge times length. Since e is the atomic unit of charge and a_0 is the atomic unit of length, $ea_0 = 4\pi\varepsilon_0\hbar^2/m_e e$ is the atomic unit of electric dipole moment. Alternatively, let $\hbar^s m_e^f e^g (4\pi\varepsilon_0)^r$ be the atomic unit of electric dipole moment. Then $\mathrm{QL} = [\hbar]^s[m_e]^f[e]^g[4\pi\varepsilon_0]^r =$ $(\mathrm{ML^2T^{-1}})^s\mathrm{M}^f\mathrm{Q}^g(\mathrm{Q^2M^{-1}L^{-3}T^2})^r$ so $s+f-r=0,\ 2s-3r=1,\ g+2r=1,\ -s+2r=0$. We get $r=1,\ s=2,\ g=-1,\ f=-1$, and the atomic unit of electric dipole moment is $\hbar^2 m_e^{-1}e^{-1}(4\pi\varepsilon_0) = ea_0$.

(b) Electric field strength is a force divided by a charge and its dimensions are the same as energy divided by (length times charge). Since the atomic units of energy, length and charge are E_h, a_0, and e, the atomic unit of electric field strength equals E_h/ea_0. Alternatively, electric field strength has dimensions of $\mathrm{MLT^{-2}Q^{-1}}$. Let $\hbar^w m_e^x e^y (4\pi\varepsilon_0)^z$ be the unit of electric field strength. We have $\mathrm{MLT^{-2}Q^{-1}} = [\hbar]^w[m_e]^x[e]^y[4\pi\varepsilon_0]^z = (\mathrm{ML^2T^{-1}})^w\mathrm{M}^x\mathrm{Q}^y(\mathrm{Q^2M^{-1}L^{-3}T^2})^z$ so $w+x-z=1,\ 2w-3z=1,\ -w+2z=-2,\ y+2z=-1$. We get $z=-3,\ y=5,\ w=-4,\ x=2$ so $\hbar^{-4}m_e^2e^5(4\pi\varepsilon_0)^{-3}$ (which equals E_h/ea_0) is the atomic unit of electric field strength.

$E_\mathrm{h}/ea_0 = (27.2114\text{ eV})(1.6022\times10^{-19}\text{ J/eV})/(1.6022\times10^{-19}\text{ C})(0.52918\ \times10^{-10}\text{ m}) =$ $5.142\times10^{11}\text{ V/m}$.

13.15 **(a)** The proton mass is 1836.15 times the electron mass m_e and m_e is the atomic unit of mass. Therefore the proton mass is 1836.15 atomic units of mass.

(b) –1, since the proton charge e is the atomic unit of charge.

(c) $h = 2\pi\hbar$ and $\hbar$ has the numerical value 1 in atomic mass units, so h has the numerical value 2π in atomic mass units.

(d) He^+ is a hydrogenlike atom with ground-state energy for infinite nuclear mass given by (6.94) as $-4[e^2/(2)4\pi\varepsilon_0 a_0]$. Since e, a_0, and $4\pi\varepsilon_0$ have numerical values of 1 in atomic units, this energy is –2 hartrees.

(e) From Prob. 13.13a, the atomic unit of time is
$\hbar/E_\mathrm{h} = (6.62607\times10^{-34}\text{ J s})/[2\pi(27.2114\text{ eV})(1.602177\times10^{-19}\text{ J/eV})] = 2.41888\times10^{-17}\text{ s}$
so one second is $(2.41888\times10^{-17})^{-1} = 4.134\times10^{16}$ atomic units of time.

(f) Speed has units of distance over time, and the atomic unit of speed is
$a_0/(\hbar/E_\mathrm{h}) = E_\mathrm{h}a_0/\hbar =$
$(27.2114\text{ eV})(1.602177\times10^{-19}\text{ J/eV})(0.529177\times10^{-10}\text{ m})2\pi/(6.62607\times10^{-34}\text{ J s}) =$
$2.1877\times10^6\text{ m/s}$. Then $(2.99792\times10^8\text{ m/s})/(2.1877\times10^6\text{ m/s}) = 137.03_5$.

(g) With infinite nuclear mass, the H-atom ground-state energy is $-\frac{1}{2}$ hartree. From (6.94), this energy is proportional to the reduced mass, which (6.105) gives as $0.99946\,m_e$, so with use of the reduced mass, the H-atom ground-state energy is $-\frac{1}{2}(0.99946) =$ –0.49973 hartrees.

(h) From Prob. 13.14a, the atomic unit of electric dipole moment is
$ea_0 = (1.6021766\times10^{-19}\text{ C})(5.2917721\times10^{-11}\text{ m}) = 8.478353\times10^{-30}\text{ C m} = 2.54175\text{ D}$,
so one debye is $1/2.54175 = 0.39343$ atomic units.

13.16 $S_{ab} = \int 1s_a^* 1s_b\,d\tau = \int (k^3/\pi)e^{-k(r_a+r_b)}\,d\tau = \int (k^3/\pi)e^{-kR\xi}\,d\tau =$
$(k^3R^3/8\pi)\int_0^{2\pi}\int_{-1}^{1}\int_1^{\infty} e^{-kR\xi}(\xi^2-\eta^2)\,d\xi\,d\eta\,d\phi =$

$$\frac{k^3R^3}{8\pi}\int_0^{2\pi}\int_{-1}^{1}\left[e^{-kR\xi}\left(-\frac{\xi^2}{kR}-\frac{2\xi}{k^2R^2}-\frac{2}{k^3R^3}\right)+\frac{\eta^2}{kR}e^{-kR\xi}\right]\Bigg|_{\xi=1}^{\infty} d\eta\,d\phi =$$

$$\frac{k^3R^3}{8\pi}\int_0^{2\pi}d\phi\int_{-1}^{1}\left[e^{-kR}\left(\frac{1}{kR}+\frac{2}{k^2R^2}+\frac{2}{k^3R^3}\right)-\frac{\eta^2}{kR}e^{-kR}\right]d\eta =$$

$$\frac{k^3R^3e^{-kR}}{4}\left[\eta\left(\frac{1}{kR}+\frac{2}{k^2R^2}+\frac{2}{k^3R^3}\right)-\frac{\eta^3}{3kR}\right]\Bigg|_{-1}^{1} =$$

$$\frac{k^3R^3e^{-kR}}{4}\left[2\left(\frac{1}{kR}+\frac{2}{k^2R^2}+\frac{2}{k^3R^3}\right)-\frac{2}{3kR}\right] = e^{-kR}(k^2R^2/3+kR+1)\quad\text{(Eq. 1)}$$

where Eq. (A.7) was used.

13.17 **(a)** $H_{aa} = \int 1s_a^*\hat{H}1s_a\,d\tau$. In atomic units, $\hat{H} = -\frac{1}{2}\nabla^2 - k/r_a + (k-1)/r_a - 1/r_b =$ $\hat{H}_a + (k-1)/r_a - 1/r_b$, where $\hat{H}_a$ is the Hamiltonian for a hydrogenlike atom with nuclear charge k. Since the orbital $1s_a$ in (13.44) is for a nuclear charge of k, we have

$\hat{H}_a 1s_a = -\frac{1}{2}k^2 1s_a$ [Eq. (6.94) in atomic units]. So

$H_{aa} = \int 1s_a \hat{H}_a 1s_a \, d\tau + (k-1)\int (1s_a^2/r_a)\, d\tau - \int (1s_a^2/r_b)\, d\tau$ (Eq. 1).

$\int 1s_a \hat{H}_a 1s_a \, d\tau = -\frac{1}{2}k^2 \int 1s_a^2 \, d\tau = -\frac{1}{2}k^2$.

$\int (1s_a^2/r_a)\, d\tau = (k^3/\pi)\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta_a \, d\theta_a \int_0^{\infty} (e^{-2kr_a}/r_a) r_a^2 \, dr_a =$
$4k^3[e^{-2kr_a}(-r_a/2k - 1/4k^2)]|_0^{\infty} = k$.

$\int (1s_a^2/r_b)\, d\tau = (k^3/\pi)\int (e^{-2kr_a}/r_b)\, d\tau =$
$(2/R)(k^3/\pi)(R^3/8)\int_0^{2\pi} d\phi \int_{-1}^{1}\int_1^{\infty} [e^{-kR(\xi+\eta)}/(\xi-\eta)](\xi^2-\eta^2)\, d\xi\, d\eta =$
$(k^3R^2/2)\int_{-1}^{1} e^{-kR\eta}\int_1^{\infty} e^{-kR\xi}(\xi+\eta)\, d\xi\, d\eta =$
$(k^3R^2/2)\int_{-1}^{1} e^{-kR\eta}[e^{-kR\xi}(-\xi/kR - 1/k^2R^2 - \eta/kR)]|_1^{\infty}\, d\eta =$
$(k^3R^2/2)\int_{-1}^{1} e^{-kR\eta}e^{-kR}(1/kR + 1/k^2R^2 + \eta/kR)\, d\eta =$
$(k^3R^2/2)e^{-kR}[e^{-kR\eta}(-1/k^2R^2 - 1/k^3R^3 - \eta/k^2R^2 - 1/k^3R^3)]|_{-1}^{1} =$
$(k^3R^2/2)e^{-kR}[e^{-kR}(-2/k^2R^2 - 2/k^3R^3) + e^{kR}(2/k^3R^3)] = -e^{-2kR}(k+1/R) + 1/R$

Then $H_{aa} = \int 1s_a \hat{H}_a 1s_a \, d\tau + (k-1)\int (1s_a^2/r_a)\, d\tau - \int (1s_a^2/r_b)\, d\tau$

$H_{aa} = -\frac{1}{2}k^2 + (k-1)k + e^{-2kR}(k+1/R) - 1/R = \frac{1}{2}k^2 - k + e^{-2kR}(k+1/R) - 1/R$

(b) $H_{ab} = H_{ba}^* = H_{ba} = \int 1s_b^* \hat{H} 1s_a \, d\tau = \int 1s_b^* [\hat{H}_a + (k-1)/r_a - 1/r_b] 1s_a \, d\tau$

$H_{ab} = \int 1s_b \hat{H}_a 1s_a \, d\tau + (k-1)\int (1s_b 1s_a/r_a)\, d\tau - \int (1s_b 1s_a/r_b)\, d\tau$.

$\int 1s_b \hat{H}_a 1s_a \, d\tau = -\frac{1}{2}k^2 \int 1s_b 1s_a \, d\tau = -\frac{1}{2}k^2 S_{ab}$

$\int 1s_b 1s_a/r_a \, d\tau = (k^3/\pi)\int (e^{-k(r_a+r_b)}/r_a)\, d\tau =$
$(2/R)(k^3/\pi)(R^3/8)\int_0^{2\pi} d\phi \int_{-1}^{1}\int_1^{\infty} [e^{-kR\xi}/(\xi+\eta)](\xi^2-\eta^2)\, d\xi\, d\eta =$
$(k^3R^2/2)\int_{-1}^{1}\int_1^{\infty} e^{-kR\xi}(\xi-\eta)\, d\xi\, d\eta = (k^3R^2/2)\int_{-1}^{1}[e^{-kR\xi}(-\xi/kR - 1/k^2R^2 + \eta/kR)]|_1^{\infty}\, d\eta =$
$(k^3R^2/2)\int_{-1}^{1} e^{-kR}(1/kR + 1/k^2R^2 - \eta/kR)\, d\eta =$
$(k^3R^2/2)e^{-kR}2(1/kR + 1/k^2R^2) = (k^2R + k)e^{-kR}$

By symmetry (just interchange the labels *a* and *b* in the definite integral)
$\int (1s_b 1s_a/r_b)\, d\tau = \int (1s_b 1s_a/r_a)\, d\tau = (k^2R + k)e^{-kR}$.

So $H_{ab} = \int 1s_b \hat{H}_a 1s_a \, d\tau + (k-1)\int (1s_b 1s_a/r_a)\, d\tau - \int (1s_b 1s_a/r_b)\, d\tau =$
$-\frac{1}{2}k^2 S_{ab} + (k-1)(k^2R+k)e^{-kR} - (k^2R+k)e^{-kR} = -\frac{1}{2}k^2 S_{ab} + (k-2)(k^2R+k)e^{-kR}$.

13.18 (a) Let $t \equiv kR$. Then Eq. (13.63) becomes

$$W_1 = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1+t)e^{-2t} + (k^2-k)(1+t)e^{-t}}{1 + e^{-t}(1 + t + t^2/3)}.$$

The R^{-1} terms in the numerator are not proportional to either *k* or k^2, so we multiply numerator and denominator by $kR \equiv t$ to get

$$W_1 = -\tfrac{1}{2}k^2 + \frac{k^2t - kt - k + k(1+t)e^{-2t} + (k^2-k)(t+t^2)e^{-t}}{t + e^{-t}(t+t^2+t^3/3)} =$$

$$k^2\left(-\tfrac{1}{2} + \frac{t^2 + (t+t^2)e^{-t}}{t + e^{-t}(t+t^2+t^3/3)}\right) + k\frac{-t - 1 + (1+t)e^{-2t} - (t+t^2)e^{-t}}{t + e^{-t}(t+t^2+t^3/3)} \equiv k^2F(t) + kG(t)$$

(b)

$\partial W_1/\partial k = 2kF + k^2(dF/dt)(\partial t/\partial k) + G + k(dG/dt)(\partial t/\partial k) = 2kF + k^2F'R + G + kG'R = 0$

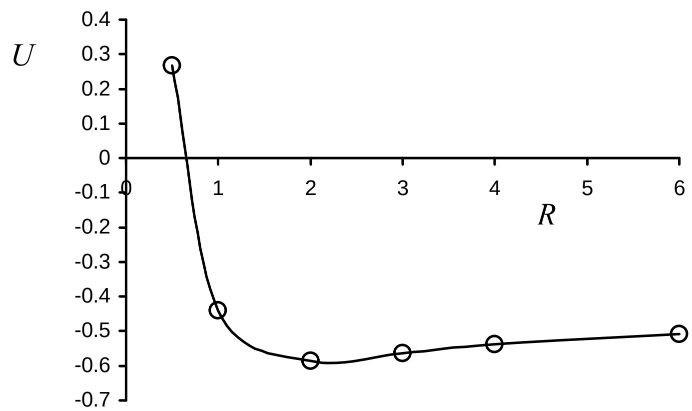
The desired result does not contain R, so we use $t \equiv kR$ to rewrite the last equation as $\partial W_1/\partial k = 2kF + ktF' + G + tG' = 0$ and we get $k = -(G + tG')/(2F + tF')$.

13.19 A C++ program is

```
#include <iostream>
#include <cmath>
using namespace std;
int main()  {
   double r, k, s, a, b, den, t, ex, num, u, umin, kmin;
   label1:
   cout  <<  " Enter R (enter -1 to quit)  ";
   cin  >>  r;
   if (r < 0)
      return 0;
   cout  <<  " Enter initial k  ";
   cin  >>  a;
   cout  <<  " Enter increment in k  ";
   cin  >> s;
   cout  <<  "Enter final k  ";
   cin  >>  b;
   umin = 1000:
   for  (k=a;  k  <=  b;  k=k+s)  {
      t=k*r;
      ex=exp(-k*r);
      num = k*k-k-1/r+(1/r)*(1+t)*ex*ex+k*(k-2)*(1+t)*ex;
      den=1+ex*(1+t+t*t/3);
      u=1/r-k*k/2+num/den;
      if (u < umin)  {
         umin = u;
         kmin = k;
      }
   }
   cout  <<  " R =  "  << r <<  " kmin =  "   << kmin  <<  " U =  "  <<  umin  <<  endl;
   goto label1;
}
```

(If more accuracy is needed, use the k accurate to 0.001 and an increment of 10^{-6} to get k accurate to 0.000001.) The results are

R/bohr	0.5	1	2	3	4	6
k	1.779	1.538	1.239	1.095	1.028	0.995
U/hartree	0.2682	–0.4410	–0.5865	–0.5644	–0.5373	–0.5091



13.20 A C++ program is

```
#include <iostream>
#include <cmath>
using namespace std;
int main()  {
   double ri, dr, rf, ki, dk, kf, umin, r, k, t, ex, num, den, u, rmin, kmin;
   label1:
   cout  <<  " Enter initial R (enter -1 to quit) ";
   cin  >>  ri;
   if (ri < 0)
      return 0;
   cout  <<  " Enter R increment ";
   cin  >> dr;
   cout  <<  " Enter final R ";
   cin  >>  rf;
   cout  <<  " Enter initial k ";
   cin  >> ki;
   cout  <<  " Enter k increment ";
   cin  >>  dk;
   cout  <<  " Enter final k ";
   cin  >> kf;
   umin = 1000;
   for (r = ri; r<= rf; r=r+dr)  {
      for (k=ki; k<=kf; k=k+dr) {
```

```
            t=k*r;
            ex=exp(-k*r);
            num = k*k-k-1/r+(1/r)*(1+t)*ex*ex+k*(k-2)*(1+t)*ex;
            den=1+ex*(1+t+t*t/3);
            u=1/r-k*k/2+num/den;
            if (u < umin)  {
               umin = u;
               kmin = k;
               rmin = r;
            }
         }
      }
      cout << "rmin = " << rmin << " kmin =  " << kmin << " umin = " << umin << endl;
      goto label1;
   }
```

We first have R go from 0.1 to 6 in steps of 0.01 and k go from 0.01 to 3 in steps of 0.01. This gives $R_{\text{min}} = 2.00$ and $k_{\text{min}} = 1.24$. Then we have R go from 1.99 to 2.01 in steps of 0.0001 and k go from 1.23 to 1.25 in steps of 0.0001. The result is $R_{\text{min}} = 2.0033$, $k_{\text{min}} = 1.2380$, and $U_{\text{min}} = -0.58651$.

13.21 **(a)** If the usual convention of having the z axis be the internuclear axis is followed, the cross-section plane is taken as the xz (or the yz) plane (and not the xy plane). In Mathcad the initial value 1.05 for k works for most of the R values and a Mathcad sheet is shown on the next page.

(b) The required statements are shown below the figures on the Mathcad sheet. In some versions of Mathcad the initial guesses for k and R must be rather close to the optimum values in order to obtain good values for the optimum values. The Minimize function works much better than trying to make both derivatives zero. If one removes the dU/dk = 0 and dU/dR = 0 statements after Given and changes Find(k,R) to Minimize(U,R,k), one gets the accurate values k = 1.2380, R = 2.0033, which agree with the results given by the Excel Solver.

13.22 If we replace R:=3.8 – FRAME/10 by R:= 10 and add k = below the root statement, we get the optimum k for R = 10. One then changes the R value. (If a converged result is not obtained at a particular R, one changes the initial k guess from 1.05 to some other value.) Optimum k values found for the bonding and antibonding MO are

R/bohrs	0.1	1	2	2.5	4	6	10
k_{bonding}	1.9799	1.5379	1.2387	1.1537	1.0283	0.9951	0.9991
$k_{\text{antibonding}}$	0.4199	0.6581	0.9004	0.9621	1.0158	1.0105	1.0009

H2+ MOs, b = 1 for bonding, b = -1 for antibonding

$b := 1$

$$U(R,k) := \frac{1}{R} - 0.5\cdot k^2 + \frac{k^2 - k - R^{-1} + R^{-1}\cdot(1 + k\cdot R)\cdot\exp(-2\cdot k\cdot R) + b\cdot k\cdot(k-2)\cdot(1 + k\cdot R)\cdot\exp(-k\cdot R)}{1 + b\cdot\exp(-k\cdot R)\cdot\left(1 + k\cdot R + k^2\cdot\frac{R^2}{3}\right)}$$

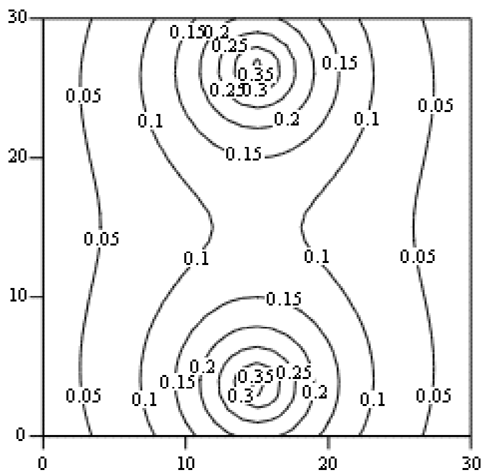
$R := 3.8 - \frac{FRAME}{10}$ $\quad k := 1.05$

$k := \mathrm{root}\left(\frac{d}{dk}U(R,k), k\right)$

$N := 30 \quad i := 0, 1 .. N \quad j := 0, 1 .. N \quad y_i := -2.5 + \frac{i}{6} \quad z_j := -2.5 + \frac{j}{6}$

$$\mathrm{phi}(y,z) := k^{1.5}\cdot\pi^{-0.5}\cdot\frac{\exp\left[-k\cdot\left[y^2 + (z + 0.5\cdot R)^2\right]^{0.5}\right] + b\cdot\exp\left[-k\cdot\left[y^2 + (z - 0.5\cdot R)^2\right]^{0.5}\right]}{\left[2 + b\cdot 2\cdot\exp(-k\cdot R)\cdot\left(1 + k\cdot R + k^2\cdot R^2\cdot 3^{-1}\right)\right]^{0.5}}$$

$M_{i,j} := \mathrm{phi}(y_i, z_j)$



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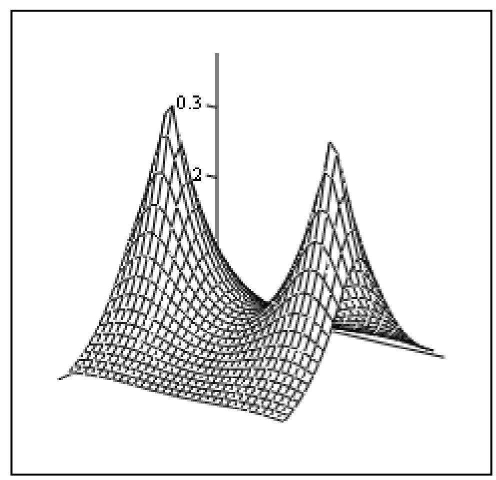


M

$b := 1 \quad k := 1.2 \qquad R := 2.$

$\frac{d}{dk}U(R,k) = -0.044 \qquad \frac{d}{dR}U(R,k) = -9.268\times 10^{-3}$

Given

$k > 0 \quad R > 0 \qquad R < 4 \qquad \frac{d}{dk}U(R,k) = 0 \qquad \frac{d}{dR}U(R,k) = 0$

$\begin{pmatrix} k \\ R \end{pmatrix} := \mathrm{Find}(k,R)$

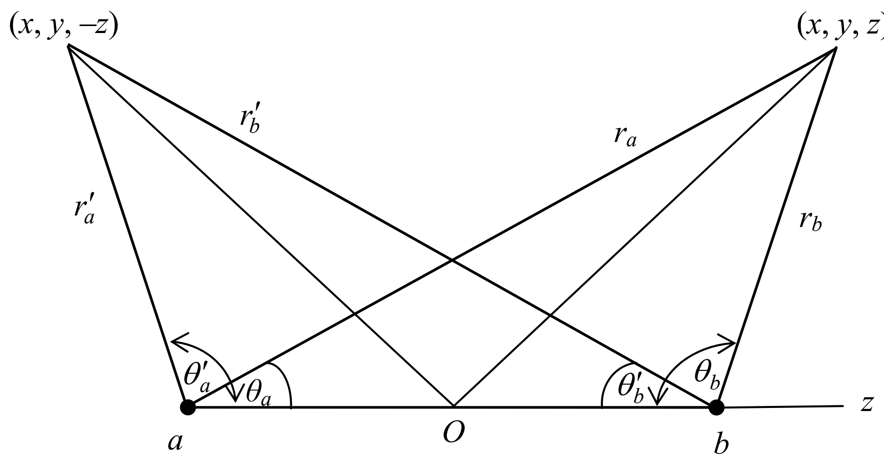
$k = 1.2348 \qquad R = 2.01933$

$\frac{d}{dk}U(R,k) = 2.5113827\times 10^{-8} \qquad \frac{d}{dR}U(R,k) = 1.47\times 10^{-3}$

13.23 The Solver is used to minimize $1/R$ plus (13.63) for each of the desired R values and for each choice of sign in (13.63); the constraint $k \geq 0.01$ is included. The results are

R	0.1	1	2	2.5	4	6	10
k_1	1.9799	1.5379	1.2387	1.1537	1.0283	0.9951	0.9991
U_1	8.02179	–0.44100	–0.58651	–0.57876	–0.53733	–0.50908	–0.50030
k_2	0.4199	0.6581	0.9004	0.9620	1.0158	1.0105	1.0009
U_2	9.58692	0.45129	–0.16581	–0.29131	–0.44500	–0.49007	–0.49970

13.24 The figure below shows that $r_b' = r_a$, $r_a' = r_b$, $\theta_b' = \theta_a$, $\theta_a' = \theta_b$, $\phi' = \phi$, where the coordinate systems are as in Fig. 13.10.



13.25 **(a)** Formation of Li_2^+ from the Li_2 ground-state electron configuration $KK(\sigma_g 2s)^2$ removes an electron from the bonding $\sigma_g 2s$ MO, thereby reducing the bond order, so we expect Li_2 to have the greater D_e. (Actually, D_e of Li_2 is 1.06 eV, less than the 1.30 eV D_e of Li_2^+. The 2.67 Å R_e of Li_2 is, as expected, less than the 3.11 Å R_e of Li_2^+.)

(b) Formation of C_2^+ from the C_2 ground-state electron configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4$ removes an electron from the bonding $\pi_u 2p$ MO, thereby reducing the bond order, so we expect C_2 to have the greater D_e.

(c) Formation of O_2^+ from the O_2 ground-state electron configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\ (\pi_g^* 2p)^2$ removes an electron from the antibonding $\pi_g^* 2p$ MO, thereby increasing the bond order, so we expect O_2^+ to have the greater D_e.

(d) Formation of F_2^+ from the F_2 ground-state electron configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\ (\pi_g^* 2p)^4$ removes an electron from the antibonding $\pi_g^* 2p$ MO, thereby increasing the bond order, so we expect F_2^+ to have the greater D_e.

13.26 **(a)** The ground-state electron configuration will resemble that of O_2 and will be $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)^2$. There are two unpaired electrons in the unfilled $\pi_g^* 3p$ shell. With four more bonding electrons than antibonding electrons, the bond order is 2.

(b) Removal of the highest-energy electron from the answer in part (a) gives the electron configuration as $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)$. With five more bonding electrons than antibonding electrons, the bond order is 2.5. There is one unpaired electron.

(c) Adding an electron to the incompletely filled shell in part (a) gives the electron configuration as $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)^3$. With three more bonding electrons than antibonding electrons, the bond order is 1.5. There is one unpaired electron.

(d) The N_2 configuration is $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$ and removal of an electron gives $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)$. The bond order is 2.5. There is one unpaired electron $(S = \frac{1}{2})$.

(e) Addition of an electron to the N_2 configuration gives the ground-state electron configuration as $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2\ (\pi_g^* 2p)$. As in part (b), there is one unpaired electron and the bond order is 2.5.

(f) Removal of an electron from the F_2 configuration gives the ground-state electron configuration as $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\ (\pi_g^* 2p)^3$. As in part (c), there is one unpaired electron and the bond order is 1.5.

(g) Addition of an electron to the F_2 configuration gives the ground-state electron configuration as $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\ (\pi_g^* 2p)^4(\sigma_u^* 2p)$. There is one unpaired electron and the bond order is $\frac{1}{2}$.

(h) Removal of an electron from the Ne_2 configuration gives the ground-state electron configuration as $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\ (\pi_g^* 2p)^4(\sigma_u^* 2p)$. As in part (g), there is one unpaired electron and the bond order is $\frac{1}{2}$.

(i) Removal of an electron from the Na_2 configuration $KKLL(\sigma_g 3s)^2$ gives $KKLL(\sigma_g 3s)$. There is one unpaired electron and the bond order is $\frac{1}{2}$.

(j) Addition of an electron to the Na_2 configuration gives $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)$. There is one unpaired electron and the bond order is $\frac{1}{2}$.

(k) Addition of an electron to the H_2 configuration gives $(\sigma_g 1s)^2(\sigma_u^* 1s)$. One unpaired electron; bond order $\frac{1}{2}$.

(l) Configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^3$; one unpaired electron; bond order 1.5.

(m) Configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4$; no unpaired electrons; bond order 2.

(n) Configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)$; one unpaired electron; bond order 2.5.

13.27 **(a)** For $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)^2$ there are two unpaired electrons in the unfilled $\pi_g^* 3p$ shell. By Hund's rule, the lowest of the three terms listed in Table 13.3 for a π^2 configuration is $^3\Sigma_g^-$.

(b) For $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)$ there is one unpaired electron, which is a π electron, and the term is $^2\Pi_g$.

(c) For $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g^* 3p)^3$ the π^3 configuration has the same term as a π configuration, namely $^2\Pi_g$.

(d) We have $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)$. As noted in Sec. 13.8, a single σ electron corresponds to a Σ^+ term, so the ground term is $^2\Sigma_g^+$.

(e) We have $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2(\pi_g^* 2p)$. As in part (b), the ground term is $^2\Pi_g$.

(f) We have $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^3$. As in part (c), the ground term is $^2\Pi_g$.

(g) We have $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4(\sigma_u^* 2p)$. The ground term is $^2\Sigma_u^+$, since the only unfilled shell has one electron in a u orbital.

(h) For $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4(\sigma_u^* 2p)$, the ground term is $^2\Sigma_u^+$, as in (g).

(i) For $KKLL(\sigma_g 3s)$, the ground term is $^2\Sigma_g^+$.

(j) For $KKLL(\sigma_g 3s)^2(\sigma_u^* 3s)$, the ground term is $^2\Sigma_u^+$.

(k) For $(\sigma_g 1s)^2(\sigma_u^* 1s)$, the ground term is $^2\Sigma_u^+$.

(l) For $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^3$, the ground term is $^2\Pi_u$.

(m) For $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4$ the ground term is ${}^1\Sigma_g^+$.

(n) For $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)$ the ground term is ${}^2\Sigma_g^+$.

13.28 **(a)** A Σ term has Λ = 0 and there is no orbital degeneracy. For a singlet term, $S = 0$ and there is no spin degeneracy. Hence a ${}^1\Sigma^-$ term has one wave function.

(b) With $S = 1$, there are three spin functions and a ${}^3\Sigma^+$ term has three wave functions.

(c) With $S = 1$, there are three spin functions; with $\Lambda \neq 0$, there is a two-fold degeneracy due to the two values (+Λ and –Λ) of M_L. Hence there are 3(2) = 6 wave functions for a ${}^3\Pi$ term.

(d) 1(2) = 2.

(e) 6(2) = 12.

13.29 The levels of a term are labeled by the value of Λ + Σ, which takes on the values Λ + S, Λ + S – 1, …, Λ – S.

(a) A ${}^1\Sigma^-$ term has Λ = 0 and $S = 0$ and has only one level. As noted in Sec. 13.8 , for a Σ term, the spin–orbit interaction is negligible and one does not put a subscript on the level, which is written as ${}^1\Sigma^-$.

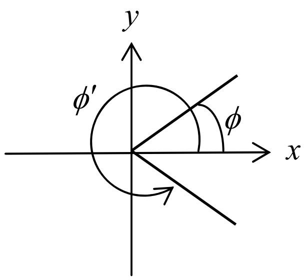
(b) For a Σ term, the spin–orbit interaction is negligible and the level is ${}^3\Sigma^+$.

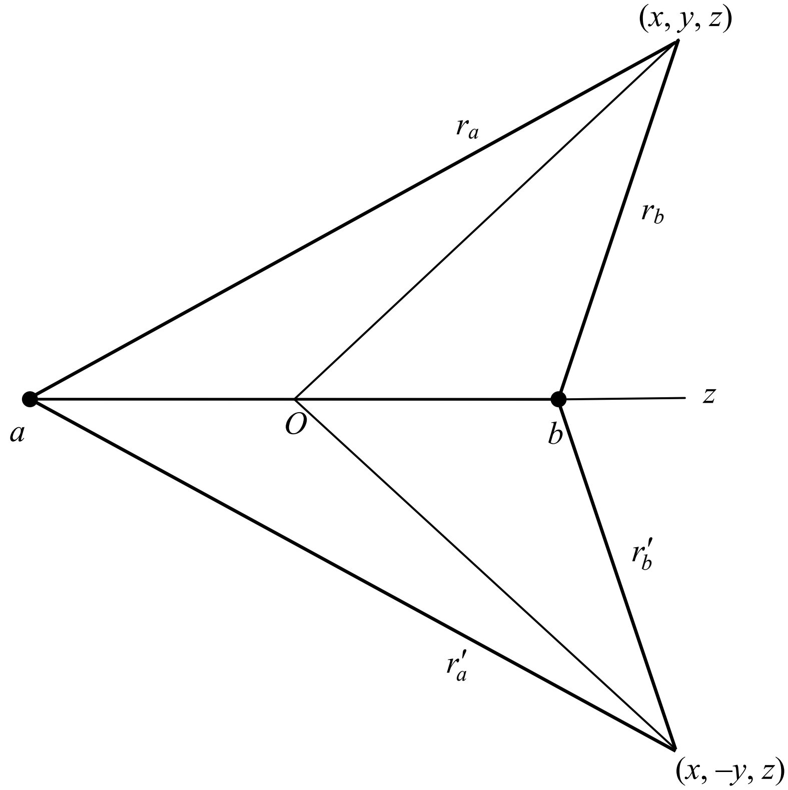
(c) $S = 1$, Λ = 1, and the levels are ${}^3\Pi_2$, ${}^3\Pi_1$, ${}^3\Pi_0$.

(d) $S = 0$, Λ = 3, and the level is ${}^1\Phi_3$.

(e) $S = 5/2$, Λ = 2, and the levels are ${}^6\Delta_{9/2}$, ${}^6\Delta_{7/2}$, ${}^6\Delta_{5/2}$, ${}^6\Delta_{3/2}$, ${}^6\Delta_{1/2}$, ${}^6\Delta_{-1/2}$.

13.30 As the figure on the next page shows, reflection in a plane containing the internuclear (z) axis does not change r_a or r_b and changes the angle of rotation ϕ about the z axis to $2\pi - \phi$, which is equivalent to changing it to $-\phi$. [The point (x, y, z) in the figure lies in front of the plane of the paper.] Each π molecular orbital (one-electron wave function) in (13.89) is an eigenfunction of $\hat{L}_z$ and so has the form $f(\xi, \eta)(2\pi)^{-1/2}e^{im\phi}$. Since r_a and r_b are unchanged by the reflection, the confocal elliptic coordinates ξ and η in (13.33) are unchanged by the reflection and f is unchanged by the reflection. The phi factor is changed by the reflection to $(2\pi)^{-1/2}e^{-im\phi}$. Therefore the $\hat{\sigma}(xz)$ reflection changes the MO π_{+1} to π_{-1} and vice versa. The first function in (13.89) is changed by $\hat{\sigma}(xz)$ to $\pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) + \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1)$, which is the same as the original function. The second function in (13.89) is changed by $\hat{\sigma}(xz)$ to $\pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) - \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1)$, which is –1 times the original function. Similarly for the third and fourth functions.





13.31 As shown in Prob. 13.30, $\hat{\sigma}_{\text{v}}(xz)$ converts ϕ to $-\phi$ and leaves ξ and η unchanged. So $[\hat{L}_z, \hat{O}_{\sigma_{\text{v}}(xz)}]e^{im\phi} = -i\hbar(\partial/\partial\phi)\hat{O}_{\sigma_{\text{v}}(xz)}e^{im\phi} + i\hbar\hat{O}_{\sigma_{\text{v}}(xz)}(\partial/\partial\phi)e^{im\phi} =$ $-i\hbar(\partial/\partial\phi)e^{-im\phi} + i\hbar\hat{O}_{\sigma_{\upsilon}(xz)}ime^{im\phi} = -m\hbar e^{-im\phi} - m\hbar e^{-im\phi} \neq 0$.

13.32 The g means the wave function is an even function; that is, ψ is unchanged on inversion of the spatial coordinates of all the electrons. From (13.78), inversion interchanges r_a and r_b and increases ϕ by π. Interchange of r_a and r_b changes η in (13.33) to $-\eta$. Replacement of η_1 and η_2 by their negatives in this trial function multiplies it by $(-1)^{j+k}$. Therefore $j+k$ must be an even number to ensure that the trial function is even. The plus sign means that the wave function is unchanged by a $\hat{\sigma}_{\text{v}}(xz)$ reflection. This reflection does not affect r_a or r_b (Prob. 13.30) and gives no restrictions on m, n, j, p.

13.33 **(a)** $S_{12} = \int f_1^* f_2 \, d\text{v} = \int\int 1s_a(1)1s_b(2)1s_a(2)1s_b(1)\, d\text{v}_1\, d\text{v}_2$

$S_{12} = \langle 1s_a(1) \mid 1s_b(1)\rangle\langle 1s_a(2) \mid 1s_b(2)\rangle = S_{ab}^2$

(b) $H_{11} = \langle 1s_a(1)1s_b(2)|\hat{H}_a(1) + \hat{H}_b(2) + \hat{H}'|1s_a(1)1s_b(2)\rangle$ For the $\hat{H}_a(1)$ integral, we have $\langle 1s_a(1)1s_b(2)|\hat{H}_a(1)|1s_a(1)1s_b(2)\rangle = \langle 1s_a(1)|\hat{H}_a(1)|1s_a(1)\rangle\langle 1s_b(2) \mid 1s_b(2)\rangle$. The Heitler–London calculation does not have an effective nuclear charge in the $1s$ function. Hence

$1s_a(1)$ is an eigenfunction of $\hat{H}_a(1)$ with eigenvalue $-\frac{1}{2}$ hartree, the hydrogen-atom ground-state energy. The $1s$ function is normalized, and we conclude that the $\hat{H}_a(1)$ integral equals $-\frac{1}{2}$ in atomic units. Similarly, the $\hat{H}_b(2)$ integral equals $-\frac{1}{2}$. Defining $Q \equiv \langle 1s_a(1)1s_b(2)|\hat{H}'|1s_a(1)1s_b(2)\rangle$, we have $H_{11} = Q-1$.

(c) $H_{12} = H_{21} = \langle 1s_a(2)1s_b(1)|\hat{H}_a(1)+\hat{H}_b(2)+\hat{H}'|1s_a(1)1s_b(2)\rangle$. The $\hat{H}_a(1)$ integral is $\langle 1s_a(2)\,|\,1s_b(2)\rangle\langle 1s_b(1)|\hat{H}_a(1)|1s_a(1)\rangle = \langle 1s_a(2)\,|\,1s_b(2)\rangle\langle 1s_b(1)|-\frac{1}{2}\cdot 1s_a(1)\rangle = -\frac{1}{2}S_{ab}^2$. Similarly, the $\hat{H}_b(2)$ integral equals $-\frac{1}{2}S_{ab}^2$. Defining A as $A \equiv \langle 1s_a(2)1s_b(1)|\hat{H}'|1s_a(1)1s_b(2)\rangle$, we have $H_{12} = A - S_{ab}^2$. Substitution in (13.98) gives

$$W_1 = \frac{H_{11}+H_{12}}{1+S_{12}} = \frac{Q-1+A-S_{ab}^2}{1+S_{ab}^2} = -1+\frac{Q+A}{1+S_{ab}^2}$$

$$W_2 = \frac{H_{11}-H_{12}}{1-S_{12}} = \frac{Q-1-A+S_{ab}^2}{1-S_{ab}^2} = -1+\frac{Q-A}{1-S_{ab}^2}$$

13.34 Addition of column 1 to column 3 and column 2 to column 4 (Theorem V of Sec. 8.5) changes (13.112) to $|(1s_a+1s_b)\overline{(1s_a+1s_b)}\,2(1s_a)\,2(\overline{1s_a})| = 4|(1s_a+1s_b)\overline{(1s_a+1s_b)}1s_a\overline{1s_a}|$, where Theorem IV was used. Subtracting column 3 from column 1 and column 4 from column 2 (Theorem V), we get $4|1s_b\overline{1s_b}1s_a\overline{1s_a}|$. Interchange of columns 1 and 3 and of columns 2 and 4 multiplies the determinant by $(-1)^2$ (Theorem VI), so we have shown that the determinant equals $4|1s_a\overline{1s_a}1s_b\overline{1s_b}|$.

13.35 For each of the AO pairs $(2p_{xa},\ 2p_{xb})$, $(2p_{ya},\ 2p_{yb})$, $(2p_{za},\ 2p_{zb})$, one AO will get spin function α and the other will have spin β. Since there are two choices for the spin assignment for each of the three pairs, there are $2^3 = 8$ possible determinants. In addition to D_1 and D_2 in (13.120) and (13.121), the other determinants are

$D_3 = |\cdots 2p_{xa}\overline{2p_{xb}}\,\overline{2p_{ya}}2p_{yb}2p_{za}\overline{2p_{zb}}\,|$ with coefficient –1;

$D_4 = |\cdots 2p_{xa}\overline{2p_{xb}}2p_{ya}\overline{2p_{yb}}\,\overline{2p_{za}}2p_{zb}\,|$ with coefficient –1;

$D_5 = |\cdots \overline{2p_{xa}}2p_{xb}\overline{2p_{ya}}2p_{yb}2p_{za}\overline{2p_{zb}}\,|$ with coefficient +1;

$D_6 = |\cdots \overline{2p_{xa}}2p_{xb}2p_{ya}\overline{2p_{yb}}\,\overline{2p_{za}}2p_{zb}\,|$ with coefficient +1;

$D_7 = |\cdots 2p_{xa}\overline{2p_{xb}}\,\overline{2p_{ya}}2p_{yb}\overline{2p_{za}}2p_{zb}\,|$ with coefficient +1;

$D_8 = |\cdots \overline{2p_{xa}}2p_{xb}\overline{2p_{ya}}2p_{yb}\overline{2p_{za}}2p_{zb}\,|$ with coefficient –1 (three interchanges).

13.36 **(a)** The $b^3\Sigma_u^+$ term is the lowest triplet term (Fig. 13.19). The Heitler–London VB functions for this term are (13.101). The spatial part of the MO function given in

Sec. 13.13 for this term is

$2^{-1/2}[1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] \approx$

$2^{-1/2}\{N[1s_a(1) + 1s_b(1)]N'[1s_a(2) - 1s_b(2)] - N[1s_a(2) + 1s_b(2)]N'[1s_a(1) - 1s_b(1)]\} =$

$2^{-1/2}NN'2[1s_b(1)1s_a(2) - 1s_a(1)1s_b(2)] = 2^{-1/2}(1 - S_{ab}^2)^{-1/2}[1s_b(1)1s_a(2) - 1s_a(1)1s_b(2)]$,

since $N = 2^{-1/2}(1 + S_{ab})^{-1/2}$ and $N' = 2^{-1/2}(1 - S_{ab})^{-1/2}$ [Eqs. (13.57) and (13.58)]. This spatial function is –1 times the VB spatial function in (13.101).

(b) The $B^1\Sigma_u^+$ MO spatial function in Sec. 13.13 is

$2^{-1/2}[1\sigma_g(1)1\sigma_u(2) + 1\sigma_g(2)1\sigma_u(1)] \approx$

$2^{-1/2}\{N[1s_a(1) + 1s_b(1)]N'[1s_a(2) - 1s_b(2)] + N[1s_a(2) + 1s_b(2)]N'[1s_a(1) - 1s_b(1)]\} =$

$2^{-1/2}NN'2[1s_a(1)1s_a(2) - 1s_b(1)1s_b(2)]$, which has only ionic terms.

13.37 **(a)** From (13.124), $\langle 1s \mid 2s_\perp\rangle = (1 - \langle 1s \mid 2s\rangle^2)^{-1/2}\langle 1s \mid [2s - \langle 1s \mid 2s\rangle 1s]\rangle =$

$(1 - \langle 1s \mid 2s\rangle^2)^{-1/2}[\langle 1s \mid 2s\rangle - \langle 1s \mid 2s\rangle\langle 1s \mid 1s\rangle] = 0$, since $\langle 1s \mid 1s\rangle = 1$. Also

$\langle 2s_\perp \mid 2s_\perp\rangle = (1 - \langle 1s \mid 2s\rangle^2)^{-1}\langle [2s - \langle 1s \mid 2s\rangle 1s] \mid [2s - \langle 1s \mid 2s\rangle 1s]\rangle =$

$(1 - \langle 1s \mid 2s\rangle^2)^{-1}[\langle 2s \mid 2s\rangle - 2\langle 1s \mid 2s\rangle\langle 1s \mid 2s\rangle + \langle 1s \mid 2s\rangle^2\langle 1s \mid 1s\rangle] =$

$(1 - \langle 1s \mid 2s\rangle^2)^{-1}[1 - \langle 1s \mid 2s\rangle^2] = 1$, since the $1s$ and $2s$ functions are real.

(b) $\phi = a(1s) + b(2s) + \cdots = c(1s) + d(2s_\perp) + \cdots = c(1s) + d[(1 - S^2)^{-1/2}(2s - S \cdot 1s)]$.

Equating the coefficients of the $1s$ orbitals and equating the coefficients of the $2s$ orbitals, we get $a = c - S(1 - S^2)^{-1/2}d$ and $b = (1 - S^2)^{-1/2}d$. So $d = (1 - S^2)^{1/2}b$ and $c = a + Sb$.

(c) From (11.14) and (7.27), $\langle 1s \mid 2s\rangle = (2\zeta_1)^{3/2}2^{-1/2}(2\zeta_2)^{5/2}(24)^{-1/2}\int_0^\infty e^{-(\zeta_1+\zeta_2)r}r^3\,dr =$

$4 \cdot 3^{-1/2}\zeta_1^{3/2}\zeta_2^{5/2}[6/(\zeta_1 + \zeta_2)^4] = 24\zeta_1^{3/2}\zeta_2^{5/2}/3^{1/2}(\zeta_1 + \zeta_2)^4$.

13.38 We will assume that the s and p valence AOs of each atom produce valence MOs whose pattern matches that in Fig. 13.17 and in the table near the beginning of Sec. 13.15.. Thus we assume the valence MOs of each molecule to be $\sigma\sigma\pi\sigma\pi\sigma$.

(a) The molecule has 10 valence electrons and filling in these valence MOs, we get a ground-state valence-electron configuration of $\sigma^2\sigma^2\pi^4\sigma^2$. There are no unpaired electrons and the filled shells give a $^1\Sigma^+$ ground term.

(b) The 8 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4$ with no unpaired electrons and a $^1\Sigma^+$ ground term if the MO order given in the table near the beginning of Sec. 13.15 is used. In fact, the ground term is actually $^3\Pi$. From Table 13.3, this suggests a $\pi^3\sigma$ configuration, perhaps $\sigma^2\sigma^2\pi^3\sigma$.

(c) The 8 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4$ with no unpaired electrons and a $^1\Sigma^+$ ground term.

(d) The 9 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma$ with one unpaired electron and a ${}^2\Sigma^+$ ground term.

(e) The 11 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma^2\pi$ with one unpaired electron and a ${}^2\Pi$ term.

(f) The 11 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma^2\pi$ with one unpaired electron and a ${}^2\Pi$ term.

(g) The 9 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma$ with one unpaired electron and a ${}^2\Sigma^+$ ground term.

(h) The 12 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma^2\pi^2$ with 2 unpaired electrons and a ${}^3\Sigma^-$ ground term (Table 13.3).

(i) The 13 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma^2\pi^3$ with one unpaired electron and a ${}^2\Pi$ term.

(j) The 14 valence electrons give the valence configuration $\sigma^2\sigma^2\pi^4\sigma^2\pi^4$ with no unpaired electrons and a ${}^1\Sigma^+$ term.

13.39 **(a)** Let $A\phi_a + B\phi_b$ be the antibonding heteronuclear MO. Then orthogonality gives
$0 = \langle c_1\phi_a + c_2\phi_b \mid A\phi_a + B\phi_b\rangle = c_1A\langle\phi_a \mid \phi_a\rangle + (c_1B + c_2A)\langle\phi_a \mid \phi_b\rangle + c_2B\langle\phi_b \mid \phi_b\rangle =$
$c_1A + (c_1B + c_2A)S_{ab} + c_2B = (c_1 + S_{ab}c_2)A + (c_2 + S_{ab}c_1)B$, so
$B = -(c_1 + S_{ab}c_2)A/(c_2 + S_{ab}c_1)$ and $A\phi_a + B\phi_b = A\phi_a - [(c_1 + S_{ab}c_2)A/(c_2 + S_{ab}c_1)]\phi_b =$
$[A/(c_2 + S_{ab}c_1)][(c_2 + S_{ab}c_1)\phi_a - (c_1 + S_{ab}c_2)\phi_b] = N''[(c_2 + S_{ab}c_1)\phi_a - (c_1 + S_{ab}c_2)\phi_b]$,
where $N'' \equiv A/(c_2 + S_{ab}c_1)$ and we assumed the orbitals are real, so $\langle\phi_a \mid \phi_b\rangle = \langle\phi_b \mid \phi_a\rangle$.
We can get the homonuclear result by setting $c_1 = c_2$ in the heteronuclear result. This gives the antibonding homonuclear MO as $N''(c_1 + S_{ab}c_1)(\phi_a - \phi_b) = N'(\phi_a - \phi_b)$, where $N' \equiv N''(c_1 + S_{ab}c_1)$.

(b) $\langle\phi_1 \mid \phi_2\rangle = \frac{1}{2}(1 - S_{ab}^2)^{-1/2}\langle 1s_a + 1s_b \mid 1s_a - 1s_b\rangle =$
$\frac{1}{2}(1 - S_{ab}^2)^{-1/2}[\langle 1s_a \mid 1s_a\rangle - \langle 1s_a \mid 1s_b\rangle + \langle 1s_b \mid 1s_a\rangle - \langle 1s_b \mid 1s_b\rangle] =$
$\frac{1}{2}(1 - S_{ab}^2)^{-1/2}(1 - S_{ab} + S_{ab} - 1) = 0$.

13.40 The simple VB method would be more useful since it gives the correct behavior when a bond is broken, whereas the simple MO wave function goes to the wrong limit on dissociation.

13.41 The zero level of potential energy corresponds to all nuclei and electrons infinitely far from one another. To reach this state, we first start with the nuclei in F_2 at a distance R_e apart and dissociate the molecule to two ground-state F atoms. This requires an energy $D_e = 1.66$ eV. Then we remove all the electrons in each F atom to infinity, one at a time.

The energy needed to do this in one F atom is the sum of the first, second,…, ninth ionization energies of F and the publication mentioned a couple of paragraphs before Eq. (10.32) gives this sum as 2715.795 eV. Thus
$U(R_e) = -[1.66 + 2(2715.795)]\text{ eV} = -5433.25\text{ eV} = -199.668E_\text{h}$.

13.42 **(a)** $N[1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$.

(b) $N[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

13.43 **(a)** False. For hydrogenlike functions, $|2p_{-1}| = |2p_1|$, but these states have different $\hat{L}_z$ eigenvalues and are different states.

(b) True. This is a one-electron system and the Hartree–Fock method gives the exact wave function.

(c) False. See Sec. 13.11.

Chapter 14

Theorems of Molecular Quantum Mechanics

14.1 $\rho_{\mathrm{VB}} = 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\phi_{\mathrm{VB}}(x, y, z, x_2, y_2, z_2)|^2 \, dx_2 \, dy_2 \, dz_2 =$

$2\cdot\frac{1}{2}(1+S_{ab}^2)^{-1}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |1s_a 1s_b(2) + 1s_a(2)1s_b|^2 \, dx_2 \, dy_2 \, dz_2 =$

$(1+S_{ab}^2)^{-1}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\{1s_a^2[1s_b(2)]^2 + [1s_a(2)]^2 1s_b^2 + 2\cdot 1s_a 1s_b 1s_a(2) 1s_b(2)\} \, dx_2 \, dy_2 \, dz_2 =$

$(1+S_{ab}^2)^{-1}[1s_a^2 + 1s_b^2 + 2\cdot 1s_a 1s_b S_{ab}]$, since $1s_b(2)$ and $1s_a(2)$ are normalized and $S_{ab} = \int 1s_a(2) 1s_b(2) \, d\upsilon_2$. (The notations $1s_a$ and $1s_b$ denote functions whose variables are x, y, z.)

$\rho_{\mathrm{MO}} = 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\phi_{\mathrm{MO}}(x, y, z, x_2, y_2, z_2)|^2 \, dx_2 \, dy_2 \, dz_2 =$

$2\cdot\frac{1}{4}(1+S_{ab})^{-2}\int (1s_a + 1s_b)^2 [1s_a(2) + 1s_b(2)]^2 \, d\upsilon_2 =$

$\frac{1}{2}(1+S_{ab})^{-2}(1s_a^2 + 1s_b^2 + 2\cdot 1s_a 1s_b)\int\{[1s_a(2)]^2 + [1s_b(2)]^2 + 2\cdot 1s_a(2) 1s_b(2)\} \, d\upsilon_2 =$

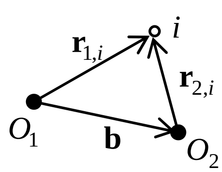
$\frac{1}{2}(1+S_{ab})^{-2}(1s_a^2 + 1s_b^2 + 2\cdot 1s_a 1s_b)(2 + 2S_{ab}) = (1+S_{ab})^{-1}(1s_a^2 + 1s_b^2 + 2\cdot 1s_a 1s_b)$.

14.2 At the midpoint (mp) between the nuclei, we have $r_a = r_b$, $e^{-r_a} = e^{-r_b}$, and $1s_a = 1s_b$. So at the midpoint, $\rho_{\mathrm{VB,mp}} = 2\cdot 1s_a^2(1+S_{ab})/(1+S_{ab}^2)$ and $\rho_{\mathrm{MO,mp}} = 4\cdot 1s_a^2/(1+S_{ab})$. Then

$$\rho_{\mathrm{MO,mp}} - \rho_{\mathrm{VB,mp}} = \frac{(1+S_{ab}^2)(4\cdot 1s_a^2) - 2\cdot 1s_a^2(1+S_{ab})^2}{(1+S_{ab})(1+S_{ab}^2)} = \frac{2\cdot 1s_a^2(1 - 2S_{ab} + S_{ab}^2)}{(1+S_{ab})(1+S_{ab}^2)} =$$

$\dfrac{2\cdot 1s_a^2(1-S_{ab})^2}{(1+S_{ab})(1+S_{ab}^2)}$. S_{ab} is positive for $R < \infty$, and $\rho_{\mathrm{MO,mp}} - \rho_{\mathrm{VB,mp}} > 0$.

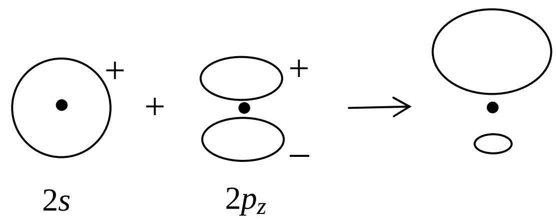
14.3 Let O_1 and O_2 be two different origins, with **b** being the vector joining them. The figure shows that $\mathbf{r}_{1,i} = \mathbf{b} + \mathbf{r}_{2,i}$. So $\sum_i Q_i \mathbf{r}_{1,i} = \sum_i Q_i(\mathbf{b} + \mathbf{r}_{2,i}) = \mathbf{b}\sum_i Q_i + \sum_i Q_i \mathbf{r}_{2,i} = \sum_i Q_i \mathbf{r}_{2,i}$, since $\sum_i Q_i = 0$.



14.4 **(a)** As noted preceding Eq. (14.19), the permanent electric dipole moment is zero for states of definite parity. Each stationary state of a many-electron atom has a definite parity that is determined by the sum of the *l* values of the spherical-harmonic factors in the wave function (Sec. 11.5). States arising from an electron configuration have even parity if $\sum_i l_i$ is even, odd parity if $\sum_i l_i$ is odd.

(b) For a one-electron atom, states with the same *n* values but different *l* values have the same energy, and a stationary state that contains contributions from spherical harmonics of different parity does not have a definite parity and need not have zero dipole moment.

(c) Two of the correct H-atom-in-an-electric-field zeroth-order functions for Prob. 9.23 are $2^{-1/2}(2s \pm 2p_0)$, which mix the even function 2*s* with the odd function $2p_z$. These two zeroth-order functions do not have definite parity. As the diagram shows, these states have an unsymmetrical distribution of electric charge and have a dipole moment.



14.5 Consider the process $\text{NaCl} \xrightarrow{(a)} \text{Na}^+ + \text{Cl}^- \xrightarrow{(b)} \text{Na} + \text{Cl}$. In step (a), an ionic NaCl molecule dissociates to ions. We can estimate ΔE_a as minus the potential energy of the ions with their centers separated by R_e. From (6.58), $E_a = e^2/4\pi\varepsilon_0 R_e =$

$$\frac{(1.6022\times 10^{-19}\ \text{C})^2}{4\pi(8.854\times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})(2.36\times 10^{-10}\ \text{m})} = (9.78\times 10^{-19}\ \text{J})\frac{1\ \text{eV}}{1.6022\times 10^{-19}\ \text{J}} = 6.10\ \text{eV}$$

Step b involves the reverse of the ionization of Na and the addition of an electron to Cl. So $\Delta E_b = -5.14\ \text{eV} + 3.61\ \text{eV} = -1.53\ \text{eV}$. Thus we estimate $D_e \approx \Delta E_a + \Delta E_b = 4.57$ eV.

With the origin at the center of one ion, the dipole moment is calculated from (14.9) as $\mu \approx eR_e = (4.803\times 10^{-10}\ \text{statC})(2.36\times 10^{-8}\ \text{cm}) = 11.3\times 10^{-18}\ \text{statC cm} =$ 11.3 D.

14.6 The sum of Hermitian operators is Hermitian. The kinetic-energy operator and the potential-energy operator in $\hat{H}_{\text{core}}$ were proved to be Hermitian in Sec. 7.2 and Prob. 7.7. Thus we only need to prove that the Coulomb and exchange operators are Hermitian. We must show that $\int [f(1)]^* \hat{J}_j(1) g(1)\, dv_1 = \int g(1)[\hat{J}_j(1) f(1)]^* dv_1$ (Eq. 1). From (14.28), the left side of Eq. 1 is $\int [f(1)]^* g(1) \int r_{12}^{-1} |\phi_j(2)|^2\, dv_2\, dv_1$. The right side of Eq. 1 is $\int g(1)[f(1)\int r_{12}^{-1} |\phi_j(2)|^2\, dv_2]^* dv_1 = \int g(1)[f(1)]^* \int r_{12}^{-1} |\phi_j(2)|^2\, dv_2\, dv_1$, which is the same as the left side and shows that $\hat{J}_j$ is Hermitian.

We now must show that $\int [f(1)]^* \hat{K}_j(1) g(1)\, dv_1 = \int g(1)[\hat{K}_j(1) f(1)]^* dv_1$ (Eq. 2). From (14.29), the left side of Eq. 2 is $\int [f(1)]^* \phi_j(1) \int r_{12}^{-1} \phi_j^*(2) g(2)\, dv_2\, dv_1$. The right side of Eq.

2 is $\int g(1)[\phi_j(1)\int r_{12}^{-1}\phi_j^*(2)f(2)\,d\upsilon_2]^*\,d\text{v}_1 = \int g(1)[\phi_j(1)]^*\int r_{12}^{-1}\phi_j(2)[f(2)]^*\,d\text{v}_2\,d\text{v}_1$ (Eq. 3). Since the integration variables in a definite integral are dummy variables, we can relabel them any way we please. If we interchange the labels 1 and 2 on the right side of Eq. 3, we get $\int\int g(2)[\phi_j(2)]^* r_{12}^{-1}\phi_j(1)[f(1)]^*\,d\text{v}_1\,d\text{v}_2$, which is the same as the left side of Eq. 2 and shows that $\hat{K}_j$ is Hermitian.

14.7 The potential-energy operator in $\hat{H}_{\text{core}}$ in (14.27) contains attractions between the electron and the several nuclei in the molecule, as compared with the attraction to the single atomic nucleus in (11.7). The Hartree–Fock operator in (14.26) contains exchange operators that are absent from the Hartree operator (11.7). The exchange operators arise from the antisymmetry of the Hartree–Fock wave function.

14.8 Equation (14.28) gives $\langle\phi_i(1)\,|\,\hat{J}_j(1)\,|\,\phi_i(1)\rangle = \int[\phi_i(1)]^*\phi_i(1)\int|\,\phi_j(2)\,|^2\,r_{12}^{-1}\,d\text{v}_2\,d\text{v}_1 =$ $\int\int[\phi_i(1)\phi_j(2)]^*\,r_{12}^{-1}\phi_i(1)\phi_j(2)\,d\upsilon_2\,d\upsilon_1 = \langle\phi_i(1)\phi_j(2)\,|\,r_{12}^{-1}\,|\,\phi_i(1)\phi_j(2)\rangle = J_{ij}$ [Eq. 14.24)]. Equation (14.29) gives $\langle\phi_i(1)\,|\,\hat{K}_j(1)\,|\,\phi_i(1)\rangle = \int[\phi_i(1)]^*\phi_j(1)\int[\phi_j(2)]^*\phi_i(2)r_{12}^{-1}\,d\text{v}_2\,d\text{v}_1 =$ $\int\int[\phi_i(1)\phi_j(2)]^* r_{12}^{-1}\phi_j(1)\phi_i(2)\,d\text{v}_1\,d\text{v}_2 = \langle\phi_i(1)\phi_j(2)\,|\,r_{12}^{-1}\,|\,\phi_j(1)\phi_i(2)\rangle = K_{ij}$.

14.9 Use of (14.29) gives $\langle\chi_r(1)\,|\,\hat{K}_j(1)\chi_s(1)\rangle = \int[\chi_r(1)]^*\phi_j(1)\int r_{12}^{-1}[\phi_j(2)]^*\chi_s(2)\,d\text{v}_2\,d\text{v}_1$. Use of the expansion (14.33) for $\phi_j(1)$ and $\phi_j(2)$ gives $\langle\chi_r(1)\,|\,\hat{K}_j(1)\chi_s(1)\rangle =$ $\sum_{t=1}^{b}\sum_{u=1}^{b} c_{tj}^* c_{uj}\int\int r_{12}^{-1}[\chi_r(1)]^*\chi_u(1)[\chi_t(2)]^*\chi_s(2)\,d\text{v}_2\,d\text{v}_1 = \sum_{t=1}^{b}\sum_{u=1}^{b} c_{tj}^* c_{uj}(ru\,|\,ts)$.

14.10 **(a)** From (14.42), $P_{rs} = 2\sum_{j=1}^{n/2} c_{rj}^* c_{sj}$ and $(P_{sr})^* = 2(\sum_{j=1}^{n/2} c_{sj}^* c_{rj})^* = 2\sum_{j=1}^{n/2} c_{rj}^* c_{sj} = P_{rs}$.

(b) $\text{Tr}(\mathbf{P}^*\mathbf{F} + \mathbf{P}^*\mathbf{H}_{\text{core}}) = \sum_{s=1}^{b}(\mathbf{P}^*\mathbf{F} + \mathbf{P}^*\mathbf{H}_{\text{core}})_{ss} = \sum_{s=1}^{b}[(\mathbf{P}^*\mathbf{F})_{ss} + (\mathbf{P}^*\mathbf{H}_{\text{core}})_{ss}] =$ $\sum_{s=1}^{b}[\sum_{r=1}^{b}(\mathbf{P}^*)_{sr}(\mathbf{F})_{rs} + \sum_{r=1}^{b}(\mathbf{P}^*)_{sr}(\mathbf{H}_{\text{core}})_{rs}] = \sum_{s=1}^{b}[\sum_{r=1}^{b}(P_{rs}F_{rs} + P_{rs}H_{rs}^{\text{core}})] =$ $\sum_{r=1}^{b}\sum_{s=1}^{b}(P_{rs}F_{rs} + P_{rs}H_{rs}^{\text{core}})$ and (14.45) follows from this result.

(c) $2(\mathbf{CC}^\dagger)_{tu} = 2\sum_{j=1}^{n/2} c_{tj}c_{ju}^\dagger = 2\sum_{j=1}^{n/2} c_{tj}c_{uj}^* = P_{tu}^*$, where (8.90) and (14.42) were used. Therefore $2\mathbf{CC}^\dagger = \mathbf{P}^*$.

14.11 **(a)** Substitution of (14.5) for ρ into $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho\,dx\,dy\,dz$ gives $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho\,dx\,dy\,dz = n\sum_{\text{all }m_s}\int\int\cdots\int|\,\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n,m_{s1},\ldots ms_n)\,|^2\,d\mathbf{r}\,d\mathbf{r}_2\cdots d\mathbf{r}_n = n$, since ψ is normalized. The vector notation (Sec. 5.2) for spatial variables is used.

(b) $n = \int \rho \, d\mathbf{r} = \int \sum_r \sum_s P_{rs}\chi_r^*\chi_s \, d\mathbf{r} = \sum_r \sum_s P_{rs} \int \chi_r^*\chi_s \, d\mathbf{r} = \sum_r \sum_s P_{rs}S_{rs} = \sum_r \sum_s P_{rs}S_{sr}^*$, where $S_{rs} = \langle \chi_r \mid \chi_s \rangle = \langle \chi_s \mid \chi_r \rangle^* = S_{sr}^*$.

(c) $\text{Tr}(\mathbf{PS}^*) = \sum_r (\mathbf{PS}^*)_{rr} = \sum_r \sum_s P_{rs}S_{sr}^* = n$, where the result of part (b) was used.

14.12 Using the expression for $\hat{H}^{\text{core}}$ given preceding these integrals, we have $H_{11}^{\text{core}} = \langle \chi_1 | \hat{H}^{\text{core}} | \chi_1 \rangle =$ $\langle \chi_1 | -\frac{1}{2}\nabla^2 - \zeta_1/r + (\zeta_1 - 2)/r \mid \chi_1 \rangle = \langle \chi_1 | -\frac{1}{2}\nabla^2 - \zeta_1/r \mid \chi_1 \rangle + (\zeta_1 - 2)\langle \chi_1 | 1/r \mid \chi_1 \rangle$. Since $-\frac{1}{2}\nabla^2 - \zeta_1/r$ is the Hamiltonian operator for a hydrogenlike atom with nuclear charge ζ_1 and χ_1 is a hydrogenlike 1*s* orbital with nuclear charge ζ_1, we have $(-\frac{1}{2}\nabla^2 - \zeta_1/r)\chi_1 = -\frac{1}{2}\zeta_1^2\chi_1$ [Eq. (6.94) in atomic units] and the first integral in H_{11}^{core} is $\langle \chi_1 | -\frac{1}{2}\nabla^2 - \zeta_1/r \mid \chi_1 \rangle = -\frac{1}{2}\zeta_1^2 \langle \chi_1 \mid \chi_1 \rangle = -\frac{1}{2}\zeta_1^2$. The function χ_1 is the same as f_1 in (9.60). After (9.60) it was shown that $\langle f_1 | 1/r_1 | f_1 \rangle = \zeta$. Hence $\langle \chi_1 | 1/r \mid \chi_1 \rangle = \zeta_1$. So $H_{11}^{\text{core}} = -\frac{1}{2}\zeta_1^2 + (\zeta_1 - 2)\zeta_1 = \frac{1}{2}\zeta_1^2 - 2\zeta_1$. The integral H_{22}^{core} is the same as H_{11}^{core} except that χ_1 (with orbital exponent ζ_1) is replaced by χ_2 (with orbital exponent ζ_2). Also $\hat{H}^{\text{core}}$ can be written as $\hat{H}^{\text{core}} = -\frac{1}{2}\nabla^2 - \zeta_2/r + (\zeta_2 - 2)/r$. So we can find H_{22}^{core} by changing ζ_1 to ζ_2 in H_{11}^{core}. We have $H_{22}^{\text{core}} = \frac{1}{2}\zeta_2^2 - 2\zeta_2$.

14.13 For real basis functions, Eq. (14.39) is $(rs \mid tu) = \int\int r_{12}^{-1}\chi_r(1)\chi_s(1)\chi_t(2)\chi_u(2) \, dv_1 \, dv_2$. Clearly, interchanging *r* and *s* does not change $(rs \mid tu)$ and interchanging *t* and *u* does not change $(rs \mid tu)$. So $(rs \mid tu) = (sr \mid tu) = (rs \mid ut) = (sr \mid ut)$. Relabeling the dummy integration variables in a definite integral does not change its value. If we interchange the labels 1 and 2 in $(rs \mid tu)$, we get $(rs \mid tu) = \int\int r_{21}^{-1}\chi_r(2)\chi_s(2)\chi_t(1)\chi_u(1) \, dv_2 \, dv_1 = (tu \mid rs)$, where (14.39) without the stars was used. Combining this result with interchanges of *t* and *u* and interchanges of *r* and *s* gives $(rs \mid tu) = (tu \mid rs) = (ut \mid rs) = (tu \mid sr) = (ut \mid sr)$.

14.14 From (14.39), $(11|11) = \int\int r_{12}^{-1}\chi_1(1)\chi_1(1)\chi_1(2)\chi_1(2) \, dv_1 \, dv_2$, where χ_1 is a 1*s* hydrogenlike function with orbital exponent ζ_1. In (9.53), $E^{(1)}$ is given by $\langle \psi^{(0)} | r_{12}^{-1} | \psi^{(0)} \rangle = \langle 1s(1)1s(2) | r_{12}^{-1} | 1s(1)1s(2) \rangle$, where the 1*s* function has orbital exponent Z [Eq. (9.49)]. Thus $(11|11)$ is the same integral as $E^{(1)}$, except that *Z* in $E^{(1)}$ is replaced by ζ_1. Hence Eq. (9.53) gives $(11|11) = 5\zeta_1/8$ in atomic units. Likewise, $(22 \mid 22)$ is the same integral as $E^{(1)}$, except that *Z* in $E^{(1)}$ is replaced by ζ_2. Hence Eq. (9.53) gives $(22 \mid 22) = 5\zeta_2/8$ in atomic units.

14.15 The approximation $F_{rs} \approx H_{rs}^{\text{core}}$ gives $F_{11} \approx H_{11}^{\text{core}} = -1.849$, $F_{22} = H_{22}^{\text{core}} = -1.586$, $F_{12} = F_{21} = H_{12} = H_{21} = -1.883$. The secular equation (14.36) is

$$\begin{vmatrix} -1.849 - \varepsilon_i & -1.883 - 0.837\varepsilon_i \\ -1.883 - 0.837\varepsilon_i & -1.586 - \varepsilon_i \end{vmatrix} = 0 = 0.299\varepsilon_i^2 + 0.283\varepsilon_i - 0.613 = 0$$

and $\varepsilon_i = -1.98$ and 1.035. With the lower root, (14.34) is

$0.13c_{11} - 0.226c_{21} = 0$ and $-0.226c_{11} + 0.394c_{21} = 0$, which gives $c_{11}/c_{21} = 1.7$.

14.16 **(a)** From (14.41) with $b = 2$, $F_{11} = H_{11}^{\text{core}} + \sum_{t=1}^{2}\sum_{u=1}^{2} P_{tu}[(11\,|\,tu) - \frac{1}{2}(1u\,|\,t1)] =$

$H_{11}^{\text{core}} + P_{11}[(11|11) - \frac{1}{2}(11|11)] + P_{12}[(11|12) - \frac{1}{2}(12|11)] + P_{21}[(11|21) - \frac{1}{2}(11|21)] +$

$P_{22}[(11|22) - \frac{1}{2}(12|21)]$. From Prob. 14.10a for real functions, $P_{12} = P_{21}$. From (14.47), $(12|11) = (11|12)$, $(11|21) = (11|12)$. Therefore

$F_{11} = H_{11}^{\text{core}} + \frac{1}{2}P_{11}(11|11) + P_{12}(11|12) + P_{22}[(11|22) - \frac{1}{2}(12|21)]$.

From (14.41) with $b = 2$, $F_{12} = H_{12}^{\text{core}} + \sum_{t=1}^{2}\sum_{u=1}^{2} P_{tu}[(12\,|\,tu) - \frac{1}{2}(1u\,|\,t2)] =$

$H_{12}^{\text{core}} + P_{11}[(12|11) - \frac{1}{2}(11|12)] + P_{12}[(12|12) - \frac{1}{2}(12|12)] + P_{21}[(12|21) - \frac{1}{2}(11|22)] +$

$P_{22}[(12|22) - \frac{1}{2}(12|22)]$. From (14.47), $(12|11) = (11|12)$ and $(12|21) = (12|12)$, so

$F_{12} = H_{12}^{\text{core}} + \frac{1}{2}P_{11}(12|11) + P_{12}[\frac{3}{2}(12|12) - \frac{1}{2}(11|22)] + \frac{1}{2}P_{22}(12|22)$.

From (14.41) with $b = 2$, $F_{22} = H_{22}^{\text{core}} + \sum_{t=1}^{2}\sum_{u=1}^{2} P_{tu}[(22\,|\,tu) - \frac{1}{2}(2u\,|\,t2)] =$

$H_{22}^{\text{core}} + P_{11}[(22|11) - \frac{1}{2}(21|12)] + P_{12}[(22|12) - \frac{1}{2}(22|12)] + P_{21}[(22|21) - \frac{1}{2}(21|22)] +$

$P_{22}[(22|22) - \frac{1}{2}(22|22)]$. From (14.47), $(22|21) = (22|12)$, $(21|22) = (22|12)$, so

$F_{22} = H_{22}^{\text{core}} + P_{11}[(22|11) - \frac{1}{2}(21|12)] + P_{12}(22|12) + \frac{1}{2}P_{22}(22|22)$.

(b) $F_{11} = H_{11}^{\text{core}} + \frac{1}{2}P_{11}(11|11) + P_{12}(11|12) + P_{22}[(11|22) - \frac{1}{2}(12|21)]$

$F_{11} = -1.8488 + \frac{1}{2}(0.9062)P_{11} + 0.9033P_{12} + [1.1826 - \frac{1}{2}(0.9536)]P_{22}$

$F_{11} - 1.8488 + 0.4531P_{11} + 0.9033P_{12} + 0.7058P_{22}$

$F_{12} = H_{12}^{\text{core}} + \frac{1}{2}P_{11}(12|11) + P_{12}[\frac{3}{2}(12|12) - \frac{1}{2}(11|22)] + \frac{1}{2}P_{22}(12|22)$

$F_{12} = -1.8826 + \frac{1}{2}P_{11}(0.9033) + P_{12}[\frac{3}{2}(0.9536) - \frac{1}{2}(1.1826)] + \frac{1}{2}P_{22}(1.2980)$

$F_{12} = -1.8826 + P_{11}(0.4516_5) + 0.8391P_{12} + P_{22}(0.6490)$

$F_{22} = H_{22}^{\text{core}} + P_{11}[(22|11) - \frac{1}{2}(21|12)] + P_{12}(22|12) + \frac{1}{2}P_{22}(22|22)$

$F_{22} = -1.5860 + P_{11}[(1.1826) - \frac{1}{2}(0.9536)] + P_{12}(1.2980) + \frac{1}{2}P_{22}(1.8188)$

$F_{22} = -1.5860 + 0.7058P_{11} + 1.2980P_{12} + 0.9094P_{22}$

14.17 $1 = \int |\phi_1|^2\, d\tau = \int (c_{11}\chi_1 + c_{21}\chi_2)^2\, d\tau = c_{11}^2 \int \chi_1^2\, d\tau + 2c_{11}c_{21} \int \chi_1\chi_2\, d\tau + c_{21}^2 \int \chi_2^2\, d\tau =$ $c_{11}^2 + 2c_{11}c_{21}S_{12} + c_{21}^2 = c_{21}^2(1 + 2S_{12}c_{11}/c_{21} + c_{11}^2/c_{21}^2) = c_{21}^2(1 + 2S_{12}k + k^2) = 1$ and $c_{21} = (1 + 2S_{12}k + k^2)^{-1/2}$, where the fact that we are dealing with real functions was used.

14.18 For this cycle, $c_{11} = 0.842$ and $c_{21} = 0.183$. From (14.49) $P_{11} = 2c_{11}^2 = 2(0.842)^2 = 1.418$, $P_{12} = 2c_{11}c_{21} = 2(0.842)0.183 = 0.308$, $P_{22} = 2c_{21}^2 = 2(0.183)^2 = 0.067$. From (14.50)–(14.52), $F_{11} = -1.8488 + 0.4531P_{11} + 0.9033P_{12} + 0.7058P_{22} =$

$-1.8488 + 0.4531(1.418) + 0.9033(0.308) + 0.7058(0.067) = -0.881$.

$F_{12} = -1.8826 + P_{11}(0.4516_5) + 0.8391P_{12} + P_{22}(0.6490) =$

$-1.8826 + 1.418(0.4516_5) + 0.8391(0.308) + 0.067(0.6490) = -0.940$.

$F_{22} = -1.5860 + 0.7058P_{11} + 1.2980P_{12} + 0.9094P_{22} =$

$-1.5860 + 0.7058(1.418) + 1.2980(0.308) + 0.9094(0.067) = -0.124_5$.

The secular equation $\det(F_{rs} - S_{rs}\varepsilon_i) = 0$ is

$$\begin{vmatrix} -0.881 - \varepsilon_i & -0.940 - 0.8366\varepsilon_i \\ -0.940 - 0.8366\varepsilon_i & -0.124_5 - \varepsilon_i \end{vmatrix} = 0 = 0.300\varepsilon_i^2 - 0.567_3\,\varepsilon_i - 0.774$$

The roots are $\varepsilon_i = -0.918,\ 2.809$. For the smaller root, we get from (14.36),

$0.037c_{11} - 0.175c_{21} = 0$

$-0.172c_{11} + 0.793_5\,c_{21} = 0$

The second equation (which has more significant figures in the coefficients) gives $c_{11}/c_{21} = 4.61$. Equation (14.48) gives $c_{21} = [1 + (4.61)^2 + 2(4.61)0.8366]^{-1/2} = -0.182_7$, and $c_{11} = 0.842$.

14.19 With $k \equiv c_{11}/c_{21} = 1$, Eq. (14.48) gives $c_{21} = (2 + 2\cdot 0.8366)^{-1/2} = 0.5218 = c_{11}$. Then (14.49) gives $P_{11} = 0.5445 = P_{12} = P_{22}$. Equations (14.50)–(14.52) give $F_{11} = -0.7255,\ F_{12} = -0.826,\ F_{22} = 0.0009$. The first estimate of the secular equation is

$$\begin{vmatrix} -0.7255 - \varepsilon_i & -0.826 - 0.8366\varepsilon_i \\ -0.826 - 0.8366\varepsilon_i & 0.0009 - \varepsilon_i \end{vmatrix} = 0 = 0.3001\varepsilon_i^2 - 0.6575\varepsilon_i - 0.683 = 0$$

with lowest root $\varepsilon_1 = -0.769$. Then

$0.043_5\,c_{11} - 0.183c_{21} = 0$

$-0.183c_{11} + 0.770c_{21} = 0$

and the second equation gives $c_{11}/c_{21} = k = 4.21$ and (14.48) gives $c_{21} = 0.197$ and $c_{11} = kc_{21} = 0.829$. Equation (14.49) gives $P_{11} = 1.374,\ P_{12} = 0.327,\ P_{22} = 0.078$. Then $F_{11} = -0.876$, $F_{12} = -0.937$, $F_{22} = -0.121$ and

$$\begin{vmatrix} -0.876 - \varepsilon_i & -0.937 - 0.8366\varepsilon_i \\ -0.937 - 0.8366\varepsilon_i & -0.121 - \varepsilon_i \end{vmatrix} = 0 = 0.3001\varepsilon_i^2 - 0.571\varepsilon_i - 0.772$$

with lowest root $\varepsilon_i = -0.913$. Then

$0.037c_{11} - 0.173c_{21} = 0$

$-0.173c_{11} + 0.792c_{21} = 0$

and the second equation gives $c_{11}/c_{21} = k = 4.58$ and (14.48) gives $c_{21} = 0.184$ and $c_{11} = kc_{21} = 0.841$. Equation (14.49) gives $P_{11} = 1.415,\ P_{12} = 0.309,\ P_{22} = 0.068$. Then $F_{11} = -0.881$, $F_{12} = -0.940,\ \ F_{22} = -0.124$. These Fock matrix elements are essentially the same as the last set of Fock matrix elements in the example in Sec, 14,3, so the remaining calculation gives essentially the same results as in the text.

14.20 **(a)** A C++ program is

```
#include <iostream>
#include <cmath>
using namespace std;
int main()  {
   int n;
   double z1, z2, s, h11, h12, h22, r1111, r2222, r1122, r1212, temp;
   double r1112, r1222, k;
   double c2, c1, p11, p12, p22, f11, f12, f22, a, b, c, rt, e1, e2, e, d2, d1, ehf, d;
   label0:
   cout << " Enter z1 ";  cin >> z1;
   cout << " Enter z2 (enter -3 to stop)  " ;  cin >> z2;
   if (z2 < 0)
      return 0;
   s=8*pow(z1*z2, 1.5)/pow(z1+z2, 3);
   h11=0.5*z1*z1-2*z1;   h22=0.5*z2*z2-2*z2;
   h12=pow(z1*z2,1.5)*(4*z1*z2-8*z1-8*z2)/pow(z1+z2,3);
   r1111=5*z1/8;   r2222=5*z2/8;
   d=pow(z1+z2,4);
   r1122=(pow(z1,4)*z2+4*pow(z1,3)*z2*z2+z1*pow(z2,4)+4*z1*z1*pow(z2,3))/d;
   r1212=20*pow(z1,3)*pow(z2,3)/pow(z1+z2,5);
   temp=(12*z1+8*z2)/pow(z1+z2,2)+(9*z1+z2)/(2*z1*z1);
   r1112=temp*16*pow(z1,4.5)*pow(z2,1.5)/pow(3*z1+z2,4);
   temp=(12*z2+8*z1)/pow(z1+z2,2)+(9*z2+z1)/(2*z2*z2);
   r1222=temp*16*pow(z2,4.5)*pow(z1,1.5)/pow(3*z2+z1,4);
   n=0;
   cout  <<  "  c1/c2  ";    cin  >>  k;
   c2=1/sqrt(1+k*k+2*k*s);   c1=k*c2;
   cout  <<  "  c1 =  "  <<  c1  <<  "  c2 =  "  << c2  << endl;
   label1:
   p11=2*c1*c1;   p12=2*c1*c2;    p22=2*c2*c2;
   f11=h11+0.5*p11*r1111+p12*r1112+p22*(r1122-0.5*r1212);
   f12=h12+0.5*p11*r1112+p12*(r1212*1.5-0.5*r1122)+0.5*p22*r1222;
   f22=h22+p11*(r1122-0.5*r1212)+p12*r1222+0.5*p22*r2222;
```

```
  a=1-s*s;    b=2*s*f12-f11-f22;    c=f11*f22-f12*f12;
  rt=sqrt(b*b-4*a*c);
  e1=(-b-rt)/(2*a);    e2=(-b+rt)/(2*a);
  e=e1;
  if (e2 < e1)
     e=e2;
  k=(e-f22)/(f12-s*e);
  d2=1/sqrt(1+k*k+2*k*s);    d1=k *d2;
  n=n+1;
  if (n> 500) {
     cout << "Did not converge";
     return 0;
  }
  cout  <<  "  c1 =  "  <<  c1  <<  "  c2 =  "  << c2  <<  "  n =  "  <<  n  <<  endl;
  cout  <<  " E =  "  <<  e  << endl;
  if (fabs(c2-d2) > 0.00001)
     goto label3;
  if (fabs(c1-d1) > 0.00001)
     goto label3;
  cout  <<  " Converged  "  <<  "  N =  "  <<  n;
  ehf = e + 0.5*(p11*h11+2*p12*h12+p22*h22);
  cout  <<  " EHF  = "  <<  ehf  << endl;
  goto label0;
  label3:  c1=d1;  c2=d2;  goto label1;
}
```

(b) In all cases, the calculation converges to the correct result. Six iterations are needed for $c_{11}/c_{21} = -1$; five iterations are needed for each of the other choices.

(c) To ensure fully converged results, we change `0.00001` in the last two `if` statements to `0.0000001`. Also, we add the statement `cout.precision(8);` to the program as a new line after `int main() {`, so as to have 8 significant figures in the output. For these orbital exponents, the program gives $E_{\text{HF}} = -2.8616726$ hartrees.

(d) For the calculations in part (d), we use the convergence test as modified in part (c). For $\zeta_1 = 1.46363$ and $\zeta_2 = 2.91093$, we get $E_{\text{HF}} = -2.8616485$. For $\zeta_1 = 1.44363$ and $\zeta_2 = 2.91093$, we get $E_{\text{HF}} = -2.8616477$. These energies are above that for the optimum orbital exponents. For $\zeta_1 = 1.45363$ and $\zeta_2 = 2.92093$, we get $E_{\text{HF}} = -2.8616718$. For $\zeta_1 = 1.45363$ and $\zeta_2 = 2.90093$, we get $E_{\text{HF}} = -2.8616721$. (Energies are given in hartrees.)

14.21 From (14.43), $\rho = P_{11}\chi_1^2 + 2P_{12}\chi_1\chi_2 + P_{22}\chi_2$. From (14.46) and (5.101), at $r = 0$, $\chi_1 = 2\zeta_1^{3/2}/(4\pi)^{1/2} = 0.9851$ and $\chi_2 = 2\zeta_2^{3/2}/(4\pi)^{1/2} = 2.8007$. So at $r = 0$, $\rho = 1.418(0.985)^2 + 2(0.308)(0.985)(2.801) + 0.067(2.801)^2 = 3.60$ electrons/bohr^3.

At $r = 1$ bohr, $\chi_1 = 2\zeta_1^{3/2}e^{-\zeta_1}/(4\pi)^{1/2} = 2(1.45)^{3/2}e^{-1.45}/(4\pi)^{1/2} = 0.2311$ and $\chi_2 = 2\zeta_2^{3/2}e^{-\zeta_2}/(4\pi)^{1/2} = 0.1526$.

So at $r = 1$, $\rho = 1.418(0.231)^2 + 2(0.308)(0.231)(0.1526) + 0.067(0.1526)^2 = 0.099$ electrons/bohr^3.

14.22 The condition that $\mathbf{C}'$ be unitary is given by (8.93) as $\boxed{\sum_s (c'_{si})^* c'_{sj} = \delta_{ij}}$. We have $\int \phi_i^* \phi_j \, d\tau = \int \sum_s (c'_{si})^* (\chi'_s)^* \sum_t c'_{tj}\chi'_t \, d\tau = \sum_s \sum_t (c'_{si})^* c'_{tj} \int (\chi'_s)^* \chi'_t \, d\tau = \sum_s \sum_t (c'_{si})^* c'_{tj}\delta_{st} =$ $\sum_s (c'_{si})^* c'_{sj} = \delta_{ij}$, where the boxed equation was used.

14.23 **(a)** $sx + 3sysz \neq s^n(x + 3yz)$, so the function is inhomogeneous.

(b) $179 = s^0 179$, so this function is homogenous of degree zero.

(c) $(sx)^2/sy(sz)^3 = s^{-2}x^2/yz^3$, so this function is homogeneous of degree –2.

(d) $[a(sx)^3 + b(sx)(sy)^2]^{1/2} = s^{3/2}(ax^3 + bxy^2)^{1/2}$, so the function is homogeneous of degree 3/2.

14.24 From (14.76), $\langle T \rangle = -E$ for an atomic stationary state. We have $E_2 > E_1$, so $0 > -E_2 + E_1$, $-E_1 > -E_2$, $\langle T \rangle_1 > \langle T \rangle_2$.

14.25 If $\hat{A}$ is a time-independent operator, then (7.113) becomes for a stationary state: $0 = 0 + i\hbar^{-1}\langle[\hat{H}, \hat{A}]\rangle$ and $\langle[\hat{H}, \hat{A}]\rangle = 0$, which is the hypervirial theorem (14.61).

14.26 **(a)** $\langle T \rangle = \langle \phi | -(\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2)\phi \rangle$. Use of Eq. (9.58) gives $\langle T \rangle = \langle \phi | (\zeta e^2/4\pi\varepsilon_0 r_1 + \zeta e^2/4\pi\varepsilon_0 r_2 - \zeta^2 e^2/4\pi\varepsilon_0 a_0)\phi \rangle =$ $\zeta(e^2/4\pi\varepsilon_0)\langle \phi | r_1^{-1} | \phi \rangle + \zeta(e^2/4\pi\varepsilon_0)\langle \phi | r_2^{-1} | \phi \rangle - (\zeta^2 e^2/4\pi\varepsilon_0 a_0)\langle \phi | \phi \rangle$. Equations after (9.60) give $\langle \phi | r_1^{-1} | \phi \rangle = \langle \phi | r_2^{-1} | \phi \rangle = \zeta/a_0$. Therefore $\langle T \rangle = \zeta^2 e^2/4\pi\varepsilon_0 a_0 + \zeta^2 e^2/4\pi\varepsilon_0 a_0 - \zeta^2 e^2/4\pi\varepsilon_0 a_0 = \zeta^2 e^2/4\pi\varepsilon_0 a_0$.
Also $\langle V \rangle = \langle \phi | -Ze^2/4\pi\varepsilon_0 r_1 - Ze^2/4\pi\varepsilon_0 r_2 + e^2/4\pi\varepsilon_0 r_{12} | \phi \rangle$. Use of $\langle \phi | r_1^{-1} | \phi \rangle = \langle \phi | r_2^{-1} | \phi \rangle = \zeta/a_0$ and the equation preceding (9.61) gives $\langle V \rangle = -2Z\zeta e^2/4\pi\varepsilon_0 a_0 + 5\zeta e^2/8(4\pi\varepsilon_0)a_0$.

(b) For $\zeta = Z - 5/16$, the results of part (a) become $\langle T \rangle = (Z - 5/16)^2 e^2/4\pi\varepsilon_0 a_0$ and $\langle V \rangle = -2Z(Z - 5/16)e^2/4\pi\varepsilon_0 a_0 + 5(Z - 5/16)e^2/8(4\pi\varepsilon_0)a_0 = -2(Z - 5/16)(e^2/4\pi\varepsilon_0 a_0)(Z - 5/16) =$ $-2(Z - 5/16)^2(e^2/4\pi\varepsilon_0 a_0) = -2\langle T \rangle$, which is (14.75).

14.27 For the harmonic oscillator, V is a homogeneous function of degree 2, so the virial theorem (14.70) gives $2\langle T\rangle = 2\langle V\rangle$ and $\langle V\rangle = \langle T\rangle = 5.0\times 10^{-19}$ J. Then $E = \langle T\rangle + \langle V\rangle = 1.00\times 10^{-18}$ J.

14.28 As shown in part (c) of the Example in Sec. 14.4, V is homogeneous of degree -1 and (14.76) gives $\langle T\rangle = -E = 59.10$ eV.

14.29 V in Cartesian coordinates is homogeneous of degree 4 and (14.72) and (14.73) give $\langle V\rangle = 2E/6 = (10\text{ eV})/3 = 3.33\text{ eV}$ and $\langle T\rangle = 4E/6 = 6.67\text{ eV}$.

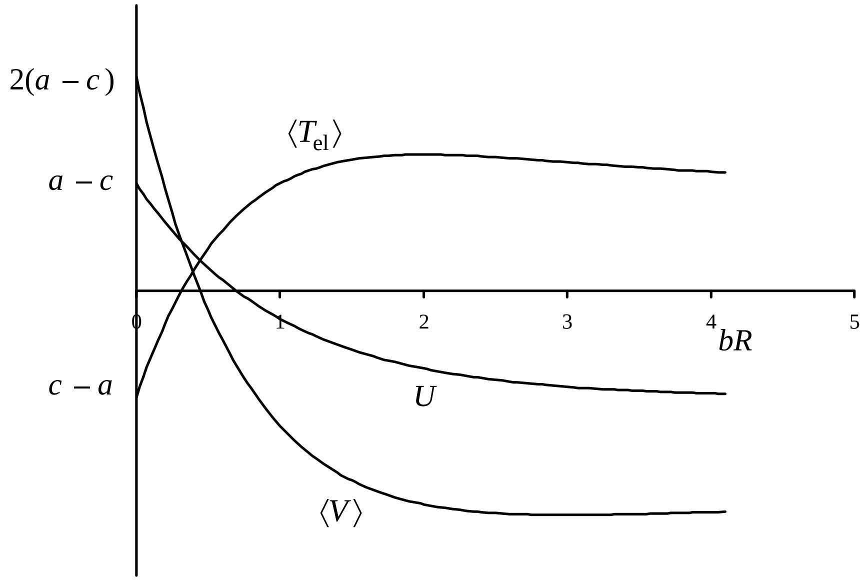
14.30 From Prob. 4.52, addition of C to V adds C to each stationary-state energy eigenvalue E. Addition of C to V leaves $\langle T\rangle = \langle\psi|\hat{T}|\psi\rangle$ unchanged (since ψ and $\hat{T}$ are unchanged) and adds C to $\langle V\rangle$. Suppose that before we added C to V, the function V was homogeneous of degree n; then the virial theorem (14.70) gives $2\langle T\rangle = n\langle V\rangle$ (Eq. 1). After we added C to V, the left side of Eq. 1 is unchanged but the right side is increased by nC. Hence Eq. 1 no longer holds. One might then think the virial theorem is violated but this is not so, because after we add the constant C to V, V is no longer a homogeneous function and (14.70) no longer applies. (For example, addition of C to the harmonic-oscillator V gives $\frac{1}{2}kx^2 + C$, which is no longer homogeneous of degree 2.)

14.31 **(a)** Use of Eqs. (5.8), (5.1), and (14.61) gives $\langle p_x\rangle = (m/i\hbar)\langle[\hat{x},\, \hat{H}]\rangle = 0$.

(b) Use of Eqs. (5.9) and (14.61) gives $\langle\partial V/\partial x\rangle = -(1/i\hbar)\langle[\hat{p}_x,\, \hat{H}]\rangle = 0$.

14.32 At $R = 0$, $U = a - c$. At $R = \infty$, $U = -c$. Between 0 and ∞, U decreases monotonically as R increases. (This is a repulsive state with no minimum in U.) We have $dU/dR = -abe^{-bR}$. The virial-theorem equation (14.94) gives $\langle T_{\text{el}}\rangle = -U - R(dU/dR) = c - ae^{-bR} + abRe^{-bR} = c + a(bR-1)e^{-bR}$. At $R = 0$, $\langle T_{\text{el}}\rangle = c - a$; at $R = \infty$, $\langle T_{\text{el}}\rangle = c$. For small R, we have $e^{-bR} \approx 1 - bR$ and $\langle T_{\text{el}}\rangle \approx c + a(bR-1)(1-bR) \approx c + a(-1+2bR)$, so $\langle T_{\text{el}}\rangle$ initially increases as R increases from 0. For large R, we can neglect the -1 in $(bR-1)$. At large R, the function Re^{-bR} decreases as R increases, since the exponential function overpowers the factor of R, so $\langle T_{\text{el}}\rangle$ decreases with increasing R at large R. Hence there must be a maximum in $\langle T_{\text{el}}\rangle$. To locate this maximum, we take the derivative: $d\langle T_{\text{el}}\rangle/dR = 0 = abe^{-bR} + abe^{-bR} - ab^2Re^{-bR}$, which gives $R = 2/b$ and $\langle T_{\text{el}}\rangle_{\max} = c + a/e^2$. The virial theorem equation (14.95) gives $\langle V\rangle = 2U + R(dU/dR) = 2ae^{-bR} - 2c - abRe^{-bR} = -2c + a(2-bR)e^{-bR}$. At $R = 0$,

$\langle V \rangle = 2a - 2c$. At $R = \infty$, $\langle V \rangle = -2c$. For small *R*, $a(2-bR)e^{-bR} \approx a(2-bR)(1-bR) \approx a(2-3bR)$, so $\langle V \rangle$ initially decreases as *R* increases from 0. For large *R*, we can neglect the 2 in $(2-bR)$, so at large *R*, $\langle V \rangle$ increases as *R* increases. Hence there must be a minimum in $\langle V \rangle$. To locate this minimum, we take the derivative:
$d\langle V \rangle/dR = 0 = -2abe^{-bR} - abe^{-bR} + ab^2Re^{-bR}$, which gives $R = 3/b$ and $\langle V \rangle_{\min} = -2c - a/e^3$. Sketches of these functions follow. (The negative values of $\langle T_{\text{el}} \rangle$ are unphysical.)



14.33 Differentiation of (14.95) gives
$d\langle V \rangle/dR = 2\,dU/dR + dU/dR + R(d^2U/dR^2) = 3dU/dR + R(d^2U/dR^2)$.
At $R = R_e$, $dU/dR = 0$ and $d\langle V \rangle/dR = R(d^2U/dR^2)$. The second derivative d^2U/dR^2 at $R = R_e$ is the force constant k_e for the bound state, and k_e must be positive: To the left of the minimum in *U* in R_e, the slope dU/dR is negative and to the right of the minimum, dU/dR is positive. Hence dU/dR is increasing as *R* increases through R_e. If a function is increasing at a point, its derivative must be positive (or zero) at that point, so $d^2U/dR^2 \geq 0$ at R_e. Hence $d\langle V \rangle/dR \geq 0$ at R_e.

Differentiation of (14.94) gives
$d\langle T_{\text{el}} \rangle/dR = -dU/dR - dU/dR - R(d^2U/dR^2) = -2dU/dR - R(d^2U/dR^2)$.
At $R = R_e$, $dU/dR = 0$ and $d\langle T_{\text{el}} \rangle/dR = -R(d^2U/dR^2)$. Since $d^2U/dR^2 \geq 0$ at R_e, we have $d\langle T_{\text{el}} \rangle/dR \leq 0$ at R_e.

14.34 This equation is valid. The molecular Hamiltonian operator (13.1) is a homogeneous function of degree –1 of the Cartesian coordinates of all the particles (electrons and nuclei) and $\hat{T}_{\text{el}} + \hat{T}_N$ is the complete kinetic energy operator for the molecule, so the equation given in the problem follows from the virial theorem (14.70).

14.35 We have $D_e = 4.75 \text{ eV} = U(\infty) - U(R_e) = -27.20 \text{ eV} - U(R_e)$ and $U(R_e) = -31.95 \text{ eV}$, where we used (6.108) and the fact that H_2 dissociates to two H atoms. At R_e, $dU/dR = 0$ and (14.95) gives $\langle V\rangle|_{R_e} = 2U(R_e) = -63.9 \text{ eV}$, $\langle T_{\text{el}}\rangle|_{R_e} = -U(R_e) = 31.95 \text{ eV}$. We have $\langle V\rangle = \langle V_{\text{el}}\rangle + V_{NN} = \langle V_{\text{el}}\rangle + e^2/4\pi\varepsilon_0 R_e$. Then

$$\frac{e^2}{4\pi\varepsilon_0 R_e} = \frac{(1.602\times10^{-19}\text{ C})^2}{4\pi(8.854\times10^{-12}\text{ C}^2\text{ N}^{-1}\text{ m}^{-2})(0.741\times10^{-10}\text{ m})} = 3.11_3\times10^{-18}\text{ J}\frac{1\text{ eV}}{1.602\times10^{-19}\text{ J}}$$

$= 19.4_3$ eV. So $\langle V_{\text{el}}\rangle|_{R_e} = \langle V\rangle|_{R_e} - e^2/4\pi\varepsilon_0 R_e = -83.3$ eV.

14.36 For the Fues function, $dU/dR = D_e(2R_e/R^2 - 2R_e^2/R^3)$. Equation (14.94) gives $\langle T_{\text{el}}\rangle = -U - R(dU/dR) = -U(\infty) + D_e(2R_e/R - R_e^2/R^2) - D_e(2R_e/R - 2R_e^2/R^2) =$ $-U(\infty) + D_e(R_e^2/R^2)$. Equation (14.95) gives $\langle V\rangle = 2U + R(dU/dR) = 2U(\infty) + 2D_e(-2R_e/R + R_e^2/R^2) + D_e(2R_e/R - 2R_e^2/R^2) =$ $2U(\infty) - 2D_e(R_e/R)$. The Fues function has $\langle T_{\text{el}}\rangle$ always increasing as R decreases and has $\langle V\rangle$ always decreasing as R decreases. These behaviors are quite wrong (see Fig. 14.1).

14.37 **(a)** For the hydrogenlike atom, $\hat{H} = -(\hbar^2/2m_e)\nabla^2 - Ze^2/4\pi\varepsilon_0 r$ and $E_n = -(Z^2/n^2)(e^2/8\pi\varepsilon_0 a)$. Let $\lambda = Z$. Then (14.123) gives $\partial E_n/\partial Z = -(2Z/n^2)(e^2/8\pi\varepsilon_0 a) = \langle\partial\hat{H}/\partial Z\rangle = \langle -e^2/4\pi\varepsilon_0 r\rangle$ and $\langle 1/r\rangle = Z/n^2 a$.

(b) From Sec. 9.6, if the secular determinant is in diagonal form, then the initially assumed unperturbed wave functions are the correct zeroth-order wave functions. The perturbation is $\hat{H}' = (\partial\hat{H}/\partial Z)\,dZ = -(e^2/4\pi\varepsilon_0 r)\,dZ$. The hydrogenlike functions of a degenerate level have the same *n*, so the off-diagonal elements of the secular determinant are $\langle nl'm'|-(e^2/4\pi\varepsilon_0 r)|nlm\rangle\,dZ$, where *nlm* denotes a hydrogenlike function with quantum numbers *n*, *l*, and *m*, and the primes indicate that at least one of l' and m' must differ from *l* and *m*, respectively. The $-(e^2/4\pi\varepsilon_0 r)$ in the integrand goes in the radial factor in the integral $\langle nl'm'|-(e^2/4\pi\varepsilon_0 r)|nlm\rangle$, and this integral must be zero because of the orthogonality of the spherical- harmonic factors in the wave functions when at least one of l' and m' differs from *l* and *m* [Eq. (7.27)]. So the secular determinant is in diagonal form.

14.38 We have $\hat{H} = \hat{p}_x^2/2m + \frac{1}{2}kx^2$. Let $\lambda = m^{-1}$. Then $\partial\hat{H}/\partial\lambda = \hat{p}_x^2/2$. Also

$E = (\text{v} + \frac{1}{2})h\nu = (\text{v} + \frac{1}{2})h(1/2\pi)(k/m)^{1/2}$ and

$\partial E/\partial(m^{-1}) = (\partial E/\partial m)[\partial m/\partial(m^{-1})] = (\partial E/\partial m)/[\partial(m^{-1})/\partial m] = -(\partial E/\partial m)/m^{-2} = -m^2(\partial E/\partial m)$

$= -m^2(\text{v} + \frac{1}{2})\hbar k^{1/2}(-\frac{1}{2}m^{-3/2}) = \frac{1}{2}m^{1/2}(\text{v} + \frac{1}{2})\hbar k^{1/2}$. So (14.123) gives

$\langle \partial H/\partial\lambda \rangle = \frac{1}{2}\langle p_x^2 \rangle = \frac{1}{2}m^{1/2}(\text{v} + \frac{1}{2})\hbar k^{1/2}$ and

$\langle p_x^2 \rangle = m^{1/2}(\text{v} + \frac{1}{2})\hbar k^{1/2} = m(\text{v} + \frac{1}{2})h(1/2\pi)(k/m)^{1/2} = m(\text{v} + \frac{1}{2})h\nu$. Equation (14.74) gives

$\langle T \rangle = \langle p_x^2/2m \rangle = \frac{1}{2}h\nu(\text{v} + \frac{1}{2})$ and $\langle p_x^2 \rangle = mh\nu(\text{v} + \frac{1}{2})$, which agrees with the Hellmann–Feynman result found in this problem.

14.39 From (9.7), $\partial\hat{H}/\partial\lambda = \hat{H}'$. From (9.14), $\partial E_n/\partial\lambda = E_n^{(1)} + 2\lambda E_n^{(2)} + \cdots + k\lambda^{k-1}E_n^{(k)} + \cdots$. Then (14.123) gives $\partial E_n/\partial\lambda = E_n^{(1)} + 2\lambda E_n^{(2)} + \cdots + k\lambda^{k-1}E_n^{(k)} + \cdots = \langle \psi_n | \hat{H}' | \psi_n \rangle$. At $\lambda = 0$, ψ_n becomes $\psi_n^{(0)}$ and we get $E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$.

14.40 Equation (14.131) gives $F_{z,a} = -\partial U/\partial z_a$ and $F_{z,b} = -\partial U/\partial z_b$. Use of the chain rule and an equation that corresponds to (14.85) gives

$$F_{z,a} = -\frac{dU(R)}{dR}\frac{\partial R}{\partial z_a} = -\frac{dU}{dR}\frac{z_a - z_b}{R} = \frac{dU}{dR}\frac{z_b - z_a}{R} = \frac{dU}{dR}\frac{\partial R}{\partial z_b} = \frac{\partial U}{\partial z_b} = -F_{z,b}$$

14.41 On the dividing surface between binding and antibinding regions, we have $Z_a \cos\theta_a\, r_a^{-2} + Z_b \cos\theta_b\, r_b^{-2} = 0$ (Eq. 1). Let *d* be the desired distance between these two intersection points. At the left intersection point, Figs. 14.4 and 14.6 give $r_a = d$, $r_b = d + R_e$, $\theta_a = \pi$, and $\theta_b = 0$. Equation 1 becomes $-Z_a/d^2 + Z_b/(d + R_e)^2 = 0$, so $Z_b d^2 = Z_a(d + R_e)^2$ and $Z_b/Z_a = (1 + R_e/d)^2 = 1 + 2(R_e/d) + (R_e/d)^2$. The quadratic formula gives $R_e/d = \{-2 + [4 - 4(1 - Z_b/Z_a)]^{1/2}\}/2 = -1 + (Z_b/Z_a)^{1/2}$ and $d = R_e/[(Z_b/Z_a)^{1/2} - 1]$.

(a) $d = (0.92\text{ Å})/(9^{1/2} - 1) = 0.46\text{ Å}$.

(b) $d = (1.27\text{ Å})/(17^{1/2} - 1) = 0.41\text{ Å}$.

(c) $d = (1.41\text{ Å})/(35^{1/2} - 1) = 0.29\text{ Å}$.

(d) $d = (1.61\text{ Å})/(53^{1/2} - 1) = 0.26\text{ Å}$.

Chapter 15

Molecular Electronic Structure

15.1 The multiplication table for a group lists the products of all pairs of operations. For $\mathcal{C}_{2v}$, the multiplication table is found to be

$\mathcal{C}_{2v}$	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$
$\hat{E}$	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$
$\hat{C}_2(z)$	$\hat{C}_2(z)$	$\hat{E}$	$\hat{\sigma}_v(yz)$	$\hat{\sigma}_v(xz)$
$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$	$\hat{E}$	$\hat{C}_2(z)$
$\hat{\sigma}_v(yz)$	$\hat{\sigma}_v(yz)$	$\hat{\sigma}_v(xz)$	$\hat{C}_2(z)$	$\hat{E}$

Each entry is the product of the element at the left end of its row and the element at the top of its column. The first row of entries and the first column of entries are easily filled in since $\hat{E}$ times any symmetry operation equals that symmetry operation. The entries on the diagonal are all $\hat{E}$ since the square of each of the $\mathcal{C}_{2v}$ symmetry operations equals $\hat{E}$. The $\hat{C}_2(z)$ operation changes the x and y coordinates to their negatives. Each reflection changes the coordinate perpendicular to the symmetry plane to its negative. Thus:
$(x, y, z)\xrightarrow{\hat{C}_2(z)}(-x, -y, z)$; $(x, y, z)\xrightarrow{\hat{\sigma}_\upsilon(xz)}(x, -y, z)$; $(x, y, z)\xrightarrow{\hat{\sigma}_\upsilon(yz)}(-x, y, z)$

We have $(x, y, z)\xrightarrow{\hat{C}_2(z)}(-x, -y, z)\xrightarrow{\hat{\sigma}_\upsilon(xz)}(-x, y, z)$. Hence $\hat{\sigma}_\upsilon(xz)\hat{C}_2(z) = \hat{\sigma}_\upsilon(yz)$. The remaining five products are found similarly, giving the preceding multiplication table. (see also Prob. 12.25.)

The eight possible combinations of the $\hat{O}_R$ eigenvalues +1 and –1 are

$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$
1	1	1	1
1	1	1	–1
1	1	–1	1
1	–1	1	1
1	1	–1	–1
1	–1	1	–1
1	–1	–1	1
1	–1	–1	–1

The first row (the totally symmetric species) is clearly a valid symmetry species.
The second row is ruled out since $\hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$, but $(-1)1 \neq 1$.

The third row is ruled out since $\hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$, but $1(-1) \neq 1$.

The fourth row is ruled out since $\hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$, but $(1)1 \neq -1$.

The fifth row is a valid representation, since $\hat{C}_2(z)\hat{\sigma}_\upsilon(xz) = \hat{\sigma}_\upsilon(xz)\hat{C}_2(z) = \hat{\sigma}_\upsilon(yz)$ and $1(-1) = (-1)1 = -1$; $\hat{C}_2(z)\hat{\sigma}_\upsilon(yz) = \hat{\sigma}_\upsilon(yz)\hat{C}_2(z) = \hat{\sigma}_\upsilon(xz)$ and $1(-1) = (-1)1 = -1$; $\hat{\sigma}_\upsilon(xz)\hat{\sigma}_\upsilon(yz) = \hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$ and $(-1)(-1) = 1$.

The sixth row is a valid representation, since $\hat{C}_2(z)\hat{\sigma}_\upsilon(xz) = \hat{\sigma}_\upsilon(xz)\hat{C}_2(z) = \hat{\sigma}_\upsilon(yz)$ and $-1(1) = 1(-1) = -1$; $\hat{C}_2(z)\hat{\sigma}_\upsilon(yz) = \hat{\sigma}_\upsilon(yz)\hat{C}_2(z) = \hat{\sigma}_\upsilon(xz)$ and $-1(-1) = -1(-1) = 1$; $\hat{\sigma}_\upsilon(xz)\hat{\sigma}_\upsilon(yz) = \hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$ and $1(-1) = -1$.

Similarly, the seventh row is found to be a valid representation.
The eighth row is ruled out since $\hat{\sigma}_\upsilon(yz)\hat{\sigma}_\upsilon(xz) = \hat{C}_2(z)$, but $(-1)(-1) \neq -1$.

15.2 The symmetry operations for $\mathcal{D}_2$ are $\hat{E},\ \hat{C}_2(x),\ \hat{C}_2(y),\ \hat{C}_2(z)$. The square of each of these operations is $\hat{E}$. The $\hat{C}_2(x)$ rotation changes the *y* and *z* coordinates to their negatives and leaves the *x* coordinate unchanged. Similarly for $\hat{C}_2(y)$ and $\hat{C}_2(z)$. Thus we have

$$(x, y, z) \xrightarrow{\hat{C}_2(x)} (x, -y, -z) \xrightarrow{\hat{C}_2(y)} (-x, -y, z)$$

$$(x, y, z) \xrightarrow{\hat{C}_2(y)} (-x, y, -z) \xrightarrow{\hat{C}_2(x)} (-x, -y, z)$$

Since $\hat{C}_2(z)$ moves the point at (x, y, z) to $(-x, -y, z)$, we have shown that

$$\boxed{\hat{C}_2(y)\hat{C}_2(x) = \hat{C}_2(x)\hat{C}_2(y) = \hat{C}_2(z)}.$$

If we perform two successive cyclic permutations, changing *x* to *y*, *y* to *z*, and *z* to *x*, the boxed equations become

$$\hat{C}_2(z)\hat{C}_2(y) = \hat{C}_2(y)\hat{C}_2(z) = \hat{C}_2(x)$$

$$\hat{C}_2(x)\hat{C}_2(z) = \hat{C}_2(z)\hat{C}_2(x) = \hat{C}_2(y)$$

The $\mathcal{D}_2$ multiplication table is therefore

$\mathcal{D}_2$	$\hat{E}$	$\hat{C}_2(x)$	$\hat{C}_2(y)$	$\hat{C}_2(z)$
$\hat{E}$	$\hat{E}$	$\hat{C}_2(x)$	$\hat{C}_2(y)$	$\hat{C}_2(z)$
$\hat{C}_2(x)$	$\hat{C}_2(x)$	$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$
$\hat{C}_2(y)$	$\hat{C}_2(y)$	$\hat{C}_2(z)$	$\hat{E}$	$\hat{C}_2(x)$
$\hat{C}_2(z)$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{E}$

The eight possible combinations of the $\hat{O}_R$ eigenvalues +1 and –1 are

$\hat{E}$	$\hat{C}_2(x)$	$\hat{C}_2(y)$	$\hat{C}_2(z)$
1	1	1	1
1	1	1	–1
1	1	–1	1
1	–1	1	1
1	1	–1	–1
1	–1	1	–1
1	–1	–1	1
1	–1	–1	–1

The first row (the totally symmetric species) is clearly a valid symmetry species. The second row is ruled out since $\hat{C}_2(y)\hat{C}_2(z) = \hat{C}_2(x)$ but $1(-1) \neq 1$. The third row is ruled out since $\hat{C}_2(x)\hat{C}_2(y) = \hat{C}_2(z)$ but $1(-1) \neq 1$. The fourth row is ruled out since $\hat{C}_2(x)\hat{C}_2(y) = \hat{C}_2(z)$ but $(-1)1 \neq 1$. The eighth row is ruled out since $\hat{C}_2(x)\hat{C}_2(y) = \hat{C}_2(z)$ but $(-1)(-1) \neq -1$. One finds that the numbers in the fifth, sixth, and seventh rows multiply the same way as the symmetry operations, and these rows and row 1 are the symmetry species.

15.3 **(a)** The E indicates the orbital degeneracy is 2. For this triplet term, $S = 1$ and M_S has three possible values. The total degeneracy is 2(3) = 6 and this is the number of independent wave functions.

(b) The orbital degeneracy is 2. $S = 0$, so $M_S = 0$. The degeneracy is 2(1) = 2.

15.4 **(a)** For each H, this set uses two *s*-type contracted Gaussians. Since the molecule has 8 H atoms, the set has 2(8) = 16 contracted functions centered on H atoms. For each non-H atom, the set has four *s*-type contracted functions and two sets of *p*-type functions. Each set of *p* functions contains the three functions p_x, p_y, p_z, so each non-H atom has $4 + 2(3) = 10$ contracted functions centered on it. There are 4 non-H atoms, for a total of 4(10) = 40 contracted functions on these atoms. The total is 40 + 16 = 56.

(b) The minimal-basis AOs are 1*s* on each H and 1*s*, 2*s*, $2p_x, 2p_y, 2p_z$ on each non-H. A double-zeta set therefore has two *s*-type contracted Gaussian functions on each H, and has four *s*-type and two sets of *p*-type functions on each non-H. This is a [4*s*2*p*/2*s*] set, as in part (a). The total number of contracted Gaussians is 10(2) + 5[4 + 2(3)] = 70.

15.5 **(a)** The minimal-basis AOs are 1*s* on each H and 1*s*, 2*s*, $2p_x, 2p_y, 2p_z$ on each non-H. A STO-3G set has one contracted Gaussian for each minimal-basis AO and so has 1 CGTF on each H and has 5 CGTFs on each C and O. The total number of CGTFs is $10(1)+5(5)=35$.

(b) In the 3-21G set, each inner-shell AO (in this case, the 1*s* AO of each C and each O) is represented by one CGTF; each valence AO is represented by a linear combination of 2 CGTFs. Thus each H atom has 2 CGTFs. Each C and O has 1 + 2(4) = 9 CGTFs. The total number of CGTFs is 10(2) + 5(9) = 65.

(c) In the 6-31G* set, each H has two *s*-type CGTFs; each C and O has one *s*-type CGTF for the 1*s* AO, two *s*-type CGTFs for the 2*s* AO, six *p*-type CGTFs for the 2*p* AOs, and six *d*-type CGTFs, for a total of 15 CGTFs per atom. Thus the total for the molecule is $10(2)+5(15)=95$.

(d) The 6-31G** set is formed from 6-31G* by adding three *p*-type functions to each H, so the molecule now has $95+10(3)=125$ CGTFs.

(e) The 6-31+G* set is formed from 6-31G* by adding four functions to each non-H, so the molecule now has $95+5(4)=115$ CGTFs.

(f) For a first-row atom such as C or O, the cc-pVTZ set is $4s3p2d1f$ and so has 4 + 3(3) + 2(5) + 1(7) = 30 CGTFs for such an atom. For an H atom, the cc-pVTZ set is $3s2p1d$ and so has 3 + 2(3) + 1(5) = 14 CGTFs. Thus for C_4H_9OH, there are 5(30) + 10(14) = 290 basis functions.

(g) For a first-row atom, the cc-pVQZ set is $5s4p3d2f1g$ and so has 5 + 4(3) + 3(5) + 2(7) + 9 = 55 CGTFs for such an atom. For an H atom, the cc-pVQZ set is $4s3p2d1f$ and so has 4 + 3(3) + 2(5) + 7 = 30 CGTFs. Thus for C_4H_9OH, there are 5(55) + 10(30) = 575 basis functions.

(h) For a first-row atom, the cc-pVDZ set is $3s2p1d$ and aug-cc-pVDZ increases the number of sets of functions for each *l* value by 1 to give $4s3p2d$, which means 4(1) + 3(3) + 2(5) = 23 CGTFs. For an H atom, the cc-pVDZ set is $2s1p$ and aug-cc-pVDZ increases the number of sets of functions for each *l* value by 1 to give $3s2p$, which means 3(1) + 2(3) = 9 CGTFs for each H. For C_4H_9OH, there are 5(23) + 10(9) = 205 basis functions.

15.6 **(a)** The minimal-basis AOs are 1*s* on each H; 1*s*, 2*s*, $2p_x, 2p_y, 2p_z$ on each O; and 1*s*, 2*s*, $2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z$ on each Si. The STO-3G set has 3 primitives for each minimal-basis AO and has one CGTF for each minimal-basis AO. The molecule has $24(9)+60(5)+24(1)=540$ CGTFs and $3(540)=1620$ primitives.

(b) In the 3-21G set, each inner-shell AO (in this case, the 1*s* AO of each O and the 1*s*, 2*s*, $2p_x, 2p_y, 2p_z$ AOs of Si) is represented by one CGTF (which consists of 3 primitives); each valence AO is represented by a linear combination of 2 CGTFs (one having 2 primitives and one having 1 primitive). Thus each H atom has 2 CGTFs and has

3 primitives. Each O has 1 + 2(4) = 9 CGTFs and has 3 + 3(4) = 15 primitives. Each Si has $5+2(4)=13$ CGTFs and has 3(5) + 3(4) = 27 primitives. The total number of CGTFs is $24(13)+60(9)+24(2)=900$. The total number of primitive Gaussians is $24(27)+60(15)+24(3)=1620$.

(c) In the 6-31G* set, each H has two *s*-type CGTFs (one of which consists of 3 primitives and one of which has 1 primitive). Each O atom has one *s*-type CGTF (which has 6 primitives) for the 1*s* AO, two *s*-type CGTFs (one with 3 primitives and one with 1 primitive) for the 2*s* AO, six *p*-type CGTFs (three having 3 primitives and three having 1 primitive) for the 2*p* AOs, and six *d*-type CGTFs (each having one primitive), for a total of 15 CGTFs and 28 primitives per oxygen. Each Si atom has one *s*-type CGTF (which has 6 primitives) for the 1*s* AO, one *s*-type CGTF (which has 6 primitives) for the 2*s* AO, three *p*-type CGTFs (each having 6 primitives) for the 2*p* AOs, two *s*-type CGTFs (one with 3 primitives and one with 1 primitive) for the 3*s* AO, six *p*-type CGTFs (three having 3 primitives and three having 1 primitive) for the 3*p* AOs, and six *d*-type CGTFs, for a total of 19 CGTFs and 52 primitives per Si atom. The total for the molecule is 24(19) + 60(15) + 24(2) = 1404 CGTFs and 24(52) + 60(28) + 24(4) = 3024 primitive Gaussians.

15.7 The CCCBDB at cccbdb.nist.gov gives these results: For HF/6-31G*, –56.184356 hartrees, 1.92 D, 1.002 Å for the NH distance, 107.2° for the HNH angle. For HF/cc-pVDZ, –56.195732 hartrees, 1.73 D, 1.008 Å, 105.9°.

15.8 The most convenient way to get most of the data at cccbdb.nist.gov is to click III Calculated Data, click D. 1. a., enter C4H10 as the formula, choose Anti, click on the HF/6-31G* energy (or the HF/cc-pVDZ energy), and you will get most of the HF/6-31G* (or cc-pVDZ) data for both conformers. Partial results follow.

For HF/6-31G* for the anti conformer:

–157.298409 hartrees, 0 D, 1.528 Å for the end CC distances, 1.529_5 Å for the middle CC distance, 1.086 Å and 1.086_5 Å for the end CH distances, 1.088 Å for the middle CH distances, 113.1° for the CCC angle, HCH angles ranging from 106.2° to 107.7°, CCH angles ranging from 109.2° to 111.3°, a CCCC dihedral of 180.0° (click on XII Geometries at the left; then click B. 1. and enter C4H10 and choose Anti; then click the HF/6-31G* box; then use the JMol model as follows: double click on an end carbon, single click on each of the next two carbons, and finally double click on the other end C).

For HF/6-31G* for the gauche conformer:

–157.296895 hartrees, 0.077 D, 1.530 Å for the end CC distances, 1.533 Å for the middle CC distance, 1.085 Å to 1.087 Å for the end CH distances, 1.088 and 1.087 Å for the middle CH distances, 114.4° for the CCC angle, HCH angles ranging from 106.2° to 107.7°, CCH angles ranging from 108.5° to 112.0°, a CCCC dihedral of 65.4°.

For HF/cc-pVDZ for the anti conformer:

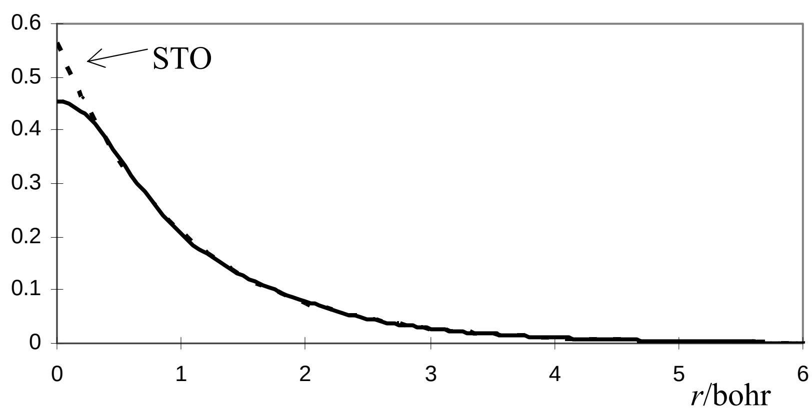
–157.310044 hartrees, 0 D, 1.526 Å for the end CC distances, 1.528 Å for the middle CC distance, 1.092 Å and 1.094 Å for the end CH distances, 1.096 Å for the middle CH distances, 113.3° for the CCC angle, HCH angles ranging from 106.1° to 107.7°, CCH angles ranging from 109.1° to 111.2°, a CCCC dihedral of 180.0°.

For HF/cc-pVDZ for the gauche conformer:
–157.308384 hartrees, 0.070 D, 1.528 Å for the end CC distances, 1.532 Å for the middle CC distance, 1.092 Å to 1.094 Å for the end CH distances, 1.094 and 1.096 Å for the middle CH distances, 114.7° for the CCC angle, HCH angles ranging from 106.1° to 107.7°, CCH angles ranging from 108.4° to 112.0°, a CCCC dihedral of 65.4°.

15.9 **(a)** $\int (S - G_{3N})^2\, d\tau = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}(S - G_{3N})^2 r^2 \sin\theta\, dr\, d\theta\, d\phi =$
$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty}(S - G_{3N})^2 r^2\, dr = 4\pi \int_0^{\infty}(S - G_{3N})^2 r^2\, dr$, since S and G_{3N} are functions of r only.

(b) We include the constraints that each orbital exponent be greater than 10^{-8}. If we start with the initial guesses 0.5, 1, and 2 for the orbital exponents and 1, 1, and 1 for the coefficients d_i and we use Options to set the Solver Tolerance to 10^{-12} and the Solver Convergence to 10^{-8} (so as to increase the accuracy of the results), the Excel Solver gives $\alpha_1 = 0.109815$, $\alpha_2 = 0.405755$, $\alpha_3 = 2.227534$, $c_1 = 0.444619$, $c_2 = 0.535335$, $c_3 = 0.154337$. The graph is shown on the next page, where the dashed line is the STO orbital and the solid line is the STO-3G function.

(c) For r between 0 and 0.35 bohr, the STO-3G function lies significantly below the STO. At other r values, the two functions are quite close to each other.



15.10 From (15.11), and the following equation, $G_i(r) = (2\alpha_i/\pi)^{3/4} e^{-\alpha_i r^2}$. Let $u \equiv \zeta r$. Then
$\sum_{i=1}^{3} c_i G_i(r, \zeta) = \sum_{i=1}^{3} c_i (2\alpha_i \zeta^2/\pi)^{3/4} e^{-\alpha_i \zeta^2 r^2} = \zeta^{3/2} \sum_{i=1}^{3} c_i (2\alpha_i/\pi)^{3/4} e^{-\alpha_i u^2} =$
$\zeta^{3/2} \sum_{i=1}^{3} c_i G_i(u) \approx \zeta^{3/2} S(u) = \zeta^{3/2}\pi^{-1/2} e^{-u} = \zeta^{3/2}\pi^{-1/2} e^{-\zeta r} \equiv S(r, \zeta)$.

15.11 **(a)** Using the information in the Sec. 15.4 example to interpret the results, we find the 1*s* CGTOs for H to be

$1s' = 0.0334946g_s(18.731137) + 0.23472695g_s(2.8253937) + 0.81375733g_s(0.6401217)$

$1s'' = g_s(0.1612778)$

where the orbital exponents are in parentheses. The polarization functions on H are $g_{p_x}(1.10),\ g_{p_y}(1.10),\ g_{p_z}(1.10)$.

(b) We find

$1s = 0.0018347g_s(3047.5249) + 0.0140373g_s(457.36951) + 0.0688426g_s(103.94869) +$
$\quad 0.2321844g_2(29.210155) + 0.4679413g_s(9.286663) + 0.362312g_s(3.163927)$

$2s' = -0.1193324g_s(7.8682724) - 0.1608542g_s(1.8812885) + 1.1434564g_s(0.5442493)$

$2s'' = g_s(0.1687144)$

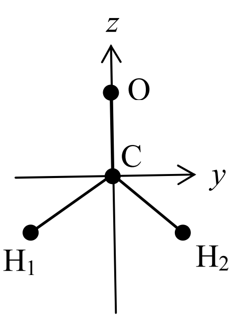
$2p'_x = 0.0689991g_{p_x}(7.8682724) + 0.316424g_{p_x}(1.8812885) + 0.7443083g_{p_x}(0.5442493)\ldots$

$2p''_x = g_{p_x}(0.1687144)\ldots$

where the dots indicate $2p_y$ and $2p_z$ functions. The polarization functions are $g_{d_{xy}}(0.800)$,…, where the dots indicate five other *d*-type functions.

15.12 These two sets differ only in that 6-31G** has additional functions on H and He. Hence for any molecule without H or He atoms, these basis sets are the same and give the same energy. Some possible answers are CO_2, C_2Cl_6, NO_2, and PCl_3.

15.13 **(a)** The molecular point group is $\mathcal{C}_{2v}$. The symmetry species are given by (15.3). For H_2CO, the minimal-basis AOs are $H_1 1s$, $H_2 1s$, C1*s*, C2*s*, C2p_x, C2p_y, C2p_z, O1*s*, O2*s*, O2p_x, O2p_y, O2p_z. The *z* axis coincides with the C_2 axis through the double bond, and we take the *x* axis as perpendicular to the molecular plane.



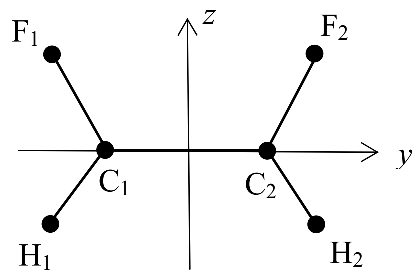
As in H_2O, $H_1 1s$ and $H_2 1s$ are transformed into each other by $\hat{C}_2(z)$ and are not eigenfunctions of $\hat{O}_{C_2(z)}$. We form symmetry orbitals as $H_1 1s + H_2 1s$ and $H_1 1s - H_2 1s$. The function $H_1 1s + H_2 1s$ is unchanged by each of the four symmetry operations and belongs to the totally symmetric species a_1. The function $H_1 1s - H_2 1s$ is unchanged by $\hat{E}$ and by $\hat{\sigma}_v(yz)$ and is multiplied by –1 by $\hat{C}_2(z)$ and by $\hat{\sigma}_v(xz)$, so it belongs to species b_2. The C1s, C2s, C2p_z, O1s, O2s, and O2p_z orbitals are unchanged by each of the symmetry operations and so belong to a_1. Each $2p_x$ AO on C and on O is unchanged by $\hat{E}$ and by $\hat{\sigma}_v(xz)$ and is multiplied by –1 by $\hat{C}_2(z)$ and by $\hat{\sigma}_v(yz)$, and their symmetry species is b_1. Each $2p_y$ AO on C and on O is unchanged by $\hat{E}$ and by $\hat{\sigma}_v(yz)$ and is multiplied by –1 by $\hat{C}_2(z)$ and by $\hat{\sigma}_v(xz)$, and their symmetry species is b_2.

(b) π MOs change sign on reflection in the molecular yz plane. The only minimal-basis symmetry orbitals that change sign on reflection in the molecular plane are $\mathrm{C}2p_x$ and $\mathrm{O}2p_x$. These two basis functions will give rise to two canonical π MOs. The remaining 10 σ symmetry orbitals will give rise to 10 σ canonical MOs. The canonical π MOs are linear combinations of the π symmetry orbitals and have the forms $c_1\mathrm{C}2p_x + c_2\mathrm{O}2p_x$ and $c_3\mathrm{C}2p_x - c_4\mathrm{O}2p_x$, where the c's are positive. In the ground electronic state, the bonding π MO $c_1\mathrm{C}2p_x + c_2\mathrm{O}2p_x$ will be occupied by two electrons and the antibonding π MO $c_3\mathrm{C}2p_x - c_4\mathrm{O}2p_x$ will be vacant. The molecule has 16 electrons, and the 14 electrons not in the bonding π MO will occupy 7 canonical σ MOs. (The symmetry species a and b indicate that all MOs in this molecule belong to orbitally nondegenerate electronic levels.)

(c) The 8 occupied energy-localized MOs are as follows. An inner-shell orbital on C that has a significant contribution from only C1s; an inner-shell orbital on O that is largely O1s; two lone-pair orbitals on oxygen, each of which is a combination of O2p_y, O2p_z, and O2s; a b($\mathrm{CH_1}$) bonding orbital that is mainly a combination of $\mathrm{H_1}1s$, C2s, C2p_z, and C2p_y; a b($\mathrm{CH_2}$) bonding orbital that is mainly a combination of $\mathrm{H_2}1s$, C2s, C2p_z, and C2p_y; a bonding σ b(CO) orbital that is composed mainly of C2s, C2p_z, O2s, and O2p_z; a bonding π MO that is composed of C2p_x and O2p_x, where it was assumed that the localized MOs for the C to O bonds are the traditional σ, π orbitals. If the double-bond localized MOs turn out to be the "banana" bonds, we have two bonding b(CO) localized orbitals, each of which is formed mainly from C2s, C2p_z, C2p_x, O2s, O2p_z, O2p_x.

(d) From part (a), there are 7 minimal-basis symmetry orbitals with a_1 symmetry, and the maximum-size secular determinant is 7 by 7.

15.14 The molecular point group is $\mathcal{C}_{2v}$. The symmetry species are given by (15.3). The minimal-basis AOs are $\mathrm{H_1}1s$, $\mathrm{H_2}1s$, $\mathrm{C_1}1s$, $\mathrm{C_1}2s$, $\mathrm{C_1}2p_x$, $\mathrm{C_1}2p_y$, $\mathrm{C_1}2p_z$, $\mathrm{C_2}1s$, $\mathrm{C_2}2s$, $\mathrm{C_2}2p_x$, $\mathrm{C_2}2p_y$, $\mathrm{C_2}2p_z$, $\mathrm{F_1}1s$, $\mathrm{F_1}2s$, $\mathrm{F_1}2p_x$, $\mathrm{F_1}2p_y$, $\mathrm{F_1}2p_z$, $\mathrm{F_2}1s$, $\mathrm{F_2}2s$, $\mathrm{F_2}2p_x$, $\mathrm{F_2}2p_y$, $\mathrm{F_2}2p_z$. The z axis coincides with the C_2 axis and we take the x axis as perpendicular to the molecular plane:



As in H_2O, $H_1 1s$ and $H_2 1s$ are transformed into each other by $\hat{C}_2(z)$ and are not eigenfunctions of $\hat{O}_{C_2(z)}$. We form symmetry orbitals as $H_1 1s + H_2 1s$ and $H_1 1s - H_2 1s$. The function $H_1 1s + H_2 1s$ is unchanged by each of the four symmetry operations and belongs to the totally symmetric species a_1. The function $H_1 1s - H_2 1s$ is unchanged by $\hat{E}$ and by $\hat{\sigma}_v(yz)$ and is multiplied by –1 by $\hat{C}_2(z)$ and by $\hat{\sigma}_v(xz)$, so it belongs to species b_2. We form the other symmetry orbitals by taking similar combinations of the AOs on C_1 and C_2, and of the AOs on F_1 and F_2, and we examine the effects of the symmetry operations on these symmetry orbitals. Consider for example, the symmetry orbital $F_1 2p_x + F_2 2p_x$. The AO $F_1 2p_x$ is transformed to $-F_2 2p_x$ by $\hat{C}_2(z)$, is transformed to $F_2 2p_x$ by $\hat{\sigma}(xz)$, and is transformed to $-F_1 2p_x$ by $\hat{\sigma}(yz)$. Therefore $F_1 2p_x + F_2 2p_x$ is unchanged by $\hat{E}$; is changed to $-F_2 2p_x - F_1 2p_x = -(F_1 2p_x + F_2 2p_x)$ by $\hat{C}_2(z)$, is unchanged by $\hat{\sigma}(xz)$, and is changed to $-(F_1 2p_x + F_2 2p_x)$ by $\hat{\sigma}(yz)$. The symmetry species of $F_1 2p_x + F_2 2p_x$ is thus b_1. Proceeding similarly with the other symmetry orbitals, we find these results, where the y axis is taken to point to the right for all nuclei:

$H_1 1s + H_2 1s$	$H_1 1s - H_2 1s$	$F_1 1s + F_2 1s$	$F_1 1s - F_2 1s$	$C_1 1s + C_2 1s$	$C_1 1s - C_2 1s$
a_1	b_2	a_1	b_2	a_1	b_2

$F_1 2s + F_2 2s$	$F_1 2s - F_2 2s$	$C_1 2s + C_2 2s$	$C_1 2s - C_2 2s$	$F_1 2p_x + F_2 2p_x$
a_1	b_2	a_1	b_2	b_1

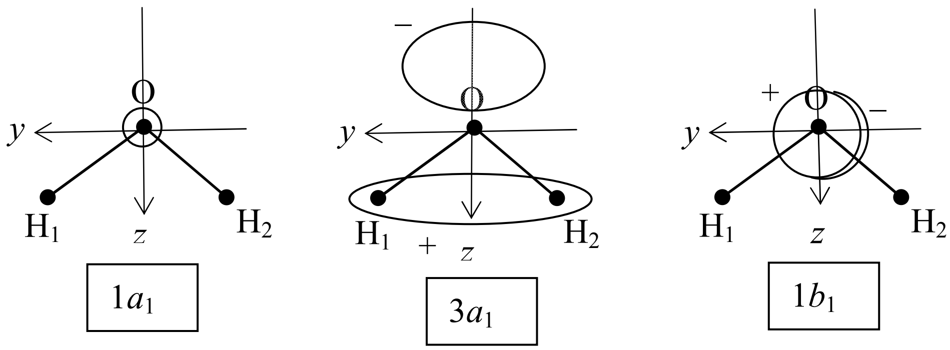
$F_1 2p_x - F_2 2p_x$	$C_1 2p_x + C_2 2p_x$	$C_1 2p_x - C_2 2p_x$	$F_1 2p_y + F_2 2p_y$	$F_1 2p_y - F_2 2p_y$
a_2	b_1	a_2	b_2	a_1

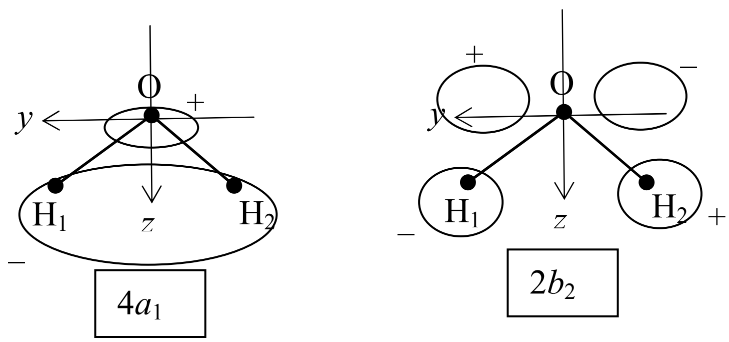
$C_1 2p_y + C_2 2p_y$	$C_1 2p_y - C_2 2p_y$	$F_1 2p_z + F_2 2p_z$	$F_1 2p_z - F_2 2p_z$

b_2	a_1	a_1	b_2

$C_1 2p_z + C_2 2p_z$	$C_1 2p_z - C_2 2p_z$
a_1	b_2

15.15 Using the MOs (15.19), (15.22), and Fig. 15.2, we have





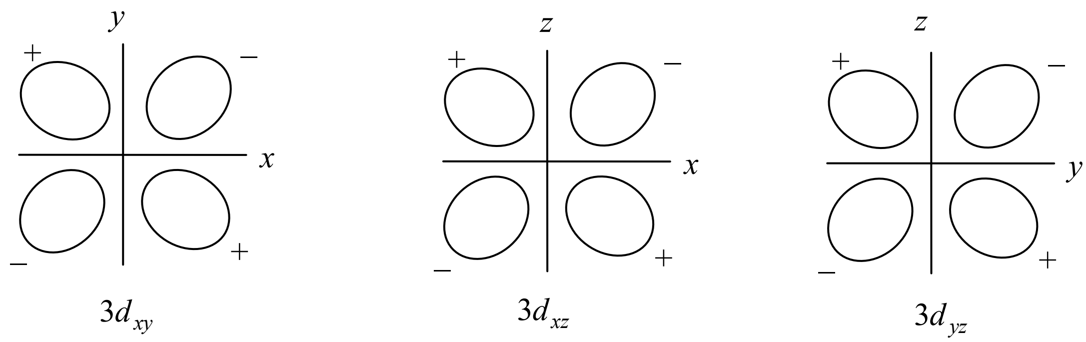
15.16 $1 = N\int(\mathrm{H}_1 1s \pm \mathrm{H}_2 1s)^2\,d\tau = N[\int(\mathrm{H}_1 1s)^2\,d\tau + \int(\mathrm{H}_2 1s)^2\,d\tau \pm 2\int(\mathrm{H}_1 1s)(\mathrm{H}_2 1s)\,d\tau] =$ $N(2 \pm 2S_{12})$ and $N = 2^{-1/2}(1 \pm S_{12})^{-1/2}$, where S_{12} is the overlap integral.

15.17 For choice c, M^-, the MO of an excited electron would be best approximated by a virtual orbital of M. All the MOs that are filled in M are filled in the excited state of M^-, so the virtual Hartree–Fock orbitals calculated for M are appropriate for use as occupied excited MOs of M^-.

15.18 We shall calculate the energy of the ion M^+ at the equilibrium geometry of the ground-state uncharged molecule M. When a ground-state molecule M is ionized, the process is so fast that the relatively heavy nuclei do not have time to adjust their locations to the equilibrium geometry of M^+, so it most probable for M^+ to be formed at a geometry close to that of ground-state M. The energy difference between M^+ and M with both species at the ground-state equilibrium geometry of M is called the *vertical ionization energy*, and it is this ionization energy that Koopmans' theorem refers to. Since the two species have the same geometry, the V_{NN} nuclear-repulsion term cancels when the energy difference is taken. Both the closed-shell species M and the ion M^+ have single-determinant Hartree–Fock wave functions, so we use (11.80), where the sums go over the occupied spin-orbitals. We assume that the MOs do not change on going from M to M^+ at the same geometry as M. The ion M^+ has one less spin-orbital than M. If the electron is removed from MO *k*, then for M^+, the term $\langle\theta_k(1)\,|\,\hat{f}_1\,|\,\theta_k(1)\rangle$ is missing from the first sum in (11.80), and all terms with *i* or *j* equal to *k* are missing from the second sum in (11.80). Let $M_{ij} \equiv J_{ij} - \delta_{m_{s,i}m_{s,j}}K_{ij}$. Then for M^+, the terms $M_{1k}, M_{2k}, \ldots, M_{k-1,k}, M_{k,k+1}, M_{k,k+2}, \ldots, M_{k,n}$ are missing from the energy expression. The Hartree–Fock energy difference $E_{HF}(\mathrm{M}^+) - E_{HF}(\mathrm{M})$ is therefore equal to minus the sum of the missing terms: $E_{HF}(\mathrm{M}^+) - E_{HF}(\mathrm{M}) = -\langle\theta_k(1)\,|\,\hat{f}_1\,|\,\theta_k(1)\rangle - \sum_{i=1}^{n} M_{ki}$ (Eq. 1), where we used $M_{ik} = M_{ki}$, which follows from $J_{ij} = J_{ji}$ and $K_{ij} = K_{ji}$ [Eq. (11.84)]. The sum $\sum_{i=1}^{n} M_{ki} = \sum_{i=1}^{n}(J_{ki} - \delta_{m_{s,k}m_{s,i}}K_{ki})$ involves the spatial orbitals of the *n* occupied spin-orbitals of the closed-shell species M. The *n* electrons reside in *n*/2 different spatial orbitals, so $\theta_1 = \theta_2, \theta_3 = \theta_4, \ldots$, etc. Hence $J_{k1} = J_{k2}, J_{k3} = J_{k4}, \ldots, J_{k,n-1} = J_{kn}$. If we define $\phi_1 \equiv \theta_1 = \theta_2, \phi_2 \equiv \theta_3 = \theta_4, \ldots, \phi_{n/2} \equiv \theta_{n-1} = \theta_n$, then for the *J* integrals, we can replace the sum over $\theta_1, \ldots, \theta_n$ with a sum over $\phi_1, \ldots, \phi_{n/2}$ if we multiply each *J* by 2. From (11.82) and (14.27), we have $\hat{f}_1 = \hat{H}^{\text{core}}(1)$, so $\langle\theta_k(1)\,|\,\hat{f}_1\,|\,\theta_k(1)\rangle = H_{kk}^{\text{core}}$ [Eq. (14.23)]. The orbitals $\theta_1, \theta_3, \theta_5, \ldots$ have the spin function α and the orbitals $\theta_2, \theta_4, \theta_6, \ldots$ have the spin function β. The Kronecker delta in $\delta_{m_{s,i}m_{s,j}}K_{ki}$ in the sum will thus alternate between 0 and 1 as we sum over *i*, and for the *K* integrals, we can replace the sum over $\theta_1, \ldots, \theta_n$ with a sum over $\phi_1, \ldots, \phi_{n/2}$. Therefore Eq. 1 becomes $E_{HF}(\mathrm{M}^+) - E_{HF}(\mathrm{M}) = -H_{kk}^{\text{core}} - \sum_{i=1}^{n/2}(2J_{ki} - K_{ki})$. Comparison with Eq. (14.30) gives $E_{HF}(\mathrm{M}^+) - E_{HF}(\mathrm{M}) = -\varepsilon_k$, which is Koopmans' theorem.

15.19 The minimal-basis AOs are $\mathrm{H_1}1s$ and $\mathrm{H_2}1s$, and the symmetry orbitals are $\mathrm{H_1}1s + \mathrm{H_2}1s$ and $\mathrm{H_1}1s - \mathrm{H_2}1s$.

15.20 From Figs. 15.1 and 6.13, we see that each of the four symmetry operations leaves $3d_{z^2}$ unchanged and leaves $3d_{x^2-y^2}$ unchanged, so these two AOs have symmetry species a_1. From the discussion on p. 146 of the text, the other *d* orbitals look like this:



We find the effects of the symmetry operators on these three AOs to be

	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_\upsilon(xz)$	$\hat{\sigma}_\upsilon(yz)$	
$3d_{xy}$	1	1	–1	–1	a_2
$3d_{xz}$	1	–1	1	–1	b_1
$3d_{yz}$	1	–1	–1	1	b_2

Therefore the $3d_{z^2}$ and $3d_{x^2-y^2}$ AOs contribute to the $1a_1$, $2a_1$, and $3a_1$ MOs in (15.19), the $3d_{xz}$ MO contributes to the $1b_1$ MO, and the $3d_{yz}$ AO contributes to the $1b_2$ MO.

15.21 **(a)** Subtraction of the $n = 3$ equation from the $n = 4$ equation and the $n = 5$ equation gives $E_{\text{SCF}}(4) - E_{\text{SCF}}(3) = A(e^{-4B} - e^{-3B})$ and $E_{\text{SCF}}(5) - E_{\text{SCF}}(3) = A(e^{-5B} - e^{-3B})$. Dividing the second equation by the first to eliminate A, we get

$$\frac{E_{\text{SCF}}(5) - E_{\text{SCF}}(3)}{E_{\text{SCF}}(4) - E_{\text{SCF}}(3)} = \frac{e^{-5B} - e^{-3B}}{e^{-4B} - e^{-3B}} = \frac{-76.06778 + 76.05777}{-76.06552 + 76.05777} = 1.291_6$$

Defining $x \equiv e^{-B}$, we get
$(x^5 - x^3)/(x^4 - x^3) = (x^2 - 1)/(x - 1) = (x + 1)(x - 1)/(x - 1) = x + 1 = 1.2916$, so
$x = 0.2916$. Then $B = -\ln x = 1.232$. (The Excel Solver can also be used to find B.) Then $E_{\text{SCF}}(4) - E_{\text{SCF}}(3) = A(e^{-4B} - e^{-3B})$ and $-76.06552 + 76.05777 = A(-0.017582)$, so $A = 0.4408$. Substitution in (15.23) with $n = 5$ gives
$-76.06778 = E_{\text{SCF}}(\infty) + 0.4408e^{-1.232(5)}$ and $E_{\text{SCF}}(\infty) = -76.0687$.

(b) Using the Excel Solver, one finds that the optimum A and B values are nearly unchanged from those in (a), and $E_{\text{SCF}}(\infty) = -76.0686$.

15.22 **(a)** The L values are 4 and 5 for these two basis sets. Subtraction of (15.88) with $n = 5$ from (15.88) with $n = 4$ gives $E_{\text{SCF}}(\text{aug-4}) - E_{\text{SCF}}(\text{aug-5}) = 5Ae^{-9\sqrt{4}} - 6Ae^{-9\sqrt{5}}$, so

$(-76.066676 + 76.068009)E_\mathrm{h} = A(6.52319 \times 10^{-8})$ and $A = 20435\ E_\mathrm{h}$, where $E_\mathrm{h} = 1$ hartree. Substitution in Eq. (15.88) with $n = 4$ gives

$-76.066676\ E_\mathrm{h} = E_\mathrm{SCF}(\infty) + (20435\ E_\mathrm{h})5e^{-9\sqrt{4}}$ and $E_\mathrm{SCF}(\infty) = -76.06823\ E_\mathrm{h}$.

(b) $E_\mathrm{SCF}(\text{aug-5}) - E_\mathrm{SCF}(\text{aug-6}) = 6Ae^{-9\sqrt{5}} - 7Ae^{-9\sqrt{6}}$ so $(-76.068009 + 76.068153)E_\mathrm{h} = A(9.05206 \times 10^{-9})$ and $A = 15908 E_\mathrm{h}$. From (15.88) with $n = 5$, $-76.068009\ E_\mathrm{h} = E_\mathrm{SCF}(\infty) + (15908\ E_\mathrm{h})6e^{-9\sqrt{5}}$ and $E_\mathrm{SCF}(\infty) = -76.06818\ E_\mathrm{h}$, as compared with $E_\mathrm{SCF}(\infty) = -76.0683\ E_\mathrm{h}$ listed in the table.

15.23 **(a)** This expression is just Eq. (15.24) written using sum notation.

(b) Use of the definitions in the equations after (15.25) followed by use of (15.25) gives $\sum_r n_r + \sum_{r>s} \sum_s n_{r\text{-}s} = \sum_r \sum_i n_{r,i} + \sum_{r>s} \sum_s \sum_i n_{r\text{-}s,i} =$
$\sum_r \sum_i n_i c_{r,i}^2 + 2\sum_{r>s} \sum_s \sum_i n_i c_{ri} c_{si} S_{rs} = \sum_i n_i (\sum_r c_{r,i}^2 + 2\sum_{r>s} \sum_s c_{ri} c_{si} S_{rs}) = \sum_i n_i = n$, where the result of part (a) was used.

15.24 The reference of Prob. 15.29c (hereafter referred to as MROO) tabulates values of the overlap integral $\langle \chi_a \mid \chi_b \rangle$ between STOs with orbital exponents ζ_a and ζ_b separated by a distance R_{ab} (in bohrs) in terms of the defined parameters

$$p \equiv \tfrac{1}{2}(\zeta_a + \zeta_b)R_{ab} \quad \text{and} \quad t \equiv (\zeta_a - \zeta_b)/(\zeta_a + \zeta_b).$$

In these tables, χ_a in $\langle \chi_a \mid \chi_b \rangle$ must be the AO with the smaller value of the quantum number *n*, or if the two *n* values are equal, χ_a must have the greater orbital exponent. The MOs (15.19) are calculated at the experimental geometry $R_\mathrm{OH} = 0.958$ Å = 1.81 bohr, $\theta = 104.5° = 1.824$ rad. The H–H distance R_HH is found from $\sin(\theta/2) = \frac{1}{2}R_\mathrm{HH}/R_\mathrm{OH}$, so $R_\mathrm{HH} = 2(1.81\ \text{bohr})\sin(1.824/2) = 2.86$ bohr. The orbital exponents are [see the paragraph preceding Eq. (15.18)]

$$\zeta_{\mathrm{H}1s} = 1.27,\ \zeta_{\mathrm{O}1s} = 7.66,\ \zeta_{\mathrm{O}2s} = 2.25,\ \zeta_{\mathrm{O}2p} = 2.21.$$

For $\langle \mathrm{O}1s \mid \mathrm{H}_1 1s \rangle$, $p = \frac{1}{2}(7.66 + 1.27)1.81 = 8.08$, $t = (7.66 - 1.27)/(7.66 + 1.27) = 0.716$. The MROO tables give the following $\langle 1s \mid 1s \rangle$ values: 0.054 at $p = 8.0$, $t = 0.7$; 0.059 at $p = 8.0$, $t = 0.8$; 0.040 at $p = 9.0$, $t = 0.7$. To allow for the increase in *t*, we add (0.016/0.1)(0.059 – 0.054) = 0.001 to the 0.054 value. To allow for the increase in *p*, we add (0.08/1)(0.040 – 0.054) = –0.001 to the 0.054 value. Thus $\langle \mathrm{O}1s \mid \mathrm{H}_1 1s \rangle$ = 0.054 + 0.001 – 0.001 = 0.054.

For $\langle \mathrm{H}_1 1s \mid \mathrm{H}_1 1s \rangle$, $p = \frac{1}{2}(1.27 + 1.27)2.86 = 3.63$, $t = 0$. The MROO tables give these $\langle 1s \mid 1s \rangle$ values at $t = 0$: 0.244 at $p = 3.6$, 0.215 at $p = 3.8$. Interpolation gives $\langle \mathrm{H}_1 1s \mid \mathrm{H}_1 1s \rangle$ = 0.240.

The MROO tables are for nonorthogonalized STOs, so we need to use (13.124) and the formula in Prob. 13.37c to write

$\langle \mathrm{O}1s \mid \mathrm{O}2s\rangle = 24(7.66)^{3/2}(2.25)^{5/2}/3^{1/2}(7.66+2.25)^4 = 0.2313$ and

$\mathrm{O}2s_\perp = [1-(0.2313)^2]^{-1/2}(\mathrm{O}2s - 0.2313\cdot \mathrm{O}1s) = 1.028\cdot \mathrm{O}2s - 0.2377\cdot \mathrm{O}1s$.

Then $\langle \mathrm{H}_1 1s \mid \mathrm{O}2s_\perp\rangle = 1.028\langle \mathrm{H}_1 1s \mid \mathrm{O}2s\rangle - 0.2377\langle \mathrm{H}_1 1s \mid \mathrm{O}1s\rangle$.

For $\langle \mathrm{H}_1 1s \mid \mathrm{O}2s\rangle$, $p = \frac{1}{2}(1.27+2.25)1.81 = 3.19$, $t = (1.27-2.25)/(1.27+2.25) = -0.278$.

The MROO tables give the following $\langle 1s \mid 2s\rangle$ values: 0.468 at $p = 3.2$, $t = -0.3$; 0.508 at $p = 3.0$, $t = -0.3$; 0.464 at $p = 3.2$, $t = -0.2$. So

$\langle \mathrm{H}_1 1s \mid \mathrm{O}2s\rangle = 0.468 + 0.002 - 0.001 = 0.469$. As found above, $\langle \mathrm{O}1s \mid \mathrm{H}_1 1s\rangle = 0.054$. So

$\langle \mathrm{H}_1 1s \mid \mathrm{O}2s_\perp\rangle = 1.028\langle \mathrm{H}_1 1s \mid \mathrm{O}2s\rangle - 0.2377\langle \mathrm{H}_1 1s \mid \mathrm{O}1s\rangle = 1.028(0.469) - 0.2377(0.054) =$ 0.469.

The MROO tables give values of $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle$ and $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\pi\rangle$; here the $2p\sigma$ AO is a $2p_{y'}$ AO on O, where the y' axis is along the OH_1 bond and points toward H_1; the $2p\pi$ AO is a $2p_{z'}$ AO on O, where the z' axis is in the molecular plane and is perpendicular to the OH_1 line. We use modified versions of Fig. 15.6 and Eq. (15.40) with *y* and *z* interchanged. In the modified Fig. 15.6, $\alpha = \frac{1}{2}(180° - 104.5°) = 37.7_5°$. The $2p_y$ and $2p_z$ AOs are proportional to *y* and *z*, respectively, and multiplication of the modified equations in (15.40) by the exponential part of a 2*p* AO gives

$2p_{y'} = 2p\sigma = 2p_y\cos\alpha + 2p_z\sin\alpha$ and $2p_{z'} = 2p\pi = -2p_y\sin\alpha + 2p_z\cos\alpha$.

From these two equations, we get

$2p_y = 2p\sigma\cos\alpha - 2p\pi\sin\alpha = 0.7907(2p\sigma) - 0.6122(2p\pi)$

$2p_z = 2p\sigma\sin\alpha + 2p\pi\cos\alpha = 0.6122(2p\sigma) + 0.7907(2p\pi)$

Then $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p_y\rangle = 0.7907\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle - 0.6122\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\pi\rangle$. The overlap of the negative half of O2*pπ* with $\mathrm{H}_1 1s$ cancels the overlap of the positive half of O2*pπ* with $\mathrm{H}_1 1s$, so $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\pi\rangle = 0$. For $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle$, $p = \frac{1}{2}(1.27+2.21)1.81 = 3.15$, $t = (1.27-2.21)/(1.27+2.21) = -0.270$. The MROO tables give the following $\langle 1s \mid 2p\sigma\rangle$ values: 0.382 at $p = 3.2$, $t = -0.3$; 0.402 at $p = 3.0$, $t = -0.3$; 0.432 at $p = 3.2$, $t = -0.2$. So $\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle = 0.382 + 0.005 + 0.015 = 0.402$ and

$\langle \mathrm{H}_1 1s \mid \mathrm{O}2p_y\rangle = 0.7907\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle = 0.318$. Finally,

$\langle \mathrm{H}_1 1s \mid \mathrm{O}2p_z\rangle = 0.6122\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle - 0.7907\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\pi\rangle = 0.6122\langle \mathrm{H}_1 1s \mid \mathrm{O}2p\sigma\rangle =$ $0.6122(0.402) = 0.246$.

15.25 **(a)** From the equation after (15.25), Eq. (15.25), and the MOs (15.19),

$n_{\mathrm{O}2s_\perp} = \sum_i n_{\mathrm{O}2s_\perp,i} = \sum_i n_i c^2_{\mathrm{O}2s_\perp,i} = 2(0.015)^2 + 2(0.820)^2 + 2(-0.502)^2 = 1.85$;

$n_{\mathrm{O}2p_x} = \sum_i n_i c^2_{\mathrm{O}2p_x,i} = 2(1)^2 = 2$; $n_{\mathrm{O}2p_y} = \sum_i n_i c^2_{\mathrm{O}2p_y,i} = 2(0.624)^2 = 0.78$;

$n_{\mathrm{O}2p_z} = \sum_i n_i c^2_{\mathrm{O}2p_z,i} = 2(0.003)^2 + 2(0.132)^2 + 2(0.787)^2 = 1.27$;

$n_{\mathrm{H_1}1s} = \sum_i n_i c^2_{\mathrm{H_1}1s,i} = 2(-0.004)^2 + 2(0.152)^2 + 2(0.424)^2 + 2(0.264)^2 = 0.54_5$;

$n_{\mathrm{H_2}1s} = \sum_i n_i c^2_{\mathrm{H_2}1s,i} = 2(-0.004)^2 + 2(0.152)^2 + 2(-0.424)^2 + 2(0.264)^2 = 0.54_5$.

(b) To find the interatomic overlap population, we take the sum of those $n_{r\text{-}s,i}$ values for basis functions *r* and *s* that lie on different atoms, using (15.25) and the overlap integrals in the Sec. 15.6 example. For $2a_1$, we have 2(2)(–0.027)0.152(0.054) + 2(2)(–0.027)0.152(0.054) + 2(2)(0.820)0.152(0.471) + 2(2)(0.820)0.152(0.471) + 2(2)0.132(0.152)0.247 + 2(2)0.132(0.152)0.247 + 2(2)0.152(0.152)0.238 = 0.53. For $1b_2$, we have 2(2)0.624(0.424)0.319 + 2(2)0.624(–0.424)(–0.319) + 2(2)0.424(–0.424)0.238 = 0.50.

(c) The contribution of MO *i* to the gross population in the basis function χ_r is given by $N_{r,i} = n_{r,i} + \frac{1}{2}\sum_{s\neq r} n_{r\text{-s}} = n_i c^2_{r,i} + \frac{1}{2} n_i \sum_{s\neq r}(2c_{ri}c_{si}S_{rs})$ [see the equation for N_r on p. 458 and (15.25)]. Since we are using an orthogonalized 2*s* AO, S_{rs} is zero for two different AOs both on O. From (15.19), the contributions to the gross population of $\mathrm{O}_{2s_\perp}$ are

$N_{\mathrm{O}2s_\perp,1a_1} = 2(0.015)^2 + 2(0.015)(-0.004)0.471(2) = 0.000$

$N_{\mathrm{O}2s_\perp,2a_1} = 2(0.820)^2 + 2(0.820)(0.152)0.471(2) = 1.580$

$N_{\mathrm{O}2s_\perp,3a_1} = 2(-0.502)^2 + 2(-0.502)(0.264)0.471(2) = 0.254$

Summing these contributions, we find $N_{\mathrm{O}2s_\perp} = 1.83$. Also,

$N_{\mathrm{O}1s,1a_1} = 2(1.000)^2 + 2(1.000)(-0.004)0.054(2) = 2.001$

$N_{\mathrm{O}1s,2a_1} = 2(-0.027)^2 + 2(-0.027)(0.152)0.054(2) = 0.001$

$N_{\mathrm{O}1s,3a_1} = 2(-0.026)^2 + 2(-0.026)(0.264)0.054(2) = 0.000$

Summing these contributions, we find $N_{\mathrm{O}1s} = 2.00$. Then

$N_{\mathrm{O}2p_x,1b_1} = 2(1)^2 = 2.000 = N_{\mathrm{O}2p_x}$

$N_{\mathrm{O}2p_y,1b_2} = 2(0.624)^2 + 2(0.624)0.424(0.319) + 2(0.624)(-0.424)(-0.319) = 1.116 = N_{\mathrm{O}2p_y}$

$N_{\mathrm{O}2p_z,1a_1} = 2(0.003)^2 + 2(0.003)(-0.004)0.247(2) = 0.000$

$N_{\mathrm{O}2p_z,2a_1} = 2(0.132)^2 + 2(0.132)(0.152)0.247(2) = 0.055$

$N_{\mathrm{O}2p_z,3a_1} = 2(0.787)^2 + 2(0.787)(0.264)0.247(2) = 1.444$

Summing these contributions, we find $N_{\mathrm{O}2p_z} = 1.50$.

$$N_{\mathrm{H_1}1s,1a_1} = 2(-0.004)^2 - 2(0.004)(1.000)0.054 - 2(0.004)(0.015)0.471 - 2(0.004)(0.003)0.247 - 2(0.004)(-0.004)0.238 = 0.000.$$

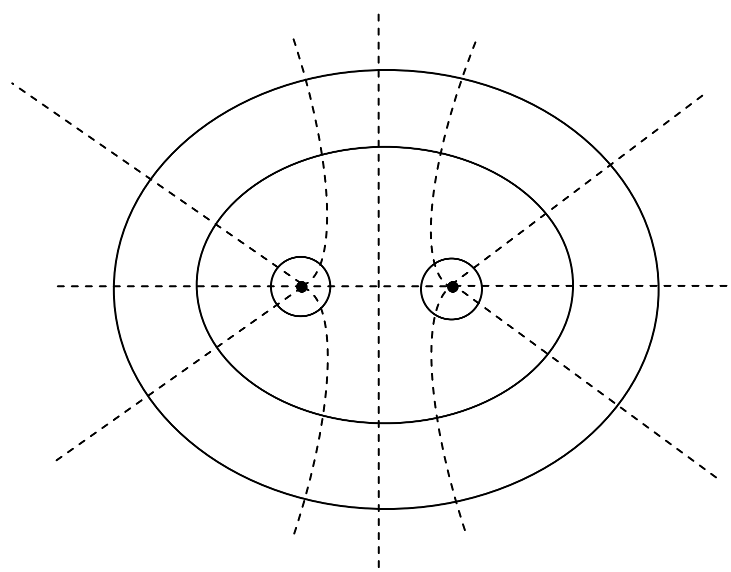
$$N_{\mathrm{H_1}1s,2a_1} = 2(0.152)^2 + 2(0.152)(-0.027)0.054 + 2(0.152)(0.820)0.471 + 2(0.152)(0.132)0.247 + 2(0.152)0.152(0.238) = 0.184.$$

$$N_{\mathrm{H_1}1s,3a_1} = 2(0.264)^2 + 2(0.264)(-0.026)0.054 + 2(0.264)(-0.502)0.471 + 2(0.264)(0.787)0.247 + 2(0.264)0.264(0.238) = 0.150.$$

$N_{\mathrm{H}_1 1s,1b_2} = 2[(0.424)^2 + 0.424(0.624)0.319 + 0.424(-0.424)0.238] = 0.443.$
Summing these contributions, we find $N_{\mathrm{H}_1 1s} = 0.77_7 = N_{\mathrm{H}_2 1s}$.

15.26 Suppose Q and Q_t have the same sign. Imagine that we reversibly push Q_t toward Q (which is located at the origin) along the *x* axis, starting at $x = \infty$ and ending at $x = d$. Reversibility means that we exert a force that differs only infinitesimally from the electrical repulsive force between the charges. The infinitesimal work *dw* we do when we displace Q_t by *dx* is $dw = F\,dx$, where *F* is the force we exert on Q_t. *F* is in the negative *x* direction and *dx* is negative, so *dw* is positive. Since *F* is in the negative *x* direction and QQ_t is positive, we have $F = -QQ_t/4\pi\varepsilon_0 x^2$ and $dw = -(QQ_t/4\pi\varepsilon_0 x^2)\,dx$. Summing up the infinitesimal elements *dw*, we get *w* as a definite integral. So
$\phi_\mathrm{P} = w_{\infty\to\mathrm{P}}/Q_t = \int_\infty^d F\,dx\,/\,Q_t = -\int_\infty^d [QQ_t/4\pi\varepsilon_0 x^2]\,dx\,/\,Q_t = (Q/4\pi\varepsilon_0)(x^{-1})\,|_\infty^d = Q/4\pi\varepsilon_0 d$.
If Q and Q_t have the opposite sign, then they attract each other, and we have to exert a force in the positive *x* direction; the expression $F = -QQ_t/4\pi\varepsilon_0 x^2$ is still valid here, since QQ_t is now negative and *F* is now in the positive *x* direction. Thus we get the same result.

15.27 Gradient paths are perpendicular to the surfaces of constant probability density.



15.28 Interchanging the *x* and *z* axes relabels the *xy* plane as the *yz* plane and relabels the *yz* plane as the *xy* plane, thereby interchanging the $\hat{\sigma}(xy)$ and $\hat{\sigma}(yz)$ operations. In Table 15.3, interchange of the $\hat{\sigma}(xy)$ and $\hat{\sigma}(yz)$ eigenvalues leaves the symmetry species A_g, A_u, B_{2g}, and B_{2u} unchanged and makes the following changes in the other species:

$B_{1g} \to B_{3g}$, $B_{1u} \to B_{3u}$, $B_{3g} \to B_{1g}$, $B_{3u} \to B_{1u}$. Thus the 1 and 3 subscripts on the b MOs are interchanged.

15.29 **(a)** No. The normalization condition for the real MO $\phi_i = \sum_r c_{ri}\chi_r$ is $1 = \int (c_{1i}\chi_1 + c_{2i}\chi_2 + \cdots)^2\, d\tau = c_{1i}^2 \int \chi_1^2\, d\tau + 2c_{1i}c_{2i}\int \chi_1\chi_2\, d\tau + \cdots = c_{1i}^2 + 2c_{1i}c_{2i}S_{12} + \cdots$. This equation can be satisfied with $c_{1i} > 1$ if $c_{1i}c_{2i}$ is negative or if S_{12} is negative. Note the negative coefficients for the H AOs in $1a_1$.

(b) In the notation of Prob. 13.37b, we have from (15.46): $c = -0.064$, $d = 0.584$. From Prob. 13.37b, $c = a + Sb$ and $d = b(1-S^2)^{1/2}$, where $S = \langle \mathrm{C}1s \mid \mathrm{C}2s\rangle =$ $24\zeta_1^{3/2}\zeta_2^{5/2}/3^{1/2}(\zeta_1+\zeta_2)^4 = 24(5.68)^{3/2}(1.76)^{5/2}/3^{1/2}(5.68+1.76)^4 = 0.2516$.
So $b = 0.584[1-(0.2516)^2]^{-1/2} = 0.603$ and $a = -0.064 - 0.2516(0.603) = -0.216$.
Then $2a_1 = 0.186(\mathrm{H}_1 1s + \mathrm{H}_2 1s + \mathrm{H}_3 1s + \mathrm{H}_4 1s) - 0.216(\mathrm{C}1s) + 0.603(\mathrm{C}2s)$.

(c) $\int (2a_1)^2 d\tau = (0.186)^2[4 + 12\langle \mathrm{H}_1 1s \mid \mathrm{H}_2 1s\rangle] + (0.216)^2 + (0.603)^2$ $-0.186(0.216)8\langle \mathrm{H}_1 1s \mid \mathrm{C}1s\rangle + 0.186(0.603)8\langle \mathrm{H}_1 1s \mid \mathrm{C}2s\rangle - 0.216(0.603)2\langle \mathrm{C}1s \mid \mathrm{C}2s\rangle$, where the equivalence of all four H atoms was used. From part (b), $\langle \mathrm{C}1s \mid \mathrm{C}2s\rangle = 0.2516$. From p. 472 of the text, the C–H bond length is $R_{\mathrm{CH}} = 1.085$ Å = 2.050 bohrs. The H–H distance is given by the law of cosines as
$R_{\mathrm{CH}} = [(2.050)^2 + (2.050)^2 - 2(2.050)^2\cos(109.47°)]^{1/2} = 3.348$ bohrs. The orbital exponents are $\zeta_{\mathrm{H}1s} = 1.17$, $\zeta_{\mathrm{C}1s} = 5.68$, $\zeta_{\mathrm{C}2s} = 1.76$, $\zeta_{\mathrm{C}2p} = 1.76$. See Prob. 15.24 for information and notations on finding the overlap integrals from the reference given. For $\langle \mathrm{H}_1 1s \mid \mathrm{H}_2 1s\rangle$, $p \equiv \frac{1}{2}(\zeta_a + \zeta_b)R_{ab} = \frac{1}{2}(1.17+1.17)3.348 = 3.92$, $t \equiv (\zeta_a - \zeta_b)/(\zeta_a + \zeta_b) =$ 0. The MROO tables give these $\langle 1s \mid 1s\rangle$ values at $t = 0$: 0.215 at $p = 3.8$, 0.189 at $p = 4.0$. Interpolation gives $\langle \mathrm{H}_1 1s \mid \mathrm{H}_1 1s\rangle = 0.199$. For $\langle \mathrm{C}1s \mid \mathrm{H}_1 1s\rangle$, $p = \frac{1}{2}(5.68+1.17)2.050 = 7.02$, $t = (5.68-1.17)/(5.68+1.17) = 0.658$. The MROO tables give these $\langle 1s \mid 1s\rangle$ values: 0.063 at p = 7.0 and t = 0.6; 0.052 at p = 7.5 and t = 0.6; 0.073 at p = 7.0 and t = 0.7. Interpolation gives $\langle \mathrm{C}1s \mid \mathrm{H}_1 1s\rangle = 0.063 - 0.011(0.02/0.50) +$ $0.010(0.058/0.10) = 0.068$. For $\langle \mathrm{H}_1 1s \mid \mathrm{C}2s\rangle$, $p = \frac{1}{2}(1.17+1.76)2.050 = 3.00$, $t = (1.17-1.76)/(1.17+1.76) = -0.201$. The MROO tables give these $\langle 1s \mid 2s\rangle$ values: 0.505 at p = 3.0 and t = –0.2; 0.508 at p = 3.0 and t = –0.3. Interpolation gives $\langle \mathrm{H}_1 1s \mid \mathrm{C}2s\rangle = 0.505$. Then $\int (2a_1)^2 d\tau = (0.186)^2[4 + 12(0.199)] + (0.216)^2 + (0.603)^2$ $-0.186(0.216)8(0.068) + 0.186(0.603)8(0.505) - 0.216(0.603)2(0.2516) = 0.997$.

15.30 We use the electron configuration given on p. 477. The lowest-energy MOs will be two inner-shell MOs that involve the C1s AOs. The $1a_g$ inner-shell MO will be almost entirely g_2. The $1b_{1u}$ inner-shell MO will be g_6. There will be six occupied bonding MOs. The g_{13} symmetry orbital will give the occupied π MO $1b_{3u}$, the highest-energy occupied

MO. The $1b_{3g}$ MO will be a bonding combination of the b_{3g} symmetry orbitals g_{11} and g_{12}, namely, $N(g_{11}+cg_{12})$. Since $\mathrm{C}_1 2p_y$ is positive near H_1 and $-\mathrm{C}_2 2p_y$ is negative near H_3, the coefficient c must be positive to give a bonding MO. The $1b_{2u}$ MO will be a bonding combination of the b_{2u} symmetry orbitals g_9 and g_{10}, namely, $N(g_9+ag_{10})$. Since $\mathrm{C}_1 2p_y$ is positive near H_1 and $\mathrm{C}_2 2p_y$ is positive near H_3, the coefficient a must be positive to give a bonding MO. The $2b_{1u}$ MO will be a bonding combination of the b_{1u} symmetry orbitals g_5, g_7, and g_8, with the inner-shell symmetry orbital g_6 making only a negligible contribution. Thus $2b_{1u}=N(g_5+\alpha g_7+\beta g_8)$. Since $\mathrm{C}_1 2s$ is positive near H_1 and H_2 and $-\mathrm{C}_2 2s$ is negative near H_3 and H_4, we see that α is positive. Since $\mathrm{C}_1 2p_z$ is negative near H_1 and H_2 and $\mathrm{C}_2 2p_z$ is positive near H_3 and H_4, we see that β is negative. The $2a_g$ and $3a_g$ MOs will each be a bonding combination of the a_g symmetry orbitals g_1, g_3, and g_4, with the inner-shell symmetry orbital g_2 making a negligible contribution. In these MOs, the g_1 and g_3 functions will have positive coefficients. Since $\mathrm{C}_1 2p_z$ is negative near H_1 and H_2 and $-\mathrm{C}_2 2p_z$ is negative near H_3 and H_4, the function g_4 will have a negative coefficient in these MOs. As noted in the problem, g_3 makes a negligible contribution to $3a_g$. Also, it turns out that the contribution of g_4 to $2a_g$ is small, and can be neglected in drawing the MO. Combining the symmetry orbitals with the signs just deduced, we get the MO sketches shown on the next page.

15.31 **(a)** $\nabla U = \mathbf{i}(\partial U/\partial x)+\mathbf{j}(\partial U/\partial y)+\mathbf{k}(\partial U/\partial z) = 2c_1 x\mathbf{i}+2c_2 y\mathbf{j}+2c_2 z\mathbf{k}$. The (i, j)th element of the Hessian is $(\partial^2 U/\partial q_i\,\partial q_j)$, where $q_1 = x$, $q_2 = y$, $q_3 = z$. So the Hessian matrix is

$$\begin{pmatrix} 2c_1 & 0 & 0 \\ 0 & 2c_2 & 0 \\ 0 & 0 & 2c_3 \end{pmatrix}$$

(b) $\nabla U = 2c(x+y+z)\mathbf{i}+2c(x+y+z)\mathbf{j}+2c(x+y+z)\mathbf{k}$. The Hessian is $\begin{pmatrix} 2c & 2c & 2c \\ 2c & 2c & 2c \\ 2c & 2c & 2c \end{pmatrix}$.

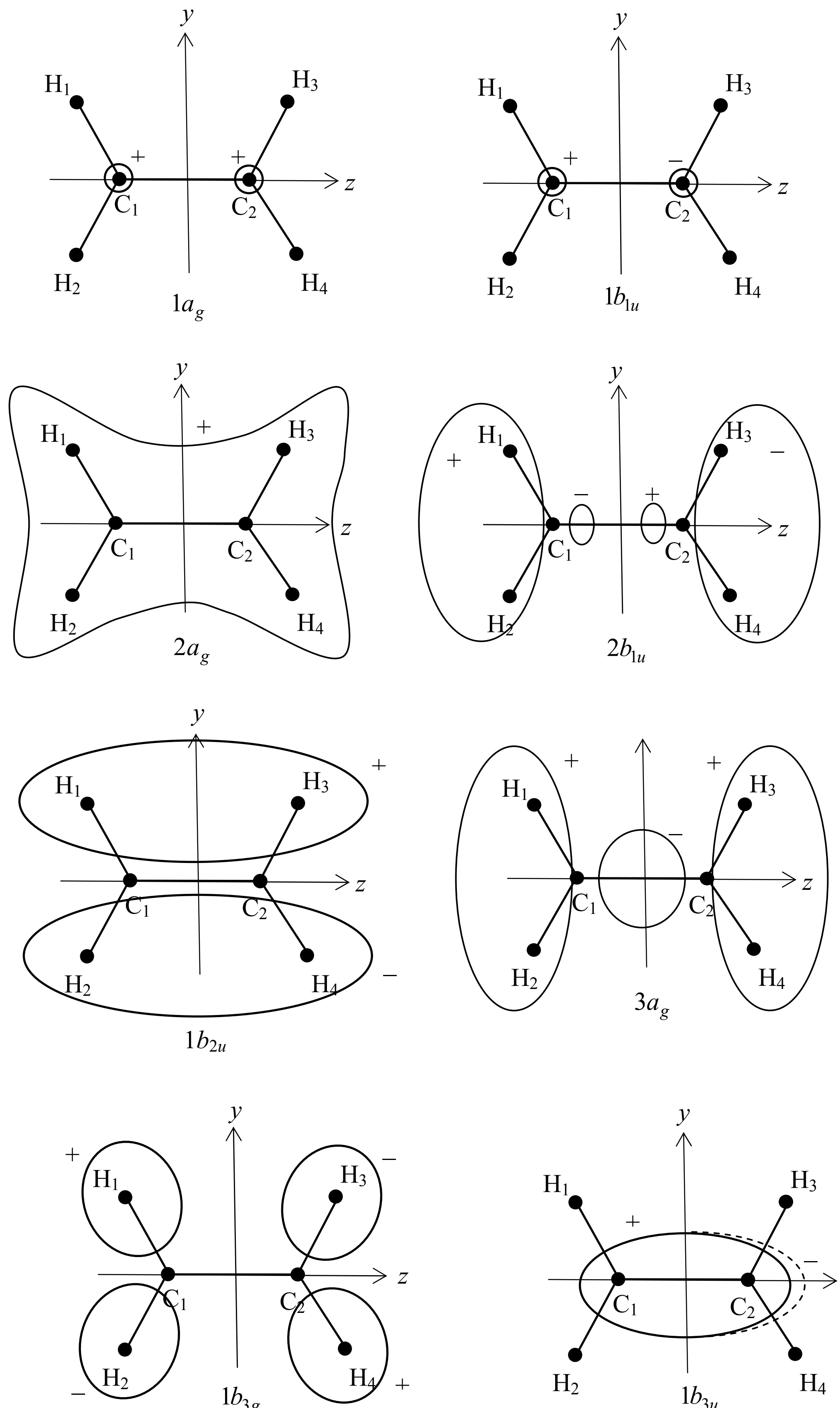
15.32 We use Table 15.5, the VSEPR method, and the rules on p. 484.

(a) R_{CH} = 1.09 Å, R_{OH} = 0.96 Å, $R(\mathrm{CO}) = 1.43$ Å, ∠HCH = ∠HCO = 109.5°, ∠COH = 106°, D(HCOH) = 60°, where D denotes a dihedral angle

(b) R_{CH} = 1.08 Å, R_{CC} = 1.34 Å, ∠HCC = 122°, ∠HCH = 116° (the deviations from 120° can be expected because the larger volume of the double bonds between the carbons produces extra repulsions on the C–H bond pairs, forcing them closer together).

(c) R_{CH} = 1.09 Å, R_{CN} = 1.47 Å, R_{NH} = 1.01 Å, ∠HCN = 109.5°, ∠CNH = 107°, D(HCNH) = 60°.

(d) $R_{CH} = 1.09$ Å, $R_{CC} = 1.52$ Å, $R_{CO} = 1.22$ Å, $\angle$HCH = $\angle$HCC = 109.5°, $\angle$CCC = 116°, $\angle$CCO = 122°, D(CCOC) = 180°. In this unusual dihedral angle, the first and fourth carbons are both bonded to the second carbon, and the second carbon is bonded to O (see p. 503 of the text). The 180° value of this dihedral angle shows that the non-H atoms lie in the same plane. D(HCCO) = 0° for one H on each C (rule 2b on p. 484).


y
z
H1
H2
H3
H4
C1
C2
+
−
1ag
1b1u
2ag
2b1u
1b2u
3ag
1b3g
1b3u

15.33 (a) A stationary point has $\nabla U = 0$, and so has $\partial U/\partial x = 0$ and $\partial U/\partial y = 0$. Hence $4x = 0$ and $-2y = 0$, so the only stationary point is at $x = 0,\ y = 0$ (the origin).

(b) For the function $2x^2 - y^2$, the stationary point (0, 0) is a minimum for the variable x, since $2x^2$ increases as x either decreases or increases from 0, and is a maximum point for y, since $-y^2$ decreases as y either increases or decreases from 0. Hence the origin is a saddle point for U.

15.34 (a) The minimum is at $x = 1,\ y = 2$, since U is zero at this point and is positive at every other point.

(b) The $^{(1)}$ superscripts in (15.72) denote the first estimates of the Hessian elements. Since we are evaluating all derivatives exactly in this problem, these superscripts are omitted. For $U = 4(x-1)^2 + 3(y-2)^2$, we have

$\partial U/\partial x = 8(x-1),\ \partial U/\partial y = 6(y-2),\ \partial^2 U/\partial x^2 = 8,\ \partial^2 U/\partial y^2 = 6,\ \partial^2 U/\partial x\,\partial y = \partial^2 U/\partial y\,\partial x = 0$

$U_{x,1} = 8(x_1 - 1),\ U_{y,1} = 6(y_1 - 2)$ and (15.72) gives

$$x_{2'} = x_1 + \frac{0\cdot 6(y_1-2) - 6\cdot 8(x_1-1)}{8\cdot 6 - 0} = x_1 - (x_1 - 1) = 1,$$

$$y_{2'} = y_1 + \frac{0\cdot 8(x_1-1) - 8\cdot 6(y_1-2)}{8\cdot 6 - 0} = 2$$

15.35 (a) The minimum is at the origin, $x = 0,\ y = 0$.

(b) $\mathbf{q}_1 = (9, 9)$, $-\nabla U = -6x\mathbf{i} - 12y\mathbf{j} = (-6x, -12y)$, $-\nabla U_1 = -54\mathbf{i} - 108\mathbf{j} = (-54, -108)$. If the vector $-\nabla U_1$ is placed with its tail at the origin, its head is at $(-54, -108)$; the slope of the gradient-vector line is $\Delta y/\Delta x = -108/(-54) = 2$. The equation of the line with slope 2 that passes through the point (9, 9) is $2 = (y-9)/(x-9)$ or $y = 2x - 9$. We must find the minimum of the function $U = 3x^2 + 6y^2$ on the line $y = 2x - 9$. On this line, $U = 3x^2 + 6(2x-9)^2 = 27x^2 - 216x + 486$. For the minimum, $\partial U/\partial x = 0 = 54x - 216$ and $x = 4$, $y = 2x - 9 = -1$. Thus the initial step (done using the steepest-descent method) is from (9, 9) to (4, –1). For point 2, $-\nabla U_2 = -6x\mathbf{i} - 12y\mathbf{j} = -24\mathbf{i} + 12\mathbf{j} = (-24, +12)$. The Fletcher–Reeves formula gives

$\beta_2 = (\nabla U_2 \cdot \nabla U_2)/(\nabla U_1 \cdot \nabla U_1) = [(24)^2 + (-12)^2]/[(54)^2 + (108)^2] = 0.0493827$. Then

$\mathbf{d}_2 = -\nabla U_2 + \beta_2 \mathbf{d}_1 = -\nabla U_2 + \beta_2(-\nabla U_1) = -24\mathbf{i} + 12\mathbf{j} + (0.0493827)(-54\mathbf{i} - 108\mathbf{j}) =$
$-26.66667\mathbf{i} + 6.66667\mathbf{j} = (-26.66667, 6.66667)$. The slope of the $\mathbf{d}_2$ vector is 6.66667/(–26.66667) = –0.250000 and the equation of the line with this slope that passes through the point (4, –1) is $-0.25000 = (y+1)/(x-4)$ or $y = -0.25000x$. We must find the minimum of the function $U = 3x^2 + 6y^2$ on the line $y = -0.25000x$. On this line, $U = 3x^2 + 6(-0.25x)^2 = 3.375x^2$. For the minimum, $\partial U/\partial x = 0 = 6.75x$ and

$x = 0,\ y = -0.25x = 0$. For point 3, $-\nabla U_3 = -6x\mathbf{i} - 12y\mathbf{j} = 0\mathbf{i} + 0\mathbf{j} = (0,\ 0)$. With a zero gradient, we have reached the minimum.

15.36 The H–H distance R_{HH} is found from $\sin(\theta/2) = \frac{1}{2}R_{\text{HH}}/R_{\text{OH}}$, so $R_{\text{HH}} = 2(0.958\ \text{Å})\sin[104.5\pi/(180)2] = 1.515\ \ \text{Å}$. The distance matrix is

$$\begin{pmatrix} 0 & 0.958\ \text{Å} & 0.958\ \text{Å} \\ 0.958\ \text{Å} & 0 & 1.515\ \text{Å} \\ 0.958\ \text{Å} & 1.515\ \text{Å} & 0 \end{pmatrix}$$

15.37 **(a)** True. Three non-collinear points determine a plane. If the nuclei are collinear, the molecule is best described as linear. **(b)** True. **(c)** True. **(d)** True.

15.38 The four symmetry operations in (15.1) each leave ω_2 unchanged and this vibration has symmetry species a_1. The operations $\hat{C}_2(z)$ and $\hat{\sigma}_{\text{v}}(xz)$ convert the vectors of ω_3 to their negatives and the other two operations leave ω_3 unchanged, so this vibration has symmetry species b_2.

15.39 $\Theta_s = h\nu_s/k = (hc/k)\tilde{\nu}_s = (6.6261\times10^{-34}\ \text{J s})(2.9979\times10^{10}\ \text{cm/s})/(1.3807\times10^{-23}\ \text{J/K})\,\nu_{\text{s}}$
$\Theta_s =\ (1.4387\ \text{cm K})\,\nu_s$.

(a) $\Theta_s = (900\ \text{cm}^{-1})(1.4387\ \text{cm K}) = 1295\ \text{K}$
$R\Theta_s/(e^{\Theta_s/T} - 1) = (8.314\ \text{J/mol-K})(1295\ \text{K})/(e^{1295/298.1} - 1) = 0.142\ \ \text{kJ/mol}$

(b) $\Theta_s = (300\ \text{cm}^{-1})(1.4387\ \text{cm K}) = 431.6\ \text{K}$
$R\Theta_s/(e^{\Theta_s/T} - 1) = (8.314\ \text{J/mol-K})(431.6\ \text{K})/(e^{431.6/298.1} - 1) = 1.103\ \text{kJ/mol}$

(c) $\Theta_s = (2000\ \text{cm}^{-1})(1.4387\ \text{cm K}) = 2877\ \text{K}$
$R\Theta_s/(e^{\Theta_s/T} - 1) = (8.314\ \text{J/mol-K})(2877\ \text{K})/(e^{2877/298.1} - 1) = 0.0015\ \text{kJ/mol}$

15.40 **(a)** $D_e/\text{hartrees} = 2(-74.783931) + (-37.680860) - (-187.634176) = 0.385454$.
$D_e = (0.385454\ \text{hartree})(27.2114\ \text{eV/hartree})\ = 10.489\ \text{eV}$.

(b) In the harmonic-oscillator approximation, each vibrational mode contributes $\frac{1}{2}h\nu = \frac{1}{2}hc\tilde{\nu}$ to the ground-state vibrational energy. Adding up these contributions, we get as the ground-state vibrational energy
$\frac{1}{2}(6.626\times10^{-34}\ \text{J s})(2.9979\times10^{10}\ \text{cm/s})0.89(5595.1\ \text{cm}^{-1}) = 4.946\times10^{-20}\ \text{J} =\ 0.309\ \text{eV}$.

So $D_0 = 10.489\ \text{eV} - 0.309\ \text{eV} = 10.180\ \text{eV}$. The predicted atomization energy is $(10.180\ \text{eV})(1.6022\times10^{-19}\ \text{J/eV})(6.0221\times10^{23}\ \text{mol}^{-1}) = 982.2\ \text{kJ/mol} = 234.8\ \text{kcal/mol}$.

(c)

$$\begin{tikzcd} \mathrm{C}(g) + 2\mathrm{O}(g) \arrow[r, "1"] \arrow[d, "2"'] & \mathrm{CO}_2(g) \\ \mathrm{C(graphite)} + \mathrm{O}_2(g) \arrow[ur, "3"'] & \end{tikzcd}$$

These three processes are at 0 K, where there is no difference between energy changes and enthalpy changes for ideal gases. Thus, from part (b), $\Delta H^\circ_{0,1}$ for step 1 is estimated as –982.2 kJ/mol. From the thermodynamic data given in the problem, $\Delta H^\circ_{0,2}/(\text{kJ/mol}) = -2(246.79) - 711.2 = -1204.78$. Also, $\Delta H_3 = \Delta H^\circ_{f,0,\mathrm{CO}_2(g)}$. From $\Delta H_1 = \Delta H_2 + \Delta H_3$, we get $\Delta H_3 = \Delta H^\circ_{f,0,\mathrm{CO}_2(g)} = (-982.2 + 1204.8)\ \text{kJ/mol} =$ 222.6 kJ/mol, which is greatly in error. To find the change in ΔH° for the formation reaction (reaction 3) on going from 0 to 298 K, we include ΔH° for taking each substance from 0 to 298 K. For each of the reaction-3 gases at 298 K, statistical mechanics gives: (a) a translational-motion contribution of $\frac{3}{2}RT$; (b) a rotational contribution of RT; (c) a vibrational contribution that is found from the formula in Prob. 15.39; (d) a negligible electronic contribution; (e) a contribution of RT to H°_{m} of each gas, arising from the definition $H \equiv U + PV$. Since the number of moles of gases is the same on each side of the formation reaction, contributions a, b, d, and e cancel, and we are left with only the vibrational contributions for the gases and the contribution from heating the graphite. From Prob. 15.39 and Table 13.2, $\Theta = (1580\ \text{cm}^{-1})(1.4387\ \text{cm K}) = 2273\ \text{K}$ for $O_2(g)$ and the vibrational contribution at 298 K is $R\Theta/(e^{\Theta/T} - 1) = (8.314\ \text{J/mol-K})(2273\ \text{K})/(e^{2273/298.1} - 1) = 0.009\ \text{kJ/mol}$. For $CO_2(g)$, the two higher-frequency vibrations make negligible contributions; for each of the two lower-frequency vibrations, $\Theta_s = 0.89(745.8\ \text{cm}^{-1})(1.4387\ \text{cm K}) = 955\ \text{K}$ and each contributes $R\Theta_s/(e^{\Theta_s/T} - 1) = (8.314\ \text{J/mol-K})(955\ \text{K})/(e^{955/298.1} - 1) = 0.336\ \text{kJ/mol}$. Thus $\Delta H^\circ_{f,298} = \Delta H^\circ_{f,0} + 2(0.336\ \text{kJ/mol}) - 1.05\ \text{kJ/mol} =$ 222.6 kJ/mol – 0.4 kJ/mol = 222.2 kJ/mol.

15.41 **(a)** To avoid a 180° angle in the Z-matrix, we use a dummy atom whose bond to the carbon makes an angle of 90° with the molecular axis, as explained on p. 503. So

C1
X2 1 1.0
O3 1 1.16 2 90.0
O4 1 1.16 2 90.0 3 180.0

Alternative answers with different orderings of the atoms are possible in this problem.

(b) See p. 503 for help on finding the dihedral angles.

C1
H2 1 1.09
H3 1 1.09 2 109.47
H4 1 1.09 2 109.47 3 120.0
H5 1 1.09 2 109.47 3 –120.0

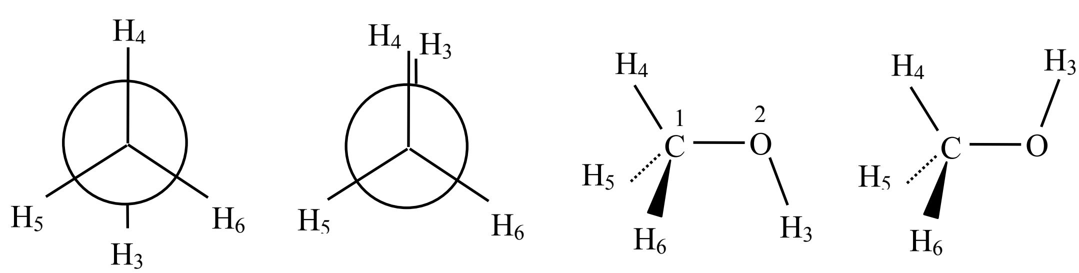
(c) C1
O2 1 1.22
H3 1 1.08 2 122.0
H4 1 1.08 2 122.0 3 180.0

(d) The simplest approach is to put a dummy atom on the other side of the C_3 axis as the hydrogens. This makes the answer similar to that of part (b):

N1
X2 1 1.0
H3 1 1.01 2 111.0
H4 1 1.01 2 111.0 3 –120.0
H5 1 1.01 2 111.0 3 120.0

(e) C1
C2 1 1.34
H3 1 1.08 2 122.0
H4 1 1.08 2 122.0 3 180.0
H5 2 1.08 1 122.0 3 0.0
H6 2 1.08 1 122.0 3 180.0

(f) In the Newman projections that follow, the O is behind the C.

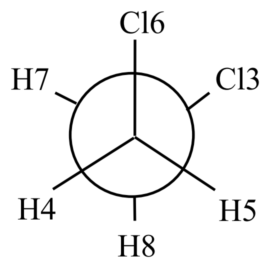


Z-matrixes for first the staggered conformation and then the eclipsed conformation are

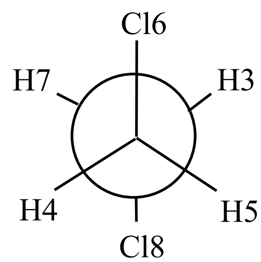
C1
O2 1 1.43
H3 2 0.96 1 106.0
H4 1 1.09 2 109.5 3 180.0
H5 1 1.09 2 109.5 3 –60.0
H6 1 1.09 2 109.5 3 60.0

C1						
O2	1	1.43				
H3	2	0.96	1	106.0		
H4	1	1.09	2	109.5	3	0.0
H5	1	1.09	2	109.5	3	120.0
H6	1	1.09	2	109.5	3	–120.0

(g) No standard C-Cl bond length is listed in Table 15.5. If one looks up bond radii, one find 0.77 and 0.99 Å for C and Cl single-bond radii, respectively, which gives a 1.76 Å length for the C-Cl bond. In the following Newman projections, C2 is behind C1.



Gauche



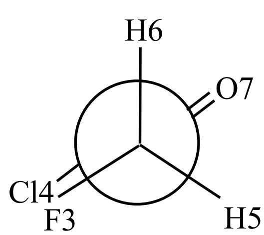
Anti

Z-matrices for the gauche and anti conformers are

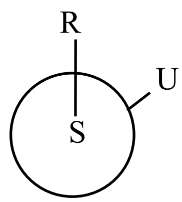
C1						
C2	1	1.54				
Cl3	2	1.76	1	109.5		
H4	1	1.09	2	109.5	3	180.0
H5	1	1.09	2	109.5	3	–60.0
Cl6	1	1.76	2	109.5	3	60.0
H7	2	1.09	1	109.5	5	180.0
H8	2	1.09	1	109.5	6	180.0

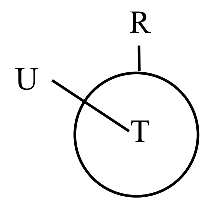
C1						
C2	1	1.54				
H3	2	1.09	1	109.5		
H4	1	1.09	2	109.5	3	180.0
H5	1	1.09	2	109.5	3	–60.0
Cl6	1	1.76	2	109.5	3	60.0
H7	2	1.09	1	109.5	5	180.0
Cl8	2	1.76	1	109.5	6	180.0

15.42 The two C's are bonded to each other. One F and two H's are bonded to C1, and an O and a Cl are bonded to C2. The O is bonded only to C2. Thus the formula is $CH_2FC(=O)Cl$. The dihedral angle D(OCCF) is 180° and D(ClCCF) is 0°. So the molecule is



15.43 If we rotate the figure at the left by 180° about a vertical axis that goes through the midpoint of the ST bond and is perpendicular to the ST bond, we get the figure at the right, which shows that D(U, T, S, R) is also 60°.



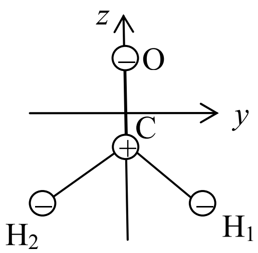


15.44 For the first atom, nothing is specified; for the second atom, one internal coordinate (IC) is specified (a bond length); for the third atom, two ICs (a bond length and a bond angle) are specified. for the fourth, fifth,…, Nth atoms, three ICs (a bond length, a bond angle, and a dihedral angle) are specified. So the total number of specified ICs is
$0 + 1 + 2 + (N - 3)3 = 3N - 6$ (since there are $N - 3$ atoms for which three ICs are specified). However, for a diatomic molecule, nothing is specified for the first atom and one IC is specified for the second atom, so one IC is specified. For a linear polyatomic molecule, the situation is complicated by the need to use a dummy atom to avoid 180° bond angles in the Z-matrix, and discussion is omitted.

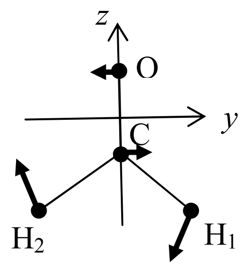
15.45 **(a)** A Z-matrix is given in the Prob. 15.41c solution. The calculated HF/3-21G equilibrium geometry, dipole moment, and harmonic vibrational wavenumbers are
R(CO) = 1.207 Å, R(CH) = 1.083 Å, ∠OCH = 122.5°; 2.66 D;
1337, 1378.5, 1693, 1916, 3162, 3233 cm^{-1}.

(b) The calculated HF/6-31G* equilibrium geometry, dipole moment, and equilibrium (harmonic) vibrational wavenumbers are R(CO) = 1.184 Å, R(CH) = 1.092 Å, ∠OCH = 122.2°; 2.67 D; 1336, 1383, 1680, 2028, 3160, 3232 cm^{-1}. Multiplication of the calculated harmonic values by the 0.895 scale factor gives as predicted fundamental wavenumbers: 1196, 1238, 1504, 1815, 2828, 2893. Experimental values are 1.205 Å, 1.111 Å, 121.9°; 2.33 D; 1167, 1249, 1500, 1746, 2783, 2843 cm^{-1}, where the wavenumbers are fundamental wavenumbers. Some sources of experimental data are the *Handbook of Chemistry and Physics* (CRC Press) and the NIST Computational Chemistry Comparison and Benchmark Database (cccbdb.nist.gov) for geometries, dipole moments and vibrational frequencies; the NIST Chemistry Webbook (webbook.nist.gov/chemistry) for vibrational frequencies; *Landolt-Börnstein*, New Series, Group II, vols. 7, 15, and 21, *Structure Data of Free Polyatomic Molecules* for geometries.

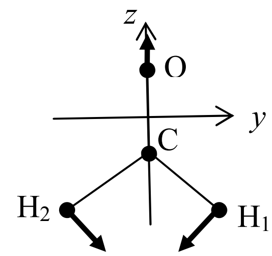
(c) The light H atoms have much larger displacements than the C and O atoms. The following diagrams (not drawn accurately to scale) show the modes. Plus and minus signs denote motions in the $+x$ and $-x$ directions, respectively.



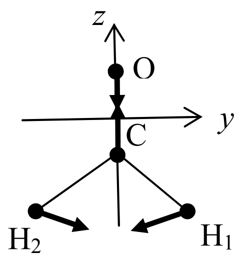
1336 cm^{-1}



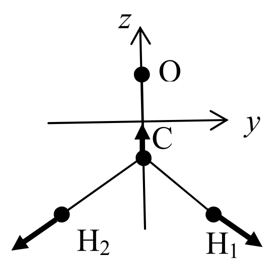
1383 cm^{-1}



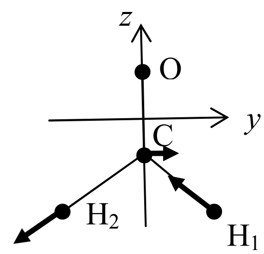
1680 cm^{-1}



2028 cm^{-1}



3160 cm^{-1}



3232 cm^{-1}

One can also use the output of the *Gaussian* program to visualize the normal modes. After each calculated vibrational wavenumber, *Gaussian* gives the *x*, *y*, *z* vibrational displacements of the atoms for that normal mode. To see where the *x*, *y*, and *z* axes have been placed by *Gaussian*, consult the standard-orientation coordinates of the atoms given by *Gaussian* preceding the frequency calculation.

(d) The predicted strongest mode is 2028 cm^{-1}. The weakest is 1336 cm^{-1}.

(e) Let the molecular plane be the *yz* plane, as in Fig. 15.1 and in the preceding normal-mode figures. For the 1336 cm^{-1} mode, $\hat{C}_2(z)$ and $\hat{\sigma}_v(yz)$ reverse each vibration vector and this is modes has symmetry species b_1 [see (15.3)]. For the 1383 and 3232 cm^{-1} modes, $\hat{C}_2(z)$ and $\hat{\sigma}_v(xz)$ reverse each vector and these modes have symmetry species b_2. For the 1680, 2028, and 3160 cm^{-1} modes, all four symmetry operations leave the vibration vectors unchanged and these are a_1 modes.

15.46 **(a)** 1842 cm^{-1} for CC stretching. 776 cm^{-1} for CCl stretching. Out of plane wavenumbers are 698, 1077, and 1093 cm^{-1}.

(b) Calculated harmonic wavenumbers scaled by 0.895 are 386, 625, 694, 964, 978, 1024, 1281, 1381, 1649, 3000, 3067, 3083 cm^{-1}. Experimental fundamental frequencies are 395, 620, 720, 896, 941, 1030, 1279, 1368, 1608, 3030, 3086, 3121 cm^{-1}.

(c) The sum of the calculated wavenumbers in (b) is $18132\ \text{cm}^{-1}$, which gives an estimated zero-point energy of $\frac{1}{2}(6.6261\times10^{-34}\ \text{J s})(2.9979\times10^{10}\ \text{cm/s})(18132\ \text{cm}^{-1})$ = $1.801\times10^{-19}\ \text{J} = 0.0413$ hartree.

15.47 The $1a_1$ MO has orbital energy $\varepsilon = -20.55787\ E_\text{h}\ (E_\text{h} = 1\ \text{hartree}),$ and is essentially the $1s$ inner-shell orbital on O. The $2a_1$ MO has $\varepsilon = -1.34613\ E_\text{h}$ and is a bonding MO that extends over all three atoms and is positive throughout The $1b_2$ MO has $\varepsilon = -0.71427\ E_\text{h}$ and is a bonding MO with two lobes of opposite sign that are separated by a nodal plane perpendicular to the molecular plane. One lobe extends over H_1 and the OH_1 bond line. The other lobe extends over H_2 and the OH_2 bond line. The $3a_1$ MO has $\varepsilon = -0.57080\ E_\text{h}$ and has two lobes of opposite sign. One lobe is centered on the side of the oxygen that is away from the hydrogens, and the other lobe extends over the two hydrogens. As discussed in the text, this is a largely lone-pair MO. The $1b_1$ MO has $\varepsilon = -0.49821\ E_\text{h}$, has two lobes of opposite sign (one above and one below the molecular plane), and is the lone pair $2p_x$ AO on oxygen.

15.48 When using WebMO it is best to use the Symmetry menu to symmetrize the molecule before running the geometry optimization, so as to ensure that the MOs have the proper symmetry. The $1a_g$ MO has orbital energy $\varepsilon = -11.22433\ E_\text{h}$ and is an inner-shell σ MO consisting of two positive lobes, the $1s$ AOs on each carbon. The $1b_{1u}$ MO has $\varepsilon = -11.22252\ E_\text{h}$ and is an inner-shell σ MO consisting of one positive and one negative lobe, the carbon 1s AOs with opposite sign. The $2a_g$ MO has $\varepsilon = -1.03317\ E_\text{h}$ and is a bonding σ MO with one lobe extending over all six atoms. The $2b_{1u}$ MO has $\varepsilon = -0.7895\ E_\text{h}$ and is a bonding σ MO with two lobes of opposite sign; each lobe extends over two hydrogens bonded to the same C and over the two CH bonds to that C. The $1b_{2u}$ MO has $\varepsilon = -0.64069\ E_\text{h}$ and is a bonding σ MO with two lobes of opposite sign; each lobe extends over two cis hydrogens and their bonds to the carbons. The $3a_g$ MO has $\varepsilon = -0.58647\ E_\text{h}$ and is a bonding σ MO with two positive lobes and one negative lobe. Each positive lobe encompasses two hydrogens bonded to the same carbon and the two CH bonds. The negative lobe extends over the CC bonds. The $1b_{3g}$ MO has $\varepsilon = -0.50194\ E_\text{h}$ and is a bonding σ MO with two positive and two negative lobes; each lobe extends over on CH bond and one H atom. The $1b_{3u}$ MO has $\varepsilon = -0.37440\ E_\text{h}$ and is a bonding π MO with one positive and one negative lobe; the lobes lie either above or below the molecular plane. See also the figures in the Prob. 15.30 solution.

15.49 **(a)** Most negative near the O atom. Most positive near the hydrogens bonded to N.

(b) Most negative on the part of the isodensity surface near the center of the double bond. Most positive near the hydrogens.

(c) Most negative on hexagonal regions (each with a hole) of the isosurface that lie above and below the interior of the ring. Most positive near the hydrogens.

(d) The most negative regions of the isodensity surface are near the carbon-carbon bonds. The most positive regions are near the hydrogens and also above and below the ring near the center of the ring.

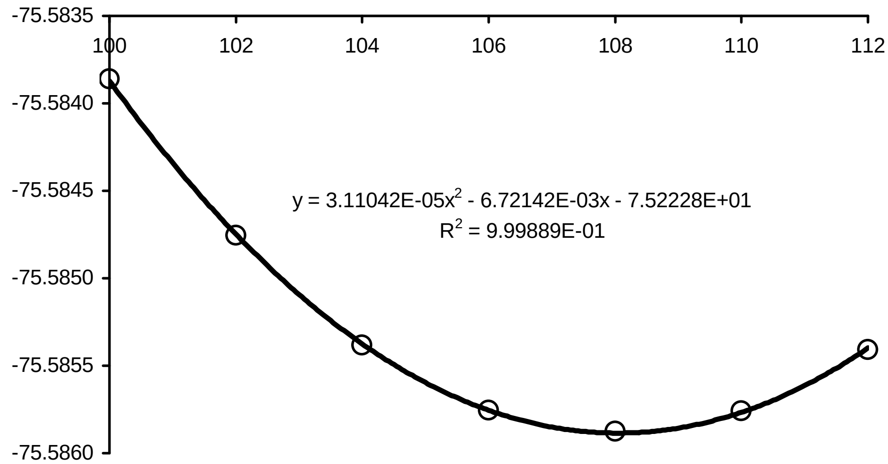
15.50 Mulliken charges: 0.434 on H, –0.869 on O.
MK charges: 0.409 on H, –0.817 on O.
CHELP charges: 0.412 on H, –0.824 on O.
CHELPG charges: 0.408 on H, –0.816 on O.

15.51 The ESP map suggests the T structure is lower energy, since it puts the negative charge near the center of one ring close to a positive hydrogen of the other ring, whereas the sandwich structure has the negative charges of the two monomers close to one another. (Two other benzene dimer structures are the parallel-displaced structure and theT-shaped tilted structure; see Figure 1 in the reference given in the text.)

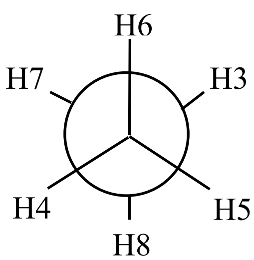
15.52 The following HF/3-21G energies as a function of bond angle are found:

100°	102°	104°	106°	108°	110°	112°
–75.583863	–75.584756	–75.585385	–75.585755	–75.585877	–75.585758	–75.585408

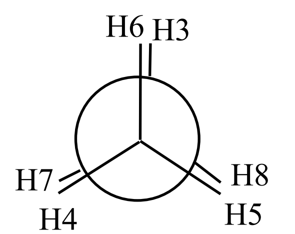
A quadratic polynomial gives a good fit, as shown by the Excel graph on the next page. The minimum of $y = ax^2 + bx + c$ is found from $dy/dx = 0 = 2ax + b$, so $x = -b/2a$ and the minimum is at $\frac{1}{2}(6.72142\times10^{-3})\,/\,(3.11042\times10^{-5}) = 108.05°$. Since the minimum is near 108°, it makes more sense to omit the points at 100° and 102° (where deviations from the harmonic-oscillator potential will be larger), and fit only the five points from 104° to 112°. This gives an R^2 value of 0.999932 and gives
$-b/2a = \frac{1}{2}(6.48631\times10^{-3})/(3.00179\times10^{-5}) = 108.04°$.



15.53 In the following Newman projections, C2 is behind C1.



staggered



eclipsed

Z-matrices for the staggered and eclipsed conformations are

C1
C2 1 R1
H3 2 R2 1 A1
H4 1 R2 2 A1 3 D1
H5 1 R2 2 A1 3 D2
H6 1 R2 2 A1 3 D3
H7 2 R2 1 A1 5 D1
H8 2 R2 1 A1 6 D1
Variables:
R1 1.54
R2 1.09
A1 109.5
Constants:
D1 180.0
D2 –60.0
D3 60.0

C1
C2 1 R1
H3 2 R2 1 A1
H4 1 R2 2 A1 3 D1
H5 1 R2 2 A1 3 D2
H6 1 R2 2 A1 3 D3
H7 2 R2 1 A1 4 D3
H8 2 R2 1 A1 5 D3
Variables:
R1 1.54
R2 1.09
A1 109.5
Constants:
D1 120.0
D2 –120.0
D3 0.

With the dihedral angles fixed, the optimized HF/6-31G** energies of the staggered and eclipsed forms are found to be –79.2382341 and –79.2334228 hartrees, respectively. The energy difference is 0.0048113 hartrees, which is equivalent to 3.02 kcal/mol.

15.54 **(a)** The SMILE string is CO or OC. The three-dimensional model shows a staggered conformation. You can either use Jmol to view the coordinates or click on PDB or MOL to download a file with the Cartesian coordinates and then use Microsoft Word to open the saved file. For the SMILES string CO, CORINA gives the following coordinates (the string OC gives the atoms in a different order):

C1	0.737	-0.015	0.000
O2	-0.690	0.068	-0.000
H3	1.070	-0.549	0.890
H4	1.070	-0.549	-0.890
H5	1.159	0.990	0.000
H6	-1.133	-0.792	-0.000

(b) The SMILES string is O=CO or OC=O. CORINA gives the conformation with the *D*(HCOH) dihedral angle equal to zero (conformer II in Prob. 15.57), which is not the lowest-energy conformer, and gives these coordinates for the string O=CO:

O1	-1.124	-0.213	0.000
C2	-0.095	0.420	-0.001
O3	1.085	-0.218	0.000
H4	-0.126	1.500	0.003
H5	1.881	0.331	-0.000

15.55 **(a)** Begin by clicking ChemicalSearch; then choose Text Search or Structure Search and enter the name or SMILES string; then click the Chemical ID number (3969407 in this case); choose XYZ-XMol XYZ format in the drop-down list, click on Chemical, and save the file to your computer. Use Microsoft Word to open the file on your computer. The result is

C	-0.01730	1.42480	0.00990
O	0.00210	-0.00410	0.00200
H	1.00530	1.80210	0.00210
H	-0.54450	1.78590	-0.87320
H	-0.52750	1.77630	0.90670
H	0.46100	-0.27290	-0.80560

(b) ChemDB gives the conformation with the two H atoms eclipsing each other (II in Prob. 15.57), which is not the lowest-energy conformer. The coordinates are given as

C	-0.01430	1.20410	0.00870
O	0.00210	-0.00410	0.00200
O	1.13890	1.89100	0.00130
H	-0.95680	1.73130	0.01600
H	1.12580	2.85790	0.00670

15.56 **(a)** Starting with the planar Z-matrix

N1
H2 1 1.0
H3 1 1.0 2 120.0
H4 1 1.0 2 120.0 3 180.0

Gaussian 09 gives the HF/6-31G* optimized geometry as the planar structure with R_{NH} = 0.988 Å, ∠HNH = 120.0°, and energy –56.173985 hartrees. A vibrational-frequency calculation gives one imaginary frequency, indicating that this structure is a saddle point, rather than a local minimum.

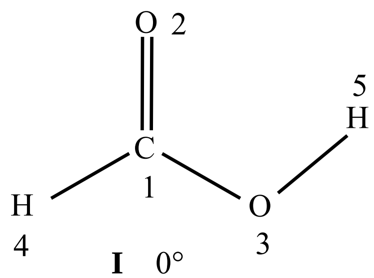
(b) Starting with the nonplanar Z-matrix

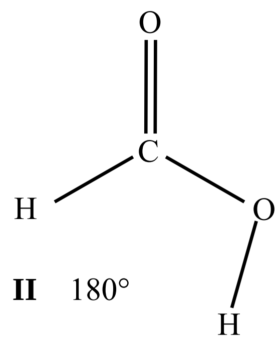
N1
X2 1 1.0
H3 1 1.0 2 100.0
H4 1 1.0 2 100.0 3 -120.0
H5 1 1.0 2 100.0 3 120.0

Gaussian converges to a pyramidal structure with the HF/6-31G* values R_{NH} = 1.002 Å, ∠HNH = 107.2°, and energy –56.184356 hartrees. A vibrational-frequency calculation gives all real frequencies, indicating that the structure is a local minimum.

(c) The HF/6-31G* equilibrium inversion barrier is (–56.173985 + 56.184356) hartrees = 0.010371 hartrees, which is 6.51 kcal/mol. (Experimental values for this barrier lie in the range 5.1 to 5.4 kcal/mol.)

15.57 **(a)** The two conformers are





where the D(OCOH) dihedral angles are given. A Z-matrix for Conformer I is

```
C1
O2  1  1.22
O3  1  1.36  2  120.0
H4  1  1.08  2  120.0  3  180.0
H5  3  0.96  1  109.5  2  0.0
```

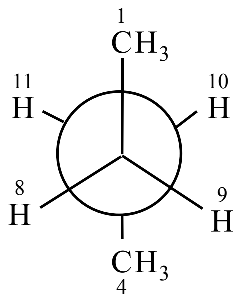
To get the Z-matrix for conformer II, we change the last entry in the last line from 0.0 to 180.0. The HF/6-31G* geometry-optimized results are planar structures with the following properties:

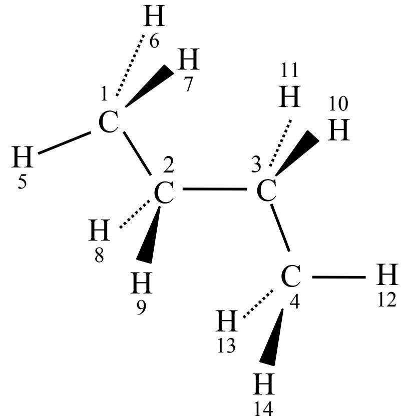
	μ	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	1.60 D	124.7°	124.9°	118.7°	1.083 Å	1.182 Å	1.323 Å	0.953 Å
II	4.37 D	123.1°	123.0°	111.5°	1.090 Å	1.176 Å	1.328 Å	0.948 Å

The energies are –188.762310 hartrees for I and –188.752546 for II. The HF/6-31G* energy difference is $E_{\rm II} - E_{\rm I} = 0.009764$ hartrees, corresponding to $E_{\rm II} - E_{\rm I} =$ 6.13 kcal/mol.

(b) The unscaled frequencies are all real (indicating that these structures are local minima). For conformer I, the unscaled HF/6-31G* wavenumbers are 692, 715, 1192, 1275, 1440, 1552, 2035, 3320, and 4042 cm^{-1}. Using the scaling factor of 0.895, we find $\frac{1}{2}hc\sum_i \tilde{\nu}_{i,\text{scaled}} = (7278\text{ cm}^{-1})hc = (7278\text{ cm}^{-1})(6.6261\times10^{-34}\text{ J s})(2.9979\times10^{10}\text{ cm/s}) =$ 1.4457×10^{-19} J. Multiplication by the Avogadro constant gives a zero-point energy of 87.06 kJ/mol = 20.81 kcal/mol for I. For conformer II, the unscaled HF/6-31G* wavenumbers are 517, 724, 1179, 1238, 1426, 1583, 2080, 3228, and 4107 cm^{-1} and the scaled frequencies give a zero-point energy of 20.58 kcal/mol. The zero-point energy difference is $E_{\rm II,ZPE} - E_{\rm I,ZPE} = -0.23$ kcal/mol. With inclusion of the zero-point vibrational energy, the HF/6-31G* calculation predicts $E_{\rm II} - E_{\rm I} = 5.90$ kcal/mol at 0 K.

15.58 **(a)** The anti conformer is





The H's on C4 are staggered with respect to the atoms bonded to C3; the H's on C1 are staggered with respect to the atoms bonded to C2. Although the *Gaussian* input procedure described in Prob. 15.53 could be use to freeze the CCCC dihedral angle D(4321) while optimizing the remaining geometry, a slightly simpler procedure is to use the keyword Opt=AddRedundant with the following Z-matrix:

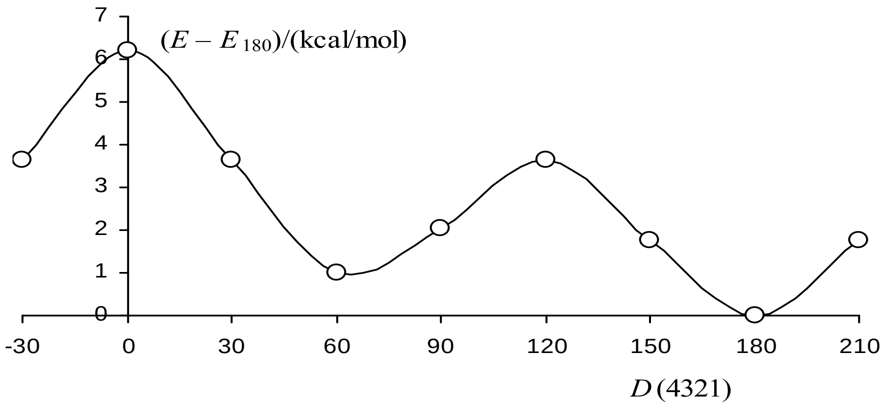
```
C1
C2   1   1.54
C3   2   1.54   1   109.5
C4   3   1.54   2   109.5   1    180.0
H5   1   1.09   2   109.5   3   180.0
H6   1   1.09   2   109.5   5   -120.0
H7   1   1.09   2   109.5   5   120.0
H8   2   1.09   1   109.5   3   -120.0
H9   2   1.09   1   109.5   3   120.0
H10  3   1.09   4   109.5   2   120.0
H11  3   1.09   4   109.5   2   -120.0
H12  4   1.09   3   109.5   2   180.0
H13  4   1.09   3   109.5   12   -120.0
H14  4   1.09   3   109.5   12   120.0

4   3   2   1    F
```

The last line (which is preceded by a blank line) freezes D(4321) at the value entered at the end of line 4. By varying this line 4 entry from 180.0 to 0.0, we generate the potential-energy curve of internal rotation. The following HF/6-31G* values are found:

D(4321)	180°	150°	120°	90°
E_{HF}/hartrees	–157.298409	–157.295624	–157.292592	–157.295152

D(4321)	60°	30°	0°
E_{HF}/hartrees	–157.296793	–157.292618	–157.288547

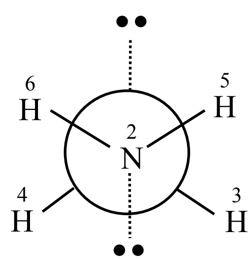
With the addition of points at –30° and 210°, Excel gives the following smoothed graph:



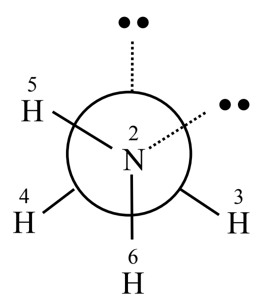
The gauche conformer occurs at slightly more than 60° with a relative energy of a bit less than 1.0 kcal/mol, the anti is at 180°, and the maximum between them occurs at 120° with relative energy 3.6 kcal/mol. The gauche → anti barrier is estimated at 2.6 kcal/mol and the anti → gauche barrier is 3.6 kcal/mol.

(b) Setting the last entry in row four of the Z-matrix in part (a) equal to 60.0, eliminating the last line, and using the keyword Opt, one finds the optimized gauche energy and CCCC dihedral angle to be –157.296895 hartrees and 65.4°. The HF/6-31G* gauche – anti energy difference is 0.001514 hartrees, or 0.95 kcal/mol.

15.59 We expect the following two conformations, with the bonds and lone pairs staggered on the N's, where N1 is behind N2:



I



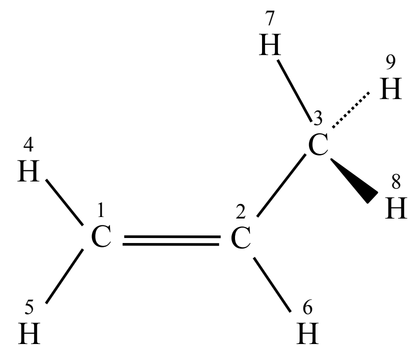
II

HF/6-31G* calculations give the following equilibrium properties:

	μ/D	R_{NN}/Å	R_{NH3}/Å	R_{NH4}/Å	∠NNH3	∠NNH4	∠314	D(5213)	D(6214)
I	0	1.451	1.004	1.004	104.8°	104.8°	103.7°	71.1°	71.1°
II	2.24	1.414	0.999	1.003	107.8°	112.2°	108.1°	150.6°	28.5°

HF/6-31G* energies are –111.1649155 hartrees for I and –111.1693737 hartrees for II. With zero-point energy (ZPE) omitted, $E_{\text{I}} - E_{\text{II}} = 0.004458$ hartrees ≙ 2.80 kcal/mol. Unscaled wavenumbers for I are 125, 1111, 1165, 1209, 1370, 1641, 1819, 1879, 3692, 3709, 3769, and 3794 cm^{-1} and for II are 473, 979, 1113, 1225, 1435, 1468, 1854, 1871, 3707, 3718, 3820, and 3826 cm^{-1}. With a scaling factor of 0.89, we find (using the procedure in the Prob. 15.57b solution) $E_{\text{I,ZPE}} = 32.16$ kcal/mol and $E_{\text{II,ZPE}} = 32.43$ kcal/mol, so with zero-point energy included, $E_{\text{I}} - E_{\text{II}} = 2.53$ kcal/mol. Since all the vibrational frequencies are real, I and II are local minima.

15.60 The doubly bonded carbons and the four atoms bonded to them will lie in the same plane. What is unclear is the conformation around the CC single bond. In the following drawing, H7 might eclipse C1 with H8 and H9 staggered with respect to H6 (as drawn) or H8 might eclipse H6 with H7 and H9 staggered with respect to C1:



HF/6-31G* optimization and frequency calculations starting from a structure with dihedral angle $D(7321) = 0°$ and from a structure with $D(7321) = 60°$, show that the 0° structure is a minimum but the 60° structure is not. Calculated properties of the 0° conformer are: $\mu = 0.31$ D, $R_{\text{C=C}} = 1.318$ Å, $R_{\text{C-C}} = 1.503$ Å, $R_{\text{CH5}} = 1.075$ Å, $R_{\text{CH4}} = 1.077$ Å, $R_{\text{CH6}} = 1.079$ Å, $R_{\text{CH7}} = 1.084$ Å, $R_{\text{CH8}} = 1.087$ Å, $\angle 512 = 121.6°$, $\angle 412 = 121.8°$, $\angle 123 = 125.2°$, $\angle 126 = 118.9°$, $\angle 237 = 111.4°$, $\angle 238 = 110.9°$, $D(7321) = 0.0°$; unscaled vibrational wavenumbers range from 212 to 3405 cm^{-1}.

15.61 There are two basis functions, namely, $1s_a$ and $1s_b$, which we shall abbreviate as a and b. With two choices for each of the four functions in $(rs\,|\,tu)$, there are 16 electron-repulsion integrals. Because of the symmetry of the molecule, we have $(aa\,|\,aa) = (bb\,|\,bb)$. Use of (14.47) gives $(aa\,|\,bb) = (bb\,|\,aa)$, $(ab\,|\,ab) = (ba\,|\,ab) = (ab\,|\,ba) = (ba\,|\,ba)$, $\boxed{(aa\,|\,ab) = (aa\,|\,ba) = (ab\,|\,aa) = (ba\,|\,aa)}$, $\boxed{(ab\,|\,bb) = (bb\,|\,ab) = (ba\,|\,bb) = (bb\,|\,ba)}$.

Because of the molecular symmetry, interchange of a and b does not change the value of an integral. Hence $(aa\,|\,ab) = (bb\,|\,ba)$ and all of the integrals in the boxed equations are equal to one another. Thus only the 4 integrals $(aa\,|\,aa)$, $(aa\,|\,bb)$, $(ab\,|\,ab)$, $(aa\,|\,ab)$ need to be calculated.

15.62 For H, $s = 0$ and $\zeta = 1$. For He, $s = 0.30$ and $\zeta = (2 - 0.30)/1 = 1.70$.
For C, $s_{2s} = s_{2p} = 3(0.35) + 2(0.85) = 2.75$ and $\zeta_{2s} = \zeta_{2p} = (6 - 2.75)/2 = 1.625$;

$s_{1s} = 0.30$ and $\zeta_{1s} = (6 - 0.30)/1 = 5.70$.

For N, $s_{2s} = s_{2p} = 4(0.35) + 2(0.85) = 3.1$ and $\zeta_{2s} = \zeta_{2p} = (7 - 3.1)/2 = 1.95$;

$s_{1s} = 0.30$ and $\zeta_{1s} = (7 - 0.30)/1 = 6.70$.

For O, $s_{2s} = s_{2p} = 5(0.35) + 2(0.85) = 3.45$ and $\zeta_{2s} = \zeta_{2p} = (8 - 3.45)/2 = 2.275$;

$s_{1s} = 0.30$ and $\zeta_{1s} = (8 - 0.30)/1 = 7.70$.

For S with electron configuration $1s^2 \,|\, 2s^2 2p^6 \,|\, 3s^2 3p^4$,

$s_{3s} = s_{3p} = 5(0.35) + 8(0.85) + 2(1.0) = 10.55$ and $\zeta_{3s} = \zeta_{3p} = (16 - 10.55)/3 = 2.1833$;

$s_{2s} = s_{2p} = 7(0.35) + 2(0.85) = 4.15$ and $\zeta_{2s} = \zeta_{2p} = (16 - 4.15)/2 = 6.075$;

$s_{1s} = 0.30$ and $\zeta_{1s} = (16 - 0.30)/1 = 15.70$.

For Ar, with electron configuration $1s^2 \,|\, 2s^2 2p^6 \,|\, 3s^2 3p^6$,

$s_{3s} = s_{3p} = 7(0.35) + 8(0.85) + 2(1.0) = 11.25$ and $\zeta_{3s} = \zeta_{3p} = (18 - 11.55)/3 = 2.15$;

$s_{2s} = s_{2p} = 7(0.35) + 2(0.85) = 4.15$ and $\zeta_{2s} = \zeta_{2p} = (18 - 4.15)/2 = 6.925$; $s_{1s} = 0.30$ and $\zeta_{1s} = (18 - 0.30)/1 = 17.70$.

The Clementi–Raimondi (CR) values compared with the Slater-rule values are

ζ values	$1s$	$2s$	$2p$	$3s$	$3p$
He, Slater	1.70				
He, CR	1.6875				
C, Slater	5.70	1.625	1.625		
C, CR	5.6727	1.6083	1.5679		
N, Slater	6.70	1.95	1.95		
N, CR	6.6651	1.9237	1.9170		
O, Slater	7.70	2.275	2.275		
O, CR	7.6579	2.2458	2.2266		
S, Slater	15.70	6.075	6.075	2.1833	2.1833
S, CR	15.5409	5.3144	5.9885	2.1223	1.8273
Ar, Slater	17.70	6.925	6.925	2.15	2.15
Ar, CR	17.5075	6.1152	7.0041	2.5856	2.2547

Chapter 16

Electron-Correlation Methods

16.1 The number of electrons is $n = 6 + 3 + 14 + 9 = 32$. For 6-31G**, each H atom has $1 + 1 + 3 = 5$ basis functions; the C atom and the F atom each have $1 + 2 + 2(3) + 6 = 15$ basis functions (see the Prob. 15.5c and d solution for details); the Si atom has one basis function for the 1*s* AO, one for the 2*s* AO, one for each of the three 2*p* AOs, two for the 3*s* AO, two for each of the three 2*p* AOs, and 6 *d*-type basis functions, for a total of 19 basis functions. The molecule thus has $5(3) + 15 + 15 + 19 = 64$ basis functions. The number of CSFs is given by (16.1) as $64!65!/16!17!48!49! = 1.862\times 10^{28}$.

16.2 Multiplication of the relation by γ gives $\frac{1}{2}\beta n\gamma^2 + (1-\beta)\gamma - 1 = 0$ and the quadratic formula gives the positive root as $\gamma = \{\beta - 1 + [(1-\beta)^2 + 2\beta n]^{1/2}\}/\beta n$. We find the following values:

n	20	20	50	50	100	100	200	200
β	0.015	0.03	0.015	0.03	0.015	0.03	0.015	0.03
γ	0.89	0.82	0.78	0.68	0.67	0.55	0.55	0.44

which indicates, for example, that for a 50-electron molecule, CISD gives 68 to 78% of the basis-set correlation energy.

16.3 Substitution in Eq. (16.2) gives
$-76.254549 + 76.243772 = (1 - a_0^2)(-76.243772 + 76.040542)$
and we get $a_0 = 0.9731$.

16.4 The H_2 ground state is a ${}^1\Sigma_g^+$ state, and only configurations that give rise to a ${}^1\Sigma_g^+$ term can contribute to the ground-state CI wave function. We can use Table 11.3.
(a) Does contribute. **(b)** By the rule on p. 378, this configuration gives *u* terms and cannot contribute. **(c)** Contributes. **(d)** This configuration gives *u* terms and does not contribute. **(e)** This gives only Π terms and does not contribute. **(f)** Contributes. **(g)** Contributes.

16.5 Equation (8.54) gives

$$(-2.862-E)c_1+0.289_5c_2=0.014c_1+0.289_5c_2=0$$
$$0.289_5c_1+(3.22_6-E)c_2=0.289_5c_1+6.102c_2=0$$

The second equation (which has more significant figures) gives $c_2=-0.0474_4c_1$, so $\psi=c_1(\Phi_1-0.0474_4\Phi_2)$. Then

$1=\langle\psi\,|\,\psi\rangle=\langle c_1(\Phi_1-0.0474_4\Phi_2)\,|\,c_1(\Phi_1-0.0474_4\Phi_2)\rangle=$

$|c_1|^2[\langle\Phi_1\,|\,\Phi_1\rangle-2(0.0474_4)\langle\Phi_1\,|\,\Phi_2\rangle+0.00225_1\langle\Phi_2\,|\,\Phi_2\rangle]=1.00225_1|c_1|^2$ and

$|c_1|=0.9989$, $c_2=-0.0474_4c_1=-0.0474$. So $\psi=0.9989\Phi_1-0.0474\Phi_2$.

16.6 **(a)** From p. 533, $\langle\Phi_2|\hat{H}|\Phi_2\rangle=\langle\phi_2(1)\,|\,\hat{H}^{\text{core}}(1)\,|\,\phi_2(1)\rangle+\langle\phi_2(2)\,|\,\hat{H}^{\text{core}}(2)\,|\,\phi_2(2)\rangle+$ $\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_2(1)\phi_2(2)\rangle=2\langle\phi_2(1)\,|\,\hat{H}^{\text{core}}(1)\,|\,\phi_2(1)\rangle+\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_2(1)\phi_2(2)\rangle$, since changing the label on the dummy integration variables from 1 to 2 does not change the value of a definite integral. From (16.5) with $i=j=2$ and $b=2$, we have

$\boxed{\langle\phi_2(1)\,|\,\hat{H}^{\text{core}}(1)\,|\,\phi_2(1)\rangle=c_{12}^2H_{11}^{\text{core}}+2c_{12}c_{22}H_{12}^{\text{core}}+c_{22}^2H_{22}^{\text{core}}}$, since the coefficients are real. From (16.6) with $i=j=k=l=2$ and $b=2$, we have

$\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_2(1)\phi_2(2)\rangle=$

$c_{12}^4(11\,|\,11)+c_{12}^3c_{22}(11\,|\,12)+c_{12}^2c_{22}c_{12}(11\,|\,21)+c_{12}^2c_{22}^2(11\,|\,22)+c_{12}c_{22}c_{12}^2(12\,|\,11)+$
$c_{12}c_{22}c_{12}c_{22}(12\,|\,12)+c_{12}c_{22}^2c_{12}(12\,|\,21)+c_{12}c_{22}^3(12\,|\,22)+$
$c_{22}c_{12}^3(21\,|\,11)+c_{22}c_{12}^2c_{22}(21\,|\,12)+c_{22}c_{12}c_{22}c_{12}(21\,|\,21)+c_{22}c_{12}c_{22}^2(21\,|\,22)+c_{22}c_{22}c_{12}^2(22\,|\,11)+$
$c_{22}^2c_{12}c_{22}(22\,|\,12)+c_{22}^3c_{12}(22\,|\,21)+c_{22}^4(22\,|\,22)$. From (14.47), we have

$(11\,|\,12)=(12\,|\,11)=(11\,|\,21)=(21\,|\,11)$, $(12\,|\,12)=(12\,|\,21)=(21\,|\,12)=(21\,|\,21)$,
$(11\,|\,22)=(22\,|\,11)$, $(12\,|\,22)=(22\,|\,12)=(21\,|\,22)=(22\,|\,21)$. So

$$\boxed{\begin{aligned}\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_2(1)\phi_2(2)\rangle&=c_{12}^4(11\,|\,11)+4c_{12}^3c_{22}(11\,|\,12)+\\&4c_{12}^2c_{22}^2(12\,|\,12)+2c_{12}^2c_{22}^2(11\,|\,22)+4c_{12}c_{22}^3(12\,|\,22)+c_{22}^4(22\,|\,22)\end{aligned}}$$

Substitution of the boxed equations gives the desired result for $\langle\Phi_2\,|\,\hat{H}\,|\,\Phi_2\rangle$.

(b) $\langle\Phi_2\,|\,\hat{H}\,|\,\Phi_1\rangle=\langle\phi_2(1)\phi_2(2)\,|\,\hat{H}^{\text{core}}(1)+\hat{H}^{\text{core}}(2)+r_{12}^{-1}\,|\,\phi_1(1)\phi_1(2)\rangle=$
$\langle\phi_2(1)\,|\,\hat{H}^{\text{core}}(1)\,|\,\phi_1(1)\rangle\langle\phi_2(2)\,|\,\phi_1(2)\rangle+\langle\phi_2(2)\,|\,\hat{H}^{\text{core}}(2)\,|\,\phi_1(2)\rangle\langle\phi_2(1)\,|\,\phi_1(1)\rangle+$
$\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_1(1)\phi_1(2)\rangle$. Since $\langle\phi_2(2)\,|\,\phi_1(2)\rangle=0=\langle\phi_2(1)\,|\,\phi_1(1)\rangle$, we have $\langle\Phi_2\,|\,\hat{H}\,|\,\Phi_1\rangle=\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_1(1)\phi_1(2)\rangle$. Equation (16.6) with $i=j=2$, $k=l=1$, and $b=2$ gives (just change the second subscript from 2 to 1 on the second and fourth coefficients in each term of the result in part (a) for $\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_2(1)\phi_2(2)\rangle$)

$\langle\phi_2(1)\phi_2(2)\,|\,r_{12}^{-1}\,|\,\phi_1(1)\phi_1(2)\rangle=\langle\Phi_2\,|\,\hat{H}\,|\,\Phi_1\rangle=$
$c_{12}^2c_{11}^2(11\,|\,11)+c_{12}^2c_{11}c_{21}(11\,|\,12)+c_{12}c_{11}c_{22}c_{11}(11\,|\,21)+c_{12}c_{11}c_{22}c_{21}(11\,|\,22)+$
$c_{12}c_{21}c_{12}c_{11}(12\,|\,11)+c_{12}c_{21}c_{12}c_{21}(12\,|\,12)+c_{12}c_{21}c_{22}c_{11}(12\,|\,21)+c_{12}c_{21}c_{22}c_{21}(12\,|\,22)+$

$c_{22}c_{11}c_{12}c_{11}(21|11)+c_{22}c_{11}c_{12}c_{21}(21|12)+c_{22}c_{11}c_{22}c_{11}(21|21)+c_{22}c_{11}c_{22}c_{21}(21|22)+$
$c_{22}c_{21}c_{12}c_{11}(22|11)+c_{22}c_{21}c_{12}c_{21}(22|12)+c_{22}c_{21}c_{22}c_{11}(22|21)+c_{22}^2c_{21}^2(22|22)$.
Use of the integral identities in part (a) gives $\langle\phi_2(1)\phi_2(2)|r_{12}^{-1}|\phi_1(1)\phi_1(2)\rangle =$
$c_{12}^2c_{11}^2(11|11)+2(c_{12}^2c_{11}c_{21}+c_{12}c_{11}^2c_{22})(11|12)+(c_{12}^2c_{21}^2+2c_{11}c_{12}c_{21}c_{22}+c_{11}^2c_{22}^2)(12|12)$
$2c_{11}c_{12}c_{21}c_{22}(11|22)+2(c_{12}c_{22}c_{21}^2+c_{22}^2c_{21}c_{11})(12|22)+c_{22}^2c_{21}^2(22|22)$.

16.7 From Table 13.1, the homonuclear diatomic MOs that arise from the 2*s* and 2*p* AOs are $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$, $3\sigma_u$. The inactive electrons are the 4 electrons in the $1\sigma_g$ and $1\sigma_u$ MOs.

(a) C_2 has 12 electrons and there are 12 – 4 = 8 active electrons. The 8 valence electrons in C_2 occupy the $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$ MOs, leaving the $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$, $3\sigma_u$ MOs available to move active electrons into. We can move as many as 8 electrons into these 4 vacant MOs, so the maximum number of electrons excited into vacant MOs is 8.

(b) N_2 has 14 electrons and there are 14 – 4 = 10 active electrons. The 10 valence electrons in N_2 occupy the $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$ MOs, leaving the $1\pi_{gx}$, $1\pi_{gy}$, $3\sigma_u$ MOs available to move active electrons into. We can move as many as 6 electrons into these 3 vacant MOs, so the maximum number of electrons excited into vacant MOs is 6.

(c) O_2 has 16 electrons and there are 16 – 4 = 12 active electrons. The 12 valence electrons in O_2 occupy the $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$ MOs and half fill each of the $1\pi_{gx}$ and $1\pi_{gy}$ MOs, leaving the $3\sigma_u$ MO and one vacancy in each of the $1\pi_{gx}$ and $1\pi_{gy}$ MOs available to move active electrons into. We can move as many as 4 electrons into these MOs, so the maximum number of electrons excited into vacant or partly vacant MOs is 4.

(d) F_2 has 18 electrons and there are 18 – 4 = 14 active electrons. The 14 valence electrons in F_2 occupy the $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$ MOs, leaving the $3\sigma_u$ MO available to move active electrons into. We can move as many as 2 electrons into this MO, so the maximum number of electrons excited is 2.

16.8 **(a)** $N=\dfrac{6!7!}{3!4!3!4!}=\dfrac{6(5)4(7)6(5)}{6(24)}=5(7)5=175$

(b) $N=\dfrac{14!15!}{7!8!7!8!}=\dfrac{14(13)12(11)10(9)8(15)14(13)12(11)10(9)}{5040(40320)}=2\,760\,615$

16.9 From (15.10), $\hat{H}=-\frac{1}{2}\sum_i\nabla_i^2-\sum_i\sum_\alpha(Z_\alpha/r_{i\alpha})+\sum_i\sum_{j>i}r_{ij}^{-1}$. From (16.9) and (16.8), $\hat{H}^0=\sum_i\hat{f}(i)=-\frac{1}{2}\sum_i\nabla_i^2-\sum_i\sum_\alpha(Z_\alpha/r_{i\alpha})+\sum_i\sum_j[\hat{j}_j(i)-\hat{k}_j(i)]$. So

$\hat{H} - \hat{H}^0 = \sum_i \sum_{j>i} r_{ij}^{-1} - \sum_i \sum_j [\hat{j}_j(i) - \hat{k}_j(i)]$, which is (16.11) with dummy variables relabeled.

16.10 **(a)** In the ground state, each of the *n* electrons is in a different spin-orbital (the Pauli exclusion principle). The occupied spin-orbitals are numbered 1 to *n* (which are the smallest and largest values that occur in the sums over *i* and *j*). In Φ_{ij}^{ab}, two electrons are excited from the occupied spin-orbitals *i* and *j* to the unoccupied spin-orbitals *a* and *b*. The spin-orbitals *i* and *j* must be different, and having $j > i$ in the sum ensures that this requirement is met. Also, having $j > i$ ensures that we do not count the same double excitation twice. Thus, we include Φ_{12}^{ab} but do not include Φ_{21}^{ab}, which is the same as Φ_{12}^{ab}. If $b = a$, then two electrons have been excited to the same spin-orbital, which makes the Slater determinant zero and violates the Pauli exclusion principle. The numbering of the vacant spin-orbitals starts at $n + 1$ and goes to infinity, and these are the smallest and largest values that occur in the sums over *a* and *b*. Having $b > a$, ensures that we do not put the two excited electrons into the same spin-orbital and ensures that we do not count the same excitation twice.

(b) From (16.11), we have
$\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \sum_l \sum_{m>l} r_{lm}^{-1} - \sum_{m=1}^n \sum_{j=1}^n [\hat{j}_j(m) - \hat{k}_j(m)] | \Phi_0 \rangle =$
$\langle \Phi_{ij}^{ab} | \sum_l \sum_{m>l} r_{lm}^{-1} | \Phi_0 \rangle - \sum_{m=1}^n \langle \Phi_{ij}^{ab} | \sum_{j=1}^n [\hat{j}_j(m) - \hat{k}_j(m)] | \Phi_0 \rangle$. The operators $\hat{j}_j(m)$ and $\hat{k}_j(m)$ are one-electron operators, and since Φ_0 and Φ_{ij}^{ab} differ by two spin-orbitals, the Condon–Slater rules in Table 11.3 give $\langle \Phi_{ij}^{ab} | \sum_{j=1}^n \hat{j}_j(m) | \Phi_0 \rangle = 0$ and $\langle \Phi_{ij}^{ab} | \sum_{j=1}^n \hat{k}_j(m) | \Phi_0 \rangle = 0$. The Condon-Slater rules for the two-electron operator r_{lm}^{-1} give
$\langle \Phi_{ij}^{ab} | \sum_l \sum_{m>l} r_{lm}^{-1} | \Phi_0 \rangle = \langle u_b(1) u_a(2) | r_{12}^{-1} | u_j(1) u_i(2) \rangle - \langle u_b(1) u_a(2) | r_{12}^{-1} | u_i(1) u_j(2) \rangle$.
Therefore $\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle = \langle u_b(2) u_a(1) | r_{12}^{-1} | u_j(2) u_i(1) \rangle - \langle u_b(2) u_a(1) | r_{12}^{-1} | u_i(2) u_j(1) \rangle$, where the dummy variables 1 and 2 were interchanged. Substitution in (16.12), use of the summation ranges discussed in part (a), and use of the $E_0^{(0)} - E_s^{(0)}$ expression in the paragraph preceding Eq. (16.13) gives Eq. (16.13).

16.11 True. As noted on p. 542, MP calculations are not variational.

16.12 **(a)** A Z-matrix is given in Prob. 15.41a. The MP2(FC)/6-31G* geometry is found to be a bond length of 1.180 Å and a bond angle of 180°. The HF/6-31G* results are 1.143 Å and 180°. The experimental values are 1.162 Å and 180°. The calculated and experimental dipole moments are zero. The calculated equilibrium unscaled and scaled vibrational wavenumbers and the experimental fundamental vibrational wavenumbers in cm^{-1} are (see the Prob. 15.45a solution for sources of data)

HF/6-31G*	746	746	1518	2585
MP2(FC)/6-31G*	636	636	1333	2448
scaled HF/6-31G*	664	664	1351	2301
scaled MP2(FC)/6-31G*	604	604	1266	2326
experimental	667	667	1333	2349

The MP2(FC)/6-31G* energy is –188.1077474 hartrees. (In *Gaussian*, this energy is found after EUMP2 = in the last cycle of calculation preceding the listing of the optimized geometry and after MP2 = in the calculation summary at the end of the output.) The MP2(FC)/6-31G* energies of C and O are found to be –37.7329745 and –74.8800367 hartrees, respectively. The calculated MP2(FC)/6-31G* D_e is

(–37.7329745) + 2(–74.8800367) – (–188.1077474) = 0.614700 hartrees = 16.727 eV. To calculate D_0, we estimate the zero-point vibrational energy as

$\frac{1}{2}\sum_i h\nu_i = \frac{1}{2}hc\sum_i \tilde{\nu}_i = \frac{1}{2}(6.626\times10^{-34}\text{ J s})(2.998\times10^{10}\text{ cm/s})(604+604+1266+2326)\text{cm}^{-1}$ = 4.768×10^{-20} J = 0.2976 eV. So the MP2(FC)/6-31G* dissociation energy is $D_0 = 16.727\text{ eV} - 0.298\text{ eV}$ = 16.43 eV, not far from the 16.56 eV experimental value.

(b) The MP2(FC)/6-31G* bond length and bond angle are found to be 0.969 Å and 103.9°. The HF/6-31G* results are 0.947 Å and 105.5°. The experimental values are 0.958 Å and 104.5°. Dipole moments are 2.24 D for MP2(FC)/6-31G*, 2.20 D for HF/6-31G*, and 1.85 D experimental. The calculated equilibrium unscaled and scaled vibrational wavenumbers and the experimental fundamental vibrational wavenumbers in cm^{-1} are

HF/6-31G*	1827	4070	4188
MP2(FC)/6-31G*	1736	3775	3917
scaled HF/6-31G*	1626	3622	3727
scaled MP2(FC)/6-31G*	1649	3586	3721
experimental	1595	3657	3756

The MP2(FC)/6-31G* energy is –76.1968475 hartrees. The MP2(FC)/6-31G* energies of H and O are found to be –0.498233 and –74.8800367 hartrees, respectively. The calculated MP2(FC)/6-31G* D_e is (–74.8800367) + 2(–0.498233) – (–76.1968475) = 0.320345 hartrees = 8.717 eV. To get D_0, we estimate the zero-point vibrational energy as

$\frac{1}{2}\sum_i h\nu_i = \frac{1}{2}hc\sum_i \tilde{\nu}_i = \frac{1}{2}(6.626\times10^{-34}\text{ J s})(2.998\times10^{10}\text{ cm/s})(1649+3586+3721)\text{cm}^{-1}$ = 8.895×10^{-20} J = 0.5552 eV. So $D_0 = 8.717\text{ eV} - 0.555\text{ eV}$ = 8.16 eV, compared with the 9.51 eV experimental value (p. 499 of the text).

16.13 In the Thermochemistry section of the *Gaussian* output (which occurs after the vibrational frequency listing), the quantity listed as E (thermal) is the sum of the molar zero-point vibrational energy and the molar translational, rotational, and vibrational energy differences between 298 K and 0 K. Therefore, subtraction of the molar zero-point vibrational energy (which is listed in the *Gaussian* thermochemistry section) from E (thermal) gives $U^\circ_{298} - U^\circ_0$. (Click on Raw Output to see the *Gaussian* output in WebMO.)

(a) 0.934 Å, 2.01 D, –100.182171 hartrees, 4041 cm^{-1}, (7.26 – 5.78) kcal/mol = 1.48 kcal/mol, 41.54 cal/mol-K.

(b) 0.935 Å, 2.01 D, –100.188436 hartrees, 4009 cm^{-1}, (7.21 – 5.73) kcal/mol = 1.48 kcal/mol, 41.54 cal/mol-K.

HF/6-31G* results are 0.911 Å, 1.97 D, –100.002907 hartrees, 4357 cm^{-1}, (7.71 – 6.23) kcal/mol = 1.48 kcal/mol, 41.44 cal/mol-K.

Experimental results are 0.917 Å (for R_e), 1.83 D, 4138 cm^{-1} (for the harmonic frequency), 1.46 kcal/mol, 41.51 cal/mol-K (at 1 atm). The CCCBDB or the *NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., 1982, give for HF:

$H^\circ_{298} - H^\circ_0 = U^\circ_{298} + R(298.15\text{ K}) - U^\circ_0 = 8.60$ kJ/mol, so $U^\circ_{298} - U^\circ_0 =$ 6.12 kJ/mol = 1.46 kcal/mol.

16.14 **(a)** $3CH_4 + C_3H_6 \rightarrow 3C_2H_6$. and $CH_4 + CH_3CHO \rightarrow C_2H_6 + H_2CO$

(b) To save time, rather than deal with the individual vibration frequencies, it is simplest to look at the zero-point energy (ZPE) reported by, for example, WebMO. HF/6-31G* results in hartrees for the electronic energies, ZPEs, and scaled ZPEs (using the scale factor 0.895) are

CH_4	CH_3CHO	C_2H_6	H_2CO
–40.195172	–152.915966	–79.228755	–113.866331
0.047777	0.059933	0.079762	0.029203
0.042760	0.053640	0.071387	0.026137

The computed energy change in hartrees for the 0 K reaction (including ZPE) is $-113.866331 - 79.228755 + 152.915966 + 40.195172 + 0.026137 + 0.071387 - 0.053640 - 0.042760$ $= 0.017176$ hartrees, which is 10.8 kcal/mol.

(c) MP2(FC)/6-31G* results in hartrees for the electronic energies, ZPEs, and scaled ZPEs (using the scale factor 0.943 given by the CCCBDB) are

CH_4	CH_3CHO	C_2H_6	H_2CO

–40.332552	–153.346919	–79.494741	–114.167748
0.046330	0.056955	0.077164	0.027283
0.043689	0.053709	0.072766	0.025728

The computed energy change is 0.018078 hartrees, which is 11.3 kcal/mol.

16.15 Use of (16.15) and equations in the paragraph after (16.20) gives $\langle \psi | \Phi_0 \rangle = \langle e^{\hat{T}} \Phi_0 | \Phi_0 \rangle = \langle \Phi_0 + \hat{T}\Phi_0 + \frac{1}{2}\hat{T}^2\Phi_0 + \cdots | \Phi_0 \rangle$. As discussed in the paragraph after (16.20), all the excited Slater determinants are orthogonal to Φ_0, so $\langle \psi | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1$. [This equation is similar to Eq. (9.15).] We have $\langle \psi | \psi \rangle = \langle e^{\hat{T}} \Phi_0 | e^{\hat{T}} \Phi_0 \rangle = \langle \Phi_0 + \hat{T}\Phi_0 + \frac{1}{2}\hat{T}^2\Phi_0 + \cdots | \Phi_0 + \hat{T}\Phi_0 + \frac{1}{2}\hat{T}^2\Phi_0 + \cdots \rangle$. We have $\langle \Phi_0 | \Phi_0 \rangle = 1$, but there is no reason for an integral like $\langle \hat{T}\Phi_0 | \hat{T}\Phi_0 \rangle$ to be zero, so $\langle \psi | \psi \rangle \neq 1$.

16.16 **(a)** If the molecule has only two electrons, then triple excitations are not possible and the CCSD and CCSD(T) energies are equal. An example is H_2.

(b) If the molecule has only two valence electrons but more than two electrons, then the frozen-core CCSD and CCSD(T) energies are equal, but the full CCSD and CCSD(T) energies differ. An example is Li_2.

(c) If the molecule has only two electrons, then $n = 2$ in (16.15) and (16.17) and the CBS CCSD energy is the exact nonrelativistic energy. H_2 is an example.

16.17 **(a)** We have $\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \cdots)\Phi_0 \rangle$, where (16.16) with $\hat{T}$ replaced by $\hat{T}_2$ was used. The determinant Φ_{ij}^{ab} is doubly excited. The quantity $\hat{T}_2^3\Phi_0$ contains only sextuply excited determinants. Hence $\langle \Phi_{ij}^{ab} | \hat{H} | \frac{1}{6}\hat{T}_2^3\Phi_0 \rangle$ is zero since the matrix elements of $\hat{H}$ between Slater determinants differing by four (or more) spin orbitals are zero (Table 11.3). The integrals involving powers of $\hat{T}$ higher than 3 involve Slater determinants differing by more than four spin-orbitals and so are zero. Thus $\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2)\Phi_0 \rangle$.

(b) $\langle \Phi_{ij}^{ab} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \cdots)\Phi_0 \rangle$. The determinant Φ_{ij}^{ab} is doubly excited. Φ_0 is unexcited. $\hat{T}_2\Phi_0$ contains only doubly excited determinants. $\hat{T}_2^2\Phi_0$ contains only quadruply excited determinants; etc. Because of the orthogonality of Slater determinants having different degrees of excitation (this follows from Table 11.3 if $\sum_i f_i$ is replaced by 1), we get $\langle \Phi_{ij}^{ab} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{T}_2\Phi_0 \rangle$.

16.18 Multiplication of (16.31) by n^3 gives $n^3 E_n^{\text{corr}} = n^3 E_\infty^{\text{corr}} + A$. Replacement of *n* by $n-1$ in this equation gives $(n-1)^3 E_{n-1}^{\text{corr}} = (n-1)^3 E_\infty^{\text{corr}} + A$. Subtracting the second equation from the first, we have $n^3 E_n^{\text{corr}} - (n-1)^3 E_{n-1}^{\text{corr}} = [n^3 - (n-1)^3] E_\infty^{\text{corr}}$, so $[n^3 E_n^{\text{corr}} - (n-1)^3 E_{n-1}^{\text{corr}}] \big/ [n^3 - (n-1)^3] = E_\infty^{\text{corr}}$.

16.19 **(a)**

$$E_n = E_\infty + \frac{B}{(n+\frac{1}{2})^4} \quad \text{and} \quad E_{n-1} = E_\infty + \frac{B}{(n-\frac{1}{2})^4} \quad \text{so } E_n - E_{n-1} = B\left[(n+\tfrac{1}{2})^{-4} - (n-\tfrac{1}{2})^{-4}\right]$$

and $B = \dfrac{E_n - E_{n-1}}{(n+\frac{1}{2})^{-4} - (n-\frac{1}{2})^{-4}}$. So

$$E_\infty = E_n - \frac{E_n - E_{n-1}}{(n+\frac{1}{2})^{-4} - (n-\frac{1}{2})^{-4}}(n+\tfrac{1}{2})^{-4} = E_n - \frac{E_n - E_{n-1}}{1 - [(n+\frac{1}{2})/(n-\frac{1}{2})]^4}$$

(b) For $n = 5$, we get $E_\infty = -76.370298 - \dfrac{-76.370298 + 76.363588}{1 - (5.5/4.5)^4} = -76.375747$

For $n = 6$, $E_\infty = -76.372559 - \dfrac{-76.372559 + 76.370298}{1 - (6.5/5.5)^4} = -76.374937$

For $n = 7$, $E_\infty = -76.373672 - \dfrac{-76.373672 + 76.372559}{1 - (7.5/6.5)^4} = -76.375113$

16.20 **(a)** The results are 0.934 Å, 4024 cm^{-1}, 1.93 D, –100.186601 hartrees, (7.23 – 5.75) kcal/mol = 1.48 kcal/mol, 41.54 cal/mol-K (where $U_{298}^\circ - U_0^\circ$ is found as in Prob. 16.13).

(b) 0.935 Å, 4003 cm^{-1}, 2.02 D, –100.188327 hartrees, (7.20 – 5.72) kcal/mol = 1.48 kcal/mol, 41.54 cal/mol-K.

(c) See Prob. 16.13.

16.21 **(a)** The indefinite integral of a function is another function, whereas a functional converts a function to a number, so the indefinite integral is not a functional.

(b) The definite integral converts a function to a number and is a functional.

(c) This is a functional. **(d)** This is not a functional. **(e)** This is a functional.

16.22 If we assume that the ground-state wave functions $\psi_{0,a}$ and $\psi_{0,b}$ of $\hat{H}_a$ and $\hat{H}_b$ are the same, then $\hat{H}_a \psi_{0,a} = E_{0,a}\psi_{0,a}$ and $\hat{H}_b \psi_{0,a} = E_{0,b}\psi_{0,a}$. Subtraction gives $(\hat{H}_a - \hat{H}_b)\psi_{0,a} = (E_{0,a} - E_{0,b})\psi_{0,a}$. But $\hat{H}_a$ and $\hat{H}_b$ differ only in $\mathbf{v}(\mathbf{r}_i)$, so $\hat{H}_a - \hat{H}_b = \sum_{i=1}^n [\mathbf{v}_a(\mathbf{r}_i) - \mathbf{v}_b(\mathbf{r}_i)]$ and we have $\sum_{i=1}^n [\mathbf{v}_a(\mathbf{r}_i) - \mathbf{v}_b(\mathbf{r}_i)]\psi_{0,a} = (E_{0,a} - E_{0,b})\psi_{0,a}$

and $\boxed{\sum_{i=1}^{n}[\mathbf{v}_a(\mathbf{r}_i) - \mathbf{v}_b(\mathbf{r}_i)] = E_{0,a} - E_{0,b}}$. By hypothesis, $\mathbf{v}_a(\mathbf{r}_i)$ and $\mathbf{v}_b(\mathbf{r}_i)$ differ by more than a constant. Since $[\mathbf{v}_a(\mathbf{r}_i) - \mathbf{v}_b(\mathbf{r}_i)]$ does not equal a constant, and since $[\mathbf{v}_a(\mathbf{r}_j) - \mathbf{v}_b(\mathbf{r}_j)]$ for $j \neq i$ depends on different variables than does $[\mathbf{v}_a(\mathbf{r}_i) - \mathbf{v}_b(\mathbf{r}_i)]$, the sum on the left side of the boxed equation does not equal a constant. But $E_{0,a} - E_{0,b}$ does equal a constant. Hence the boxed equation cannot be true. We were led to this erroneous equation by the assumption that the ground-state wave functions $\psi_{0,a}$ and $\psi_{0,b}$ of $\hat{H}_a$ and $\hat{H}_b$ are the same. Hence this assumption must be false.

16.23 **(a)** We use Eq. (16.51). Comparison of (16.61) with the equation preceding (16.51) gives $g = -(9/8)(3/\pi)^{1/3}\alpha\rho^{4/3}$. Here, g depends on ρ but not on ρ_x, ρ_y, or ρ_z, so $\delta E_x^{X\alpha}/\delta\rho = \delta g/\delta\rho = -(3/2)(3/\pi)^{1/3}\alpha\rho^{1/3}$.

(b) Here $g = \rho^{-1}\nabla\rho \cdot \nabla\rho = \rho^{-1}[(\partial\rho/\partial x)^2 + (\partial\rho/\partial y)^2 + (\partial\rho/\partial z)^2] = \rho^{-1}(\rho_x^2 + \rho_y^2 + \rho_z^2)$ where Eqs. (5.31) and (5.23) were used. Equation (16.51) gives $\delta F/\delta\rho = -\rho^{-2}(\rho_x^2 + \rho_y^2 + \rho_z^2) - (\partial/\partial x)(2\rho^{-1}\rho_x) - (\partial/\partial y)(2\rho^{-1}\rho_y) - (\partial/\partial z)(2\rho^{-1}\rho_z)$. We have $(\partial/\partial x)(2\rho^{-1}\rho_x) = -2\rho^{-2}(\partial\rho/\partial x)\rho_x + 2\rho^{-1}(\partial\rho_x/\partial x) = -2\rho^{-2}\rho_x^2 + 2\rho^{-1}\rho_{xx}$, where $\rho_{xx} \equiv \partial^2\rho/\partial x^2$. So $\delta F/\delta\rho = \rho^{-2}(\rho_x^2 + \rho_y^2 + \rho_z^2) - 2\rho^{-1}(\rho_{xx} + \rho_{yy} + \rho_{zz}) =$ $\rho^{-2}(\rho_x^2 + \rho_y^2 + \rho_z^2) - 2\rho^{-1}\nabla^2\rho$, where (3.46) was used.

16.24 The operator $\hat{h}^{\text{KS}}$ in (16.49) is given by the terms in brackets in Eq. (16.47). The first two terms in these brackets match the first two terms in the right side of Eq. (16.8) (except that different labels are used for the electron). The third term in brackets in (16.47) is given by (16.45) to be $\int r_{12}^{-1}\rho(\mathbf{r}_2)\,d\mathbf{r}_2 = \sum_{i=1}^{n}\int |\theta_i^{\text{KS}}(\mathbf{r}_2)|^2 r_{12}^{-1}\,d\mathbf{r}_2$ (Eq. 1). From (16.8) and (14.28), $\sum_{j=1}^{n}\hat{j}_j(m) = \sum_{j=1}^{n}\int |\phi_j(2)|^2\, r_{12}^{-1}\,d\upsilon_2$ (Eq. 2). [The summation over the spin coordinates of electron *j* that is mentioned after (16.8) gives 1 for each $\hat{j}_j$ term.] The right sides of Eq. 1 and 2 are the same, except that different letters are used for the dummy summation variables and the Kohn–Sham orbitals are used in Eq. 1 instead of the Hartree–Fock orbitals used in Eq. 2. Thus the only difference between the Hartree–Fock operator (16.8) and the Kohn–Sham Hamiltonian in (16.47) is that $-\sum_{j=1}^{n}\hat{k}_j(m)$ is replaced by $\upsilon_{xc}(m)$.

16.25 Use of (16.54) in (16.52) gives $E_{xc}^{\text{LDA}}[\rho] = \int(\rho\varepsilon_x + \rho\varepsilon_c)\,d\mathbf{r}$. From (16.50) and (16.51), $\upsilon_{xc}^{\text{LDA}} \equiv \delta E_{xc}^{\text{LDA}}/\delta\rho = (\partial/\partial\rho)(\rho\varepsilon_x + \rho\varepsilon_c) = \varepsilon_x + \rho(\partial\varepsilon_x/\partial\rho) + \varepsilon_c + \rho(\partial\varepsilon_c/\partial\rho)$. Let $\upsilon_x^{\text{LDA}} \equiv \varepsilon_x + \rho(\partial\varepsilon_x/\partial\rho)$ and $\upsilon_c^{\text{LDA}} \equiv \varepsilon_c + \rho(\partial\varepsilon_c/\partial\rho)$. So $\upsilon_{xc}^{\text{LDA}} = \upsilon_x^{\text{LDA}} + \upsilon_c^{\text{LDA}}$. Then $\upsilon_x^{\text{LDA}} \equiv \varepsilon_x + \rho(\partial\varepsilon_x/\partial\rho) = -(3/4)(3/\pi)^{1/3}\rho^{1/3} + \rho(-3/4)(3/\pi)^{1/3}(1/3)\rho^{-2/3} = -(3/\pi)^{1/3}\rho^{1/3}$, where (16.55) was used. Also $\upsilon_c^{\text{LDA}} \equiv \varepsilon_c + \rho(\partial\varepsilon_c/\partial\rho) = \varepsilon_c^{\text{VWN}} + \rho(\partial\varepsilon_c^{\text{VWN}}/\partial\rho) \equiv \upsilon_c^{\text{VWN}}$, where (16.56) was used. Finally, $E_x^{\text{LDA}} \equiv \int \rho\varepsilon_x\, d\mathbf{r} = -0.75(3/\pi)^{1/3} \int \rho^{4/3} d\mathbf{r}$, where (16.55) was used.

16.26 The Hartree–Fock exchange energy $E_{x,\text{HF}}$ is given by the K_{ij} terms in (14.22) and is $E_{x,\text{HF}} = -\sum_{i=1}^{n/2} \sum_{j=1}^{n/2} K_{ij}$ (Eq. 1), where each sum goes over the *n*/2 different occupied spatial orbitals of the *n*-electron molecule, and the exchange integrals are defined by (14.24). If, instead of summing over the *n*/2 occupied MOs, we sum over the *n* electrons, then each sum will have *n* (instead of *n*/2) terms, with each MO occurring twice in each sum, since each MO is occupied by two electrons. We thus want to consider the relation between the double sum $\sum_{i=1}^{n} \sum_{j=1}^{n} K_{ij}$ (Eq. 2) and the double sum in Eq. 1.

In the double sum in Eq. 1, we have two types of terms: those that involve only one MO and those that involve two different MOs. Consider first the terms that involve only one MO. Let *r* be a particular MO in the sums in Eq. 1. In each sum in Eq. 2, the MO *r* will occur twice, once for each electron that occupies MO *r*. Let *ra* and *rb* denote these two occurrences of MO *r*. In place of the term K_{rr} in Eq. 1, we will get the four terms $K_{ra,ra}$, $K_{ra,rb}$, $K_{rb,ra}$, $K_{rb,rb}$. Since *ra* and *rb* are the same MOs as each other, these four terms are each equal to K_{rr} and their sum equals $4K_{rr}$.

Now consider terms that involve the two different MOs *r* and *p*. In the Eq. 1 double sum, these terms give the contribution $K_{rp} + K_{pr}$. In the Eq. 2 double sum, these terms give the contribution $K_{ra,pa} + K_{ra,pb} + K_{rb,pa} + K_{rb,pb} + K_{pa,ra} + K_{pa,rb} + K_{pb,ra} + K_{pb,rb}$. Since *ra* and *rb* are the same MOs and *pa* and *pb* are the same MOs, we have $K_{ra,pa} + K_{ra,pb} + K_{rb,pa} + K_{rb,pb} + K_{pa,ra} + K_{pa,rb} + K_{pb,ra} + K_{pb,rb} = 4(K_{rp} + K_{pr})$ [which could be simplified using (11.84)].

Thus we see that the double sum in Eq. 2 is four times the double sum in Eq. 1, which justifies the factor 1/4 in Eq. (16.60). Changing the upper limits to *n* in Eq. 1 and multiplying by 1/4 to compensate, and replacing the Hartree–Fock MOs by the Kohn–Sham MOs in the exchange integrals (14.24), we get Eq. (16.60).

16.27 The electron density is the sum of the densities due to the spin-α electrons and the spin-β electrons: $\rho = \rho^\alpha + \rho^\beta$. If $\rho^\alpha = \rho^\beta$, then $\rho = 2\rho^\alpha$ and $(\rho^\alpha)^{4/3} + (\rho^\beta)^{4/3} = 2(\rho^\alpha)^{4/3} = 2(\frac{1}{2}\rho)^{4/3} = 2^{-1/3}\rho^{4/3}$ and the right side of (16.65) becomes $-(3/4)(6/\pi)^{1/3}(1/2)^{1/3} \int \rho^{4/3}\, d\mathbf{r} = -(3/4)(3/\pi)^{1/3} \int \rho^{4/3}\, d\mathbf{r}$, which is (16.58).

16.28 **(a)** $n\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle = n\sum_{\text{all } m_s} \int\int\cdots\int |\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, m_{s1}, \ldots, m_{sn})|^2 \delta(\mathbf{r}-\mathbf{r}_1)\, d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_n$, where the vector notation for spatial variables (Sec. 5.2) is used. In the integral over $\mathbf{r}_1$

(which is really a triple integral), the Dirac delta function $\delta(\mathbf{r}-\mathbf{r}_1)$ has the same effect as $\delta(\mathbf{r}_1-\mathbf{r})$ (this will be proved below), so use of (7.91) to do the $\mathbf{r}_1$ integration gives $n\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle = n\sum_{\text{all } m_s}\int\cdots\int|\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n,m_{s1},\ldots,m_{sn})|^2\,d\mathbf{r}_2\cdots d\mathbf{r}_n$ **(Eq. 1)**. Equation (14.5) then gives $n\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle = \rho(\mathbf{r})$ **(Eq. 2)**. To verify the statement made about the delta function, we start with Eq. (7.91): $f(a)=\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx$. Let $w\equiv -x$. Then $dw=-dx$ and $f(a)=-\int_{\infty}^{-\infty} f(-w)\delta(-w-a)\,dw=\int_{-\infty}^{\infty} f(-w)\delta(-a-w)\,dw$. Let $b\equiv -a$. Then $f(-b)=\int_{-\infty}^{\infty} f(-w)\delta(b-w)\,dw$ **(Eq. 3)**. Let $g(w)\equiv f(-w)$. [For example, if $f(w)=2w^2+w$, then $f(-w)=2w^2-w$ and $g(w)=2w^2-w$.] Then Eq. 3 becomes $g(b)=\int_{-\infty}^{\infty} g(w)\delta(b-w)\,dw=\int_{-\infty}^{\infty} g(x)\delta(b-x)\,dx$, where the dummy integration variable was changed to *x*. Comparison with (7.91) shows that $\delta(b-x)$ in the integrand has the same effect as $\delta(x-b)$.

Also, $\langle\psi|\sum_{i=1}^{n}\delta(\mathbf{r}-\mathbf{r}_i)|\psi\rangle=\sum_{i=1}^{n}\langle\psi|\delta(\mathbf{r}-\mathbf{r}_i)|\psi\rangle$ **(Eq. 4)**. When $\mathbf{r}_1$ is changed to $\mathbf{r}_i$ in Eq. 1, we get an integrand on the right side of the equation in which $\mathbf{r}_i$ (instead of $\mathbf{r}_1$) is replaced by $\mathbf{r}$. As discussed after Eq. (14.4), the location of the $\mathbf{r}$ in ψ does not affect the value of the integral, so $\langle\psi|\delta(\mathbf{r}-\mathbf{r}_i)|\psi\rangle=\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle$ and Eq. 4 becomes $\langle\psi|\sum_{i=1}^{n}\delta(\mathbf{r}-\mathbf{r}_i)|\psi\rangle=\sum_{i=1}^{n}\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle=n\langle\psi|\delta(\mathbf{r}-\mathbf{r}_1)|\psi\rangle=\rho(\mathbf{r})$ **(Eq. 5)**, where Eq. 2 was used.

(b) Starting with Eq. 5 and using Eq. (11.78) with $D=\psi$ and $\hat{f}_i=\delta(\mathbf{r}-\mathbf{r}_i)$, we get $\rho(\mathbf{r})=\langle\psi|\sum_{i=1}^{n}\delta(\mathbf{r}-\mathbf{r}_i)|\psi\rangle=\sum_{i=1}^{n}\langle\theta_i(1)|\,\delta(\mathbf{r}-\mathbf{r}_1)\,|\,\theta_i(1)\rangle=\sum_{i=1}^{n}|\theta_i(\mathbf{r})|^2$.

16.29 **(a)** The following results are found

	R_{CO}/Å	$\tilde{\nu}_i/\text{cm}^{-1}$	E_{CO_2}/E_h	E_C/E_h	E_O/E_h
SVWN/6-31G*	1.171	624, 624, 1359, 2459	–187.616774	–37.566160	–74.643343
BLYP/6-31G*	1.183	601, 601, 1304, 2346	–188.563058	–37.832017	–75.046947
B3LYP/6-31G*	1.169	640, 640, 1372, 2436	–188.580940	–37.846279	–75.060611

where E_h = 1 hartree and the equilibrium bond angle is 180° in all cases. (A spin multiplicity of 3 must be entered for C and for O in the input.) The calculated D_e values are found from $E_C+2E_O-E_{CO_2}$. The D_0 values are found by adding the zero-point energy $E_{ZPE}=\frac{1}{2}h\sum_i \nu_i$ to D_e, as in Prob. 16.12a. Using the conversion factor in Table A.2, we find the atomization energies ΔE_{at} from the D_0 values. We find

	D_e/E_h	D_e/eV	E_{ZPE}/eV	D_0/eV	ΔE_{at}/(kcal/mol)
SVWN/6-31G*	0.763928	20.79	0.314	20.47	472
BLYP/6-31G*	0.637147	17.34	0.301	17.04	393

B3LYP/6-31G*	0.613437	16.69	0.315	16.38	378

The experimental ΔE_{at} found from thermodynamic data is 382 kcal/mol.

(b) The results found for H_2O are

	R_{OH}/Å	∠HOH	$\tilde{\nu}_i/\text{cm}^{-1}$	E_{H_2O}/E_h	E_H/E_h
SVWN/6-31G*	0.975	103.7°	1649, 3673, 3805	–76.040301	–0.493937
BLYP/6-31G*	0.980	102.7°	1682, 3567, 3689	–76.388543	–0.495446
B3LYP/6-31G*	0.969	103.6°	1713, 3727, 3849	–76.408953	–0.500273

(A spin multiplicity of 2 must be entered for H when doing the calculations.) The calculated D_e values are found from $E_O + 2E_H - E_{H_2O}$. We find

	D_e/E_h	D_e/eV	E_{ZPE}/eV	D_0/eV	ΔE_{at} /(kcal/mol)
SVWN/6-31G*	0.409085	11.132	0.566	10.566	243.7
BLYP/6-31G*	0.350704	9.543	0.554	8.989	207.3
B3LYP/6-31G*	0.347796	9.464	0.576	8.888	205.0

The experimental ΔE_{at} found from thermodynamic data is 219.4 kcal/mol.

16.30 Figures and Z-matrixes for the two conformers are given in Prob. 15.57. The B3LYP/6-31G* geometry-optimized structures are planar with the following properties:

	μ	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	1.43 D	125.5°	125.2°	106.6°	1.100 Å	1.205 Å	1.347 Å	0.977 Å
II	3.87 D	123.8°	122.7°	109.5°	1.108 Å	1.198 Å	1.353 Å	0.972 Å

The energies are –189.755456 hartrees for I and –189.747166 for II. The B3LYP/6-31G* electronic energy difference is $E_{II} - E_I$ = 0.008290 hartrees, corresponding to $E_{II} - E_I$ = 5.20 kcal/mol. The vibrational wavenumbers are 626, 707, 1055, 1147, 1326, 1423, 1855, 3086, and 3666 cm^{-1} for I and 533, 658, 1041, 1132, 1299, 1450, 1901, 2978, and 3722 cm^{-1} for II. The CCCBDB gives the scale factor for B3LYP/6-31G* frequencies as 0.96. For conformer I, we find $\frac{1}{2}hc\sum_i \tilde{\nu}_{i,\text{scaled}} = (7148\ \text{cm}^{-1})hc =$ $(7148\ \text{cm}^{-1})(6.6261\times10^{-34}\ \text{J s})(2.9979\times10^{10}\ \text{cm/s}) = 1.420\times10^{-19}\ \text{J}$. Multiplication by the Avogadro constant gives a zero-point energy of 85.51 kJ/mol = 20.44 kcal/mol. For conformer II, we find a zero-point energy of 20.19 kcal/mol. With inclusion of zero-point energies, we have $E_{II} - E_I$ = 4.95 kcal/mol.

16.31 B3LYP/6-31G* results in hartrees for the electronic energies, ZPEs, and scaled ZPEs (using the scale factor 0.960 given by the CCCBDB) are

CH_4	CH_3CHO	C_2H_6	H_2CO
–40.518389	–153.830119	–79.830417	–114.500472
0.045224	0.055825	0.075234	0.026837
0.043415	0.053592	0.072225	0.025764

The computed energy change in hartrees for the 0 K reaction (including ZPE) is 0.018601 hartrees, which is 11.7 kcal/mol.

16.32 **(a)** With the definition $\tau \equiv it/\hbar$, we write (7.100) as $\Psi = \sum_n c_n e^{-E_n\tau}\psi_n(q)$, where the c_n's are constants. In the computer simulation, τ is considered as a real variable. The ratio of the coefficient of an excited-state (es) wave function with energy E_{es} to the coefficient of the ground-state (gs) wave function in the sum is $(c_{es}/c_{gs})e^{-(E_{es}-E_{gs})\tau}$. Since $E_{es} > E_{gs}$, this ratio goes to zero as $\tau \to \infty$, so the contributions of terms involving excited states become negligible as $\tau \to \infty$. From Prob. 4.52, the addition of $-V_{\text{ref}}$ to $\hat{H}$ changes each energy from E_n to $E_n - V_{\text{ref}}$.

(b) Equation (7.97) with V_{ref} subtracted from $\hat{H}$ is $-(\hbar/i)\partial\Psi/\partial t = (\hat{T} + V - V_{\text{ref}})\Psi$. We have $-(\hbar/i)\partial\Psi/\partial t = -(\hbar/i)(\partial\Psi/\partial\tau)(\partial\tau/\partial t) = -(\hbar/i)(\partial\Psi/\partial\tau)(i/\hbar) = -(\partial\Psi/\partial\tau)$, from which the equation given in the problem follows. Atomic units are used, so $\hbar$ and m_e are missing from the kinetic-energy operator.

16.33 **(a)** The Pauli exclusion principle allows us to put two electrons (with opposite spins) into the $n = 1$ particle-in-a-box orbital and one electron into the $n = 2$ orbital. Let the notation 1(1) and 2(1) denote electron 1 in the $n = 1$ orbital and electron 1 in the $n = 2$ orbital, respectively. From (10.48) (which is the expansion of a Slater determinant), we have

$$\begin{aligned}\psi_{gs} = {} & 6^{-1/2}[1(1)2(2)1(3) - 1(1)1(2)2(3)]\beta(1)\alpha(2)\alpha(3) + \\ & 6^{-1/2}[1(1)1(2)2(3) - 2(1)1(2)1(3)]\alpha(1)\beta(2)\alpha(3) + \\ & 6^{-1/2}[2(1)1(2)1(3) - 1(1)2(2)1(3)]\alpha(1)\alpha(2)\beta(3) \\ \equiv {} & a\beta(1)\alpha(2)\alpha(3) + b\alpha(1)\beta(2)\alpha(3) + c\alpha(1)\alpha(2)\beta(3)\end{aligned}.$$

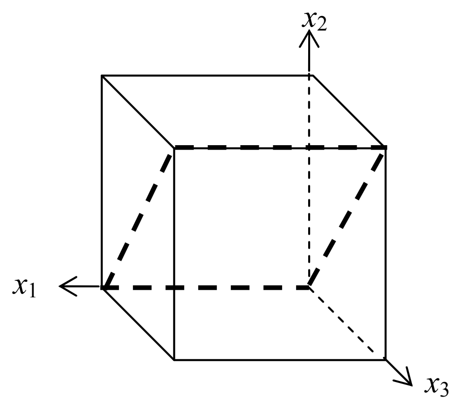
(b) Multiplication of $\hat{H}\psi_{gs} = (\hat{H}a)\beta(1)\alpha(2)\alpha(3) + (\hat{H}b)\alpha(1)\beta(2)\alpha(3) + (\hat{H}c)\alpha(1)\alpha(2)\beta(3) = E_{gs}[a\beta(1)\alpha(2)\alpha(3) + b\alpha(1)\beta(2)\alpha(3) + c\alpha(1)\alpha(2)\beta(3)]$ by $\beta(1)\alpha(2)\alpha(3)$ followed by summation over all the spin variables gives $\hat{H}a = E_{gs}a$, where orthogonality of different spin functions was used. The nodes of a are where $a = 1(1)2(2)1(3) - 1(1)1(2)2(3) = 0$. Since the function $1(1) = (2/l)^{1/2}\sin(\pi x_1/l)$ is never zero for $0 < x_1 < l$, we can divide by 1(1), and the nodes of a are where $2(2)1(3) - 1(2)2(3) = 0$. This equation is $\sin(2\pi x_2/l)\sin(\pi x_3/l) = \sin(\pi x_2/l)\sin(2\pi x_3/l)$. Use of $\boxed{\sin 2z = 2\sin z\cos z}$ gives

$2\sin(\pi x_2/l)\cos(\pi x_2/l)\sin(\pi x_3/l) = 2\sin(\pi x_2/l)\sin(\pi x_3/l)\cos(\pi x_3/l)$ and $\cos(\pi x_2/l) = \cos(\pi x_3/l)$. The cosine functions in this equation decrease from 1 to –1 as x_2 and x_3 go from 0 to *l*. Only when $x_2 = x_3$ is this equation satisfied, and this defines the location of the nodal surface.

(c) The heavy dashed line in the figure shows the nodal plane where $x_2 = x_3$. With use of the boxed identity for sin 2*z*, the equation $a = 1(1)[2(2)1(3) - 1(2)2(3)]$ becomes

$$a = (2/l)^{3/2}\sin(\pi x_1/l)2[\sin(\pi x_2/l)\cos(\pi x_2/l)\sin(\pi x_3/l) - \sin(\pi x_2/l)\sin(\pi x_3/l)\cos(\pi x_3/l)]$$

$a = (2/l)^{3/2}\sin(\pi x_1/l)2\sin(\pi x_2/l)\sin(\pi x_3/l)[\cos(\pi x_2/l) - \cos(\pi x_3/l)]$. The sine functions in *a* are never negative in the range 0 to *l*, and the cosine functions continually decrease as x_2 and x_3 increase from 0 to *l*. Hence *a* is positive when $x_2 > x_3$ (above the nodal plane) and *a* is negative below the nodal plane, where $x_2 < x_3$. If x_2 and x_3 in *a* are interchanged, *a* is multiplied by –1.



16.34 **(a)** The isotropic shielding constants in ppm are: 159.91 for the methyl carbon, 4.26 for the carbonyl carbon, 22.17 for the carbonyl hydrogen, and 30.41, 30.18, 30.18 for the methyl hydrogens. Because of the nearly free rotation about the CC single bond, we average the methyl shielding constants to get 30.33 ppm. (If you are using WebMO, first run a geometry optimization; then click on New Job Using This Geometry; then click the right arrow, choose *Gaussian*, and choose NMR as the Calculation.)

(b) Subtraction [see (16.73)] gives the shifts in ppm as 29.87 for the methyl C, 185.52 for the carbonyl C, 10.01 for the carbonyl hydrogen, and 1.85 for the methyl hydrogens.

(c) Clicking on Scaling Factors, we get Table 1a, which gives for gas-phase B3LYP/6-31G* calculations the following values. For ^1H, $m = -0.9957$, $b = 32.288$; for ^{13}C, $m = -0.9269$, $b = 187.474$. Therefore the equation $\delta_i = (\sigma_i - b)/m$ in Sec. 16.9 gives as the predicted ^{13}C shifts: $-(159.91 - 187.47)/0.9269 = 29.73$ ppm for the methyl C and $-(4.26 - 187.47)/0.9269 = 197.66$ ppm for the carbonyl carbon. The predicted proton shifts are $-(22.17 - 32.29)/0.9957 = 10.16$ ppm for the carbonyl H and $-(30.33 - 32.29)/0.9957 = 1.97$ ppm for the methyl hydrogens. The database at sdbs.riodb.aist.go.jp gives carbon shifts in chloroform as 30.89 and 199.93 and gives the proton shifts as 9.79 and 2.21.

16.35 **(a)** The isotropic shielding constants in ppm are: 175.24 for the methyl carbon, 25.84 for the carbonyl carbon, 22.19 for the carbonyl hydrogen, and 29.93, 29.81, 29.81 for the methyl hydrogens. Because of the nearly free rotation about the CC single bond, we average the methyl shielding constants to get 29.85 ppm. (If you are using WebMO, choose Other as the Basis Set and enter the desired basis set; see also Prob. 16.34a.)

(b) Subtraction [see (16.73)] gives the shifts in ppm as 14.54 for the methyl C, 163.96 for the carbonyl C, 9.99 for the carbonyl hydrogen, and 2.33 for the methyl hydrogens.

(c) Clicking on Scaling Factors, we get Table 1a, which gives for gas-phase GIAO MP2/6-31+G(d,p) calculations the following values. For ^{1}H, $m = -1.0565$, $b = 32.019$; for ^{13}C, $m = -0.9077$, $b = 202.752$. Therefore the equation $\delta_i = (\sigma_i - b)/m$ in Sec. 16.9 gives as the predicted ^{13}C shifts: $-(175.24 - 202.75)/0.9077 = 30.31$ ppm for the methyl C and $-(25.84 - 202.75)/0.9077 = 194.90$ ppm for the carbonyl carbon. The predicted proton shifts are $-(22.19 - 32.02)/1.0565 = 9.30$ ppm for the carbonyl H and $-(29.85 - 32.02)/1.0565 = 2.05$ ppm for the methyl hydrogens. The database at sdbs.riodb.aist.go.jp gives carbon shifts in chloroform as 30.89 and 199.93 and gives the proton shifts as 9.79 and 2.21.

16.36 From (14.76), (6.94), and (6.63),
$\langle T\rangle = \langle \frac{1}{2}\mu\upsilon^2\rangle = -E = Z^2e^2/8\pi\varepsilon_0 a = Z^2e^2\mu e^2/8\pi\varepsilon_0(4\pi\varepsilon_0)\hbar^2$, where we use the reduced mass μ in $\langle T\rangle$, since it is μ that occurs in the kinetic-energy part of the Hamiltonian for internal motion; $\langle T\rangle$ is the kinetic energy of the electron's motion relative to the nucleus. We get $\langle\upsilon^2\rangle = Z^2e^4/(4\pi\varepsilon_0)^2\hbar^2$ and $\langle\upsilon^2\rangle^{1/2}/c = Ze^2/4\pi\varepsilon_0\hbar c =$
$Z(1.6022\times10^{-19}\text{ C})^2 2\pi\big/4\pi(8.854\times10^{-12}\text{ C}^2/\text{N-m}^2)(6.626\times10^{-34}\text{ J s})(2.9979\times10^{8}\text{ m/s})$
$= 0.0072974Z = Z/137.04$.

16.37 From the p. 583 definition, $\sum_i n_i = \sum_i c_i^* \sum_j c_j S_{ij} = \sum_i \sum_j c_i^* c_j S_{ij}$. We have $\psi = \sum_i c_i \Phi_i$ and $1 = \langle\psi\,|\,\psi\rangle = \langle\sum_i c_i\Phi_i\,|\sum_j c_j\Phi_j\rangle = \sum_i\sum_j c_i^* c_j\langle\Phi_i\,|\,\Phi_j\rangle = \sum_i\sum_j c_i^* c_j S_{ij}$. So $\sum_i n_i = 1$.

16.38 We have $\Phi_B = N\,|\cdots \overset{\frown}{p_y p_z}\,\overset{\frown}{s_1 s_2}\,| =$

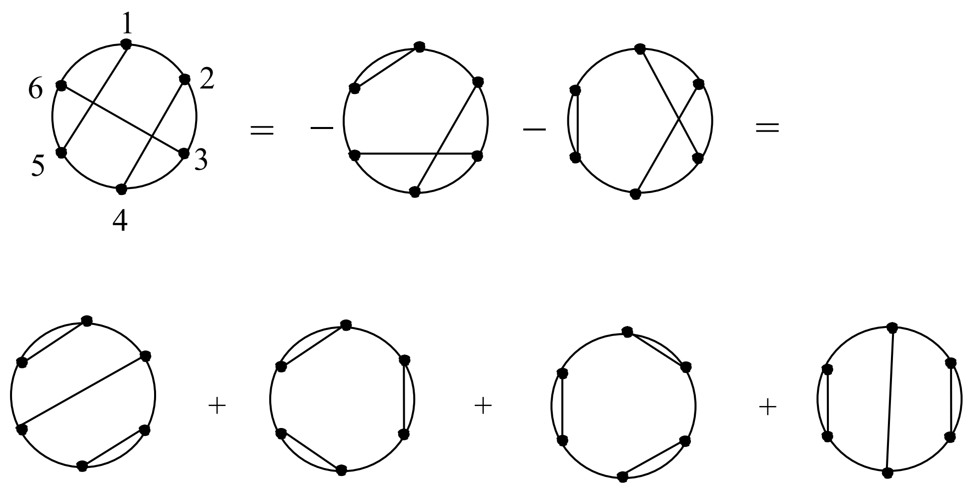
$$N\,|\cdots p_y\overline{p_z}s_1\overline{s_2}\,| - N\,|\cdots \overline{p_y}p_z s_1\overline{s_2}\,| - N\,|\cdots p_y\overline{p_z}\,\overline{s_1}s_2\,| + N\,|\cdots \overline{p_y}p_z\overline{s_1}s_2\,| =$$

$$N\,|\cdots p_y\overline{p_z}s_1\overline{s_2}\,| + N\,|\cdots \overline{p_y}s_1 p_z\overline{s_2}\,| + N\,|\cdots p_y\overline{s_1}\,\overline{p_z}s_2\,| + N\,|\cdots \overline{p_y}p_z\overline{s_1}s_2\,|,$$

where Theorem II on in Sec. 8.3 was used. Adding this equation to (16.74), we get

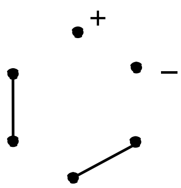
$\Phi_A + \Phi_B = N|\cdots p_y \bar{s}_1 p_z \bar{s}_2| + N|\cdots \bar{p}_y s_1 \bar{p}_z s_2| + N|\cdots p_y \bar{p}_z s_1 \bar{s}_2| + N|\cdots \bar{p}_y p_z \bar{s}_1 s_2|$.
Also $\Phi_C = N|\cdots p_y s_2 p_z s_1| =$
$N|\cdots p_y \bar{s}_2 p_z \bar{s}_1| - N|\cdots p_y \bar{s}_2 \bar{p}_z s_1| - N|\cdots \bar{p}_y s_2 p_z \bar{s}_1| + N|\cdots \bar{p}_y s_2 \bar{p}_z s_1|$. Let the last four columns of each determinant in Φ_C be numbered 1, 2, 3, and 4. We now interchange columns 2 and 4 of the first determinant in Φ_C, interchange columns 2 and 3 of the second determinant in Φ_C and then interchange columns 3 and 4 in the resulting determinant, interchange columns 2 and 3 of the third determinant in Φ_C and then interchange columns 3 and 4 in the resulting determinant, and interchange columns 2 and 4 of the last determinant in Φ_C. This gives
$\Phi_C = -N|\cdots p_y \bar{s}_1 p_z \bar{s}_2| - N|\cdots p_y \bar{p}_z s_1 \bar{s}_2| - N|\cdots \bar{p}_y p_z \bar{s}_1 s_2| - N|\cdots \bar{p}_y s_1 \bar{p}_z s_2|$, which is seen to equal $-(\Phi_A + \Phi_B)$.

16.39 Using (16.78), we have

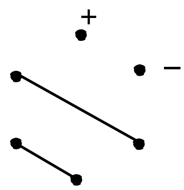


where each diagram stands for a bond eigenfunction.

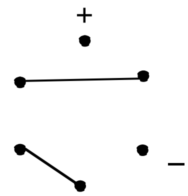
16.40 The types of singly polar VB structures are



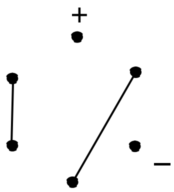
VI



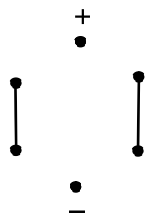
VII



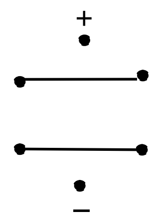
VIII



IX



X



XI

There are 12 individual structures of the form VI, since the plus sign can be put on each of 6 carbons and the minus sign can be put on the preceding or following carbon. Similarly, there are 12 individual structures of the form VII, 12 of the form VIII, and 12 of the form IX. There are 6 of the form X and 6 of the form XI.

16.41 **(a)** There are 4 π AOs (one on each C) to be paired. Equation (16.77) gives $4!/2!3! = 2$ canonical covalent VB π-electron structures.

(b) If we put the four carbons on a ring, the pairings with no lines crossing are 1–2 3–4 and 4–1 2–3, so the canonical covalent structures are

$\mathrm{CH_2{=}CH{-}CH{=}CH_2}$ $\qquad$ $\mathrm{CH_2{-}CH{=}CH{-}CH_2}$

(c) The singly polar structures are

$\overset{+}{\mathrm{CH_2}}{-}\overset{-}{\mathrm{CH}}{-}\mathrm{CH{=}CH_2}$ $\qquad$ $\overset{-}{\mathrm{CH_2}}{-}\overset{+}{\mathrm{CH}}{-}\mathrm{CH{=}CH_2}$ $\qquad$ $\mathrm{CH_2{=}CH{-}}\overset{+}{\mathrm{CH}}{-}\overset{-}{\mathrm{CH_2}}$

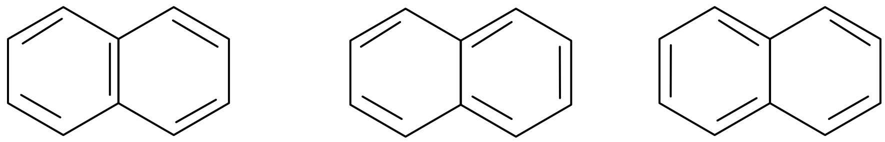
$\mathrm{CH_2{=}CH{-}}\overset{-}{\mathrm{CH}}{-}\overset{+}{\mathrm{CH_2}}$ $\qquad$ $\mathrm{CH_2{-}}\overset{+}{\mathrm{CH}}{-}\overset{-}{\mathrm{CH}}{-}\mathrm{CH_2}$ $\qquad$ $\mathrm{CH_2{-}}\overset{-}{\mathrm{CH}}{-}\overset{+}{\mathrm{CH}}{-}\mathrm{CH_2}$

$\overset{-}{\mathrm{CH_2}}{-}\mathrm{CH{-}}\overset{+}{\mathrm{CH}}{-}\mathrm{CH_2}$ $\qquad$ $\overset{+}{\mathrm{CH_2}}{-}\mathrm{CH{-}}\overset{-}{\mathrm{CH}}{-}\mathrm{CH_2}$ $\qquad$ $\mathrm{CH_2{-}}\overset{-}{\mathrm{CH}}{-}\mathrm{CH{-}}\overset{+}{\mathrm{CH_2}}$

$\mathrm{CH_2{-}}\overset{+}{\mathrm{CH}}{-}\mathrm{CH{-}}\overset{-}{\mathrm{CH_2}}$ $\qquad$ $\overset{+}{\mathrm{CH_2}}{-}\mathrm{CH{=}CH{-}}\overset{-}{\mathrm{CH_2}}$ $\qquad$ $\overset{-}{\mathrm{CH_2}}{-}\mathrm{CH{=}CH{-}}\overset{+}{\mathrm{CH_2}}$

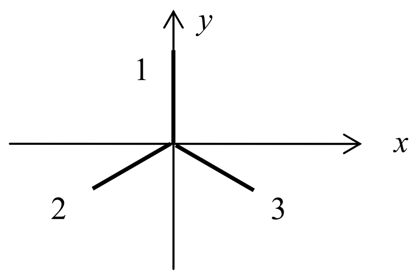
16.42 **(a)** For naphthalene, there are 10 π AOs (one on each C) to be paired, and (16.77) gives $10!/5!6! = 42$ canonical covalent π-electron structures.

(b) There are only the following three ways to draw 5 pairs of double bonds between adjacent carbons in naphthalene:



(c) The 1–2, 3–4, 5–6, and 7–8 bonds (see Fig. 17.6 for the numbering) are double bonds in two of the three Kekulé structures, so these bonds are predicted to be the shortest.

16.43 Let the maxima of these hybrids lie in the *xy* plane, as follows:



The direction cosines of lines 1, 2, and 3 are the cosines of the angles each line makes with the positive halves of the *x*, *y*, and *z* axes. These angles and their cosines are

	α	β	γ	$\cos\alpha$	$\cos\beta$	$\cos\gamma$
line 1	90°	0°	90°	0	1	0
line 2	210°	120°	90°	$-\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}$	0
line 3	330°	240°	90°	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}$	0

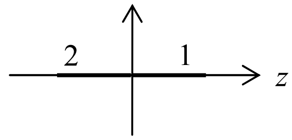
From the discussion after (16.81), the coefficients of the 2*p* AOs in the hybrids are proportional to the direction cosines, and the sp^2 hybrids h_1, h_2, h_3 have the forms:

$h_1 = b(\mathrm{C}2s) + c(\mathrm{C}2p_y)$, $\quad h_2 = b(\mathrm{C}2s) + c[-\frac{1}{2}\sqrt{3}(\mathrm{C}2p_x) - \frac{1}{2}(\mathrm{C}2p_y)]$

$h_3 = b(\mathrm{C}2s) + c[\frac{1}{2}\sqrt{3}(\mathrm{C}2p_x) - \frac{1}{2}(\mathrm{C}2p_y)]$

The orthonormality conditions give $b^2 + c^2 = 1$ and $b^2 - \frac{1}{2}c^2 = 0$. We get $b = 1/3^{1/2}$ and $c = (2/3)^{1/2}$ and substitution in the preceding equations gives the hybrids.

16.44 Let the maxima of these hybrids lie on the *z* axis as follows:



The direction cosines of lines 1 and 2 are the cosines of the angles each line makes with the positive halves of the *x*, *y*, and *z* axes. These angles and their cosines are

	α	β	γ	$\cos\alpha$	$\cos\beta$	$\cos\gamma$
line 1	90°	90°	0°	0	0	1
line 2	90°	90°	180°	0	0	–1

From the discussion after (16.81), the coefficients of the 2*p* AOs in the hybrids are proportional to the direction cosines, and the *sp* hybrids h_1, h_2 have the forms:

$$h_1 = b(\mathrm{C}2s) + c(\mathrm{C}2p_z)$$
$$h_2 = b(\mathrm{C}2s) + c[-(\mathrm{C}2p_z)]$$

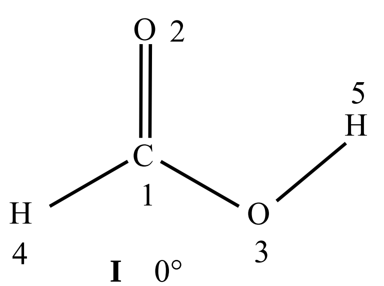
The orthonormality conditions give $b^2 + c^2 = 1$ and $b^2 - c^2 = 0$. We get $b = 1/2^{1/2}$ and $c = 1/2^{1/2}$. Substitution in the preceding equations gives the hybrids as

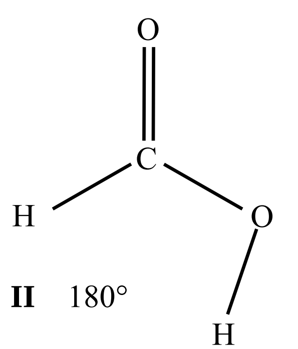
$$h_1 = 2^{-1/2}[(\mathrm{C}2s) + (\mathrm{C}2p_z)] \qquad h_2 = 2^{-1/2}[(\mathrm{C}2s) - (\mathrm{C}2p_z)]$$

16.45 **(a)** To avoid the 180° angle in the Z-matrix, we use a dummy atom, as in Prob. 15.41a. The HF/6-31G* geometries are found to be R_{CH} = 1.059 Å, R_{CN} = 1.132 Å, ∠HCN = 180° for HCN; R_{NH} = 0.985 Å, R_{NC} = 1.154 Å, ∠HNC = 180° for HNC.

(b) The HF/6-31G* transition-state structure is found to be R_{CH} = 1.155 Å, R_{CN} = 1.169 Å, ∠HCN = 77.5°.

16.46 **(a)** HF/6-31G* calculations give the stable conformers as the following planar structures:





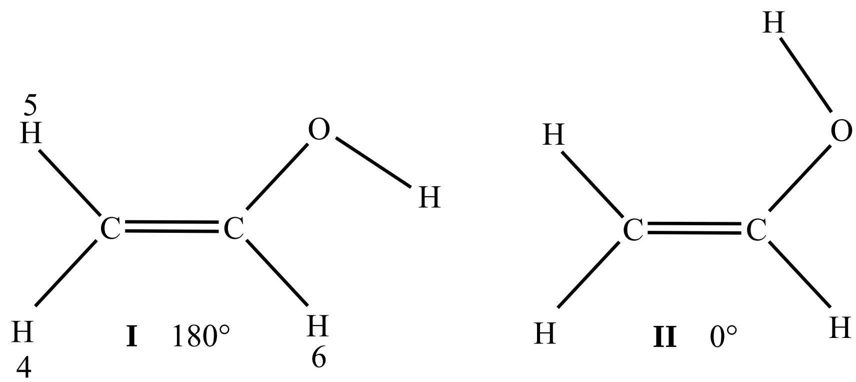
where the *D*(OCOH) dihedral angles are given. A Z-matrix for Conformer I is given in Prob. 15.57. A good starting pointing for the search for the transition state is to take *D*(OCOH) equal to 90°. One finds the following HF/6-31G* properties for the conformers and the transition state (TS):

	μ	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	1.60 D	124.7°	124.9°	108.7°	1.083 Å	1.182 Å	1.323 Å	0.953 Å
II	4.37 D	123.1°	123.0	111.5°	1.090 Å	1.176 Å	1.328 Å	0.948 Å
TS	3.20 D	123.0	123.9	112.0	1.087 Å	1.174 Å	1.351 Å	0.950 Å

	D(OCOH)	E_{HF}/hartrees
I	0°	–188.762310
II	180°	–188.752546
TS	96.0°	–188.740756

The energy difference between the more-stable conformer I and the transition state is 0.021554 hartrees (zero-point energies omitted), corresponding to a 13.5 kcal/mol barrier. The energy difference between I and II is predicted to be 6.1 kcal/mol.

(b) HF/6-31G* calculations give the following two stable planar conformers:



where the D(CCOH) dihedral angles are given. A good starting point for the search for the transition state is to take D(CCOH) equal to 90°. One finds the following HF/6-31G* properties for the conformers and the transition state (TS):

	μ/D	∠H5C=C	∠HCH	∠CCO	∠HCO	∠COH	R_{CH4}/Å	R_{CH5}/Å	$R_{C=C}$/Å
I	2.09	121.4°	118.5°	122.7°	115.6°	110.7°	1.073	1.074	1.315
II	1.06	122.3°	117.5	126.9°	110.6°	110.3°	1.073	1.077	1.318
TS	1.76	121.5	118.1°	123.7	114.1°	110.2	1.074	1.075	1.314

	R_{CH6}/Å	R_{CO}/Å	R_{OH}/Å	D(CCOH)	E_{HF}/hartrees
I	1.077	1.354	0.945	180°	–152.885390
II	1.074	1.347	0.948	0°	–152.888887
TS	1.077	1.368	0.948	85.7°	–152.881576

Although conformers I and II are predicted to be planar, the six atoms CH_2CHO of the transition state are slightly nonplanar; for example, D(OCCH5) is –1.3°. The energy difference between the more-stable conformer II and the transition state is 0.007311 hartrees (zero-point energies omitted), corresponding to a 4.6 kcal/mol barrier.

Chapter 17

Semiempirical and Molecular-Mechanics Treatments of Molecules

17.1 **(a)** The carbons are numbered 1, 2, and 3, with 1 bonded to 2 and 2 bonded to 3. The assumptions (17.11) to (17.13) give $H_{11}^{\text{eff}} = H_{22}^{\text{eff}} = H_{33}^{\text{eff}} = \alpha$, $H_{12}^{\text{eff}} = H_{23}^{\text{eff}} = \beta$, $H_{13}^{\text{eff}} = 0$.
The secular equation (17.10) is

$$\begin{vmatrix} \alpha - e_k & \beta & 0 \\ \beta & \alpha - e_k & \beta \\ 0 & \beta & \alpha - e_k \end{vmatrix} = 0$$

Division of each row by β gives

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

where $x \equiv (\alpha - e_k)/\beta$. Use of (17.21) gives $\prod_{j=1}^{3}[x - 2\cos(j\pi/4)] = 0$ and $x = 2\cos(j\pi/4),\ j = 1, 2, 3;\ \ x = 1.414, 0, -1.414$. The energies (lowest first) are $e_k = \alpha - \beta x = \alpha + 1.414\beta,\ \alpha,\ \alpha - 1.414\beta$.

The equations for the HMO coefficients are

$$\begin{aligned} xc_{1j} + c_{2j} \qquad &= 0 \\ c_{1j} + xc_{2j} + c_{3j} &= 0 \\ c_{2j} + xc_{3j} &= 0 \end{aligned}$$

For the root $x = -1.414$, we get $c_2 = -xc_1 = 1.414c_1$,
$c_3 = -c_2/x = 0.707c_2 = 0.707(1.414c_1) = c_1$. Normalization gives
$1 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + (1.414)^2 c_1^2 + c_1^2 = 4c_1^2$ and $c_1 = 0.5$. So $c_2 = 0.707$ and $c_3 = 0.5$.
For the root $x = 0$, we get $c_2 = 0$ and $c_3 = -c_1$. Normalization gives $1 = c_1^2 + c_3^2 = 2c_1^2$, so $c_1 = 0.707$, $c_2 = 0$, and $c_3 = -0.707$.
For the root $x = 1.414$, we get $c_2 = -xc_1 = -1.414c_1$,
$c_3 = -c_2/x = -0.707c_2 = -0.707(-1.414c_1) = c_1$. Normalization gives
$1 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + (1.414)^2 c_1^2 + c_1^2 = 4c_1^2$ and $c_1 = 0.5$. So $c_2 = -0.707$ and $c_3 = 0.5$.
The HMOs from lowest to highest are

$\phi_1 = 0.5f_1 + 0.707f_2 + 0.5f_3$

$\phi_2 = 0.707f_1 - 0.707f_3$

$\phi_3 = 0.5f_1 - 0.707f_2 + 0.5f_3$

(b) We use (17.54): $p_{rs} = \sum_i n_i c_{ri} c_{si}$ for real HMOs. This species has three π electrons, two of which are in ϕ_1 and one in ϕ_2. So $p_{12} = 2(0.5)0.707 + 1(0.707)0 = 0.707 = p_{23}$.

(c) Use of (17.53) gives $q_1 = 2(0.5)^2 + 1(0.707)^2 = 1$, $q_2 = 2(0.707)^2 + 1(0) = 1$, $q_3 = 2(0.5)^2 + 1(-0.707)^2 = 1$.

(d) $F_1 = 3^{1/2} - p_{12} = 3^{1/2} - 0.707 = 1.025$. $F_2 = 3^{1/2} - p_{12} - p_{23} = 3^{1/2} - 0.707 - 0.707 =$ 0.318. $F_3 = 1.025$.

(e) The π-electron energy is due to the two electrons in ϕ_1 and the one electron in ϕ_2, and is $2(\alpha + 1.414\beta) + \alpha = 3\alpha + 2.828\beta$. The Hückel energy of a nonconjugated double bond is $\alpha + \beta$ and the Hückel energy of a nonconjugated electron on a carbon atom is [see (17.11)] α, so the nonconjugated Hückel π-electron energy is $2(\alpha + \beta) + \alpha$, and the delocalization energy is $3\alpha + 2.828\beta - (3\alpha + 2\beta) = 0.828\beta$.

17.2 **(a)** The conjugated-carbon structure is the same for these ions as for the allyl radical, so the HMOs and HMO energies are the same as in Prob. 17.1a.

(b) The cation has two π electrons and these go in the HMO ϕ_1. The anion has four π electrons, two in ϕ_1 and two in ϕ_2. For the cation, $p_{12} = 2(0.5)0.707 = 0.707 = p_{23}$. For the anion, $p_{12} = 2(0.5)0.707 + 2(0.707)0 = 0.707 = p_{23}$.

(c) For the cation, $q_1 = 2(0.5)^2 = 0.5$, $q_2 = 2(0.707)^2 = 1$, $q_3 = 2(0.5)^2 = 0.5$. For the anion, $q_1 = 2(0.5)^2 + 2(0.707)^2 = 1.5$, $q_2 = 2(0.707)^2 + 2(0) = 1$, $q_3 = 2(0.5)^2 + 2(-0.707)^2 = 1.5$.

(d) p_{12} and p_{23} are the same for neutral allyl, for the cation, and for the anion, so the free valences of the ions are the same as in Prob. 17.1d.

(e) For the cation, the π-electron energy is $2(\alpha + 1.414\beta) = 2\alpha + 2.828\beta$ and the nonconjugated Hückel π-electron energy is $2(\alpha + \beta)$, so the delocalization energy is $2\alpha + 2.828\beta - 2\alpha - 2\beta = 0.828\beta$. For the anion, the π-electron energy is $2(\alpha + 1.414\beta) + 2\alpha = 4\alpha + 2.828\beta$ and the nonconjugated Hückel π-electron energy is $2(\alpha + \beta) + 2\alpha$, so the delocalization energy is $4\alpha + 2.828\beta - 4\alpha - 2\beta = 0.828\beta$. The stabilities are predicted to be the same.

17.3 For the polyenes (17.28), $n_C = 2s + 2$. Equation (17.31) gives $\lambda_{HMO} = \{4(37300\ \text{cm}^{-1})\sin[\pi/(4s+6)]\}^{-1} = (67.0\ \text{nm})/\sin[\pi/(4s+6)]$. We find

s	0	1	2	3	4	5	6	7	9
λ_{exper}/nm	162.5	217	268	303	334	364	390	410	447
λ_{HMO}	134	217	301	386	471	556	641	726	897

HMO error	–18%	0	12%	27%	41%	53%	64%	77%	101%

The average absolute error is 44% for the HMO method.

17.4 For $x = -0.618$, the first equation of (17.25) gives $c_2 = 0.618c_1$; the second equation gives $c_3 = -c_1 + 0.618c_2 = -c_1 + 0.618(0.618)c_1 = -0.618c_1$; the fourth equation gives $c_4 = c_3/0.618 = -c_1$. Normalization gives $1 = c_1^2 + c_2^2 + c_3^2 + c_4^2 =$ $c_1^2 + (0.618)^2 c_1^2 + (0.618)^2 c_1^2 + c_1^2 = 2.76c_1^2$ and $c_1 = 0.602$. Then $c_2 = 0.618c_1 = 0.372$; $c_3 = -0.618c_1 = -0.372$; $c_4 = -c_1 = -0.602$.

For $x = 0.618$, the first equation of (17.25) gives $c_2 = -0.618c_1$; the second equation gives $c_3 = -c_1 - 0.618c_2 = -c_1 - 0.618(-0.618)c_1 = -0.618c_1$; the fourth equation gives $c_4 = -c_3/0.618 = c_1$. Normalization gives $1 = c_1^2 + c_2^2 + c_3^2 + c_4^2 =$ $c_1^2 + (0.618)^2 c_1^2 + (0.618)^2 c_1^2 + c_1^2 = 2.76c_1^2$ and $c_1 = 0.602$. Then $c_2 = -0.618c_1 = -0.372$; $c_3 = -0.618c_1 = -0.372$; $c_4 = c_1 = 0.602$.

For $x = 1.618$, the first equation of (17.25) gives $c_2 = -1.618c_1$; the second equation gives $c_3 = -c_1 - 1.618c_2 = -c_1 - 1.618(-1.618)c_1 = 1.618c_1$; the fourth equation gives $c_4 = -c_3/1.618 = -c_1$. Normalization gives $1 = c_1^2 + c_2^2 + c_3^2 + c_4^2 =$ $c_1^2 + (1.618)^2 c_1^2 + (1.618)^2 c_1^2 + c_1^2 = 7.24c_1^2$ and $c_1 = 0.372$. Then $c_2 = -1.618c_1 = -0.602$; $c_3 = 1.618c_1 = 0.602$; $c_4 = -c_1 = -0.372$.

17.5 **(a)** Similar to the first equation in (17.25), the first equation satisfied by the coefficients is $xc_{1j} + c_{2j} = 0$. Substitution of (17.30) and the equation preceding (17.29) gives

$$-2\cos\frac{j\pi}{n_C+1}\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{j\pi}{n_C+1} + \left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{2j\pi}{n_C+1} = 0$$

Use of $\sin 2\theta = 2\sin\theta\cos\theta$ gives

$$-2\cos\frac{j\pi}{n_C+1}\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{j\pi}{n_C+1} + \left(\frac{2}{n_C+1}\right)^{1/2} 2\sin\frac{j\pi}{n_C+1}\cos\frac{j\pi}{n_C+1} = 0$$

$$0 = 0$$

Similar to the second and third equations in (17.25), equations that are not the first or last have the form $c_{r-1,j} + xc_{rj} + c_{r+1,j} = 0$. Substitution of (17.30) and the equation preceding (17.29) gives

$$\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{j(r-1)\pi}{n_C+1} - 2\cos\frac{j\pi}{n_C+1}\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{jr\pi}{n_C+1} + \left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{j(r+1)\pi}{n_C+1} = 0$$

Use of the identity in the problem to combine the first and last terms on the left side gives

$$\left(\frac{2}{n_C+1}\right)^{1/2} 2\sin\frac{jr\pi}{n_C+1}\cos\frac{j\pi}{n_C+1} - 2\cos\frac{j\pi}{n_C+1}\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{jr\pi}{n_C+1} = 0$$

$$0 = 0$$

Similar to the last equation in (17.25), the last equation satisfied by the coefficients is $c_{n_C-1,j} + xc_{n_C,j} = 0$. Substitution of (17.30) and the equation preceding (17.29) gives

$$\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{j(n_C-1)\pi}{n_C+1} - 2\cos\frac{j\pi}{n_C+1}\left(\frac{2}{n_C+1}\right)^{1/2}\sin\frac{jn_C\pi}{n_C+1} = 0$$

Division by $[2/(n_C+1)]^{1/2}$ and use of $\sin A\cos B = \frac{1}{2}[\sin(A+B)+\sin(A-B)]$ gives

$$\sin\frac{j(n_C-1)\pi}{n_C+1} - \sin\frac{j(n_C+1)\pi}{n_C+1} - \sin\frac{j(n_C-1)\pi}{n_C+1} = 0$$

$$-\sin j\pi = 0$$

$$0 = 0$$

(b) From (17.8) and (17.30), $\phi_j = \sum_{r=1}^{n_C} c_{rj} f_r = \sum_{r=1}^{n_C}\left(\frac{2}{n_C+1}\right)^{1/2}\left(\sin\frac{jr\pi}{n_C+1}\right) f_r$ and

$$\int \phi_j^*\phi_j\,d\tau = \int \sum_{r=1}^{n_C}\left(\frac{2}{n_C+1}\right)^{1/2}\left(\sin\frac{jr\pi}{n_C+1}\right) f_r \sum_{s=1}^{n_C}\left(\frac{2}{n_C+1}\right)^{1/2}\left(\sin\frac{js\pi}{n_C+1}\right) f_s\,d\tau =$$

$$\left(\frac{2}{n_C+1}\right)\sum_{r=1}^{n_C}\sum_{s=1}^{n_C}\left(\sin\frac{jr\pi}{n_C+1}\right)\left(\sin\frac{js\pi}{n_C+1}\right)\int f_r^* f_s\,d\tau =$$

$$\left(\frac{2}{n_C+1}\right)\sum_{r=1}^{n_C}\sum_{s=1}^{n_C}\left(\sin\frac{jr\pi}{n_C+1}\right)\left(\sin\frac{js\pi}{n_C+1}\right)\delta_{rs} =$$

$$\left(\frac{2}{n_C+1}\right)\sum_{r=1}^{n_C}\left(\sin\frac{jr\pi}{n_C+1}\right)^2 = -\left(\frac{2}{n_C+1}\right)\frac{1}{4}\sum_{r=1}^{n_C}\left[\exp\left(\frac{i\,jr\pi}{n_C+1}\right) - \exp\left(-\frac{i\,jr\pi}{n_C+1}\right)\right]^2 =$$

$$-\frac{1}{2n_C+2}\left[\sum_{r=1}^{n_C}\exp\left(\frac{2i\,jr\pi}{n_C+1}\right) - \sum_{r=1}^{n_C}2 + \sum_{r=1}^{n_C}\exp\left(-\frac{2i\,jr\pi}{n_C+1}\right)\right] =$$

$$-\frac{1}{2n_C+2}\left[\sum_{r=1}^{n_C}(e^w)^r - 2n_C + \sum_{r=1}^{n_C}(e^{-w})^r\right] \quad \text{where } w \equiv 2i\,j\pi/(n_C+1)$$

where a formula in Prob. 1.28 was used. The formula for the sum of a geometric series is $\sum_{r=1}^{n} b^r = \dfrac{b-b^{n+1}}{1-b}$. Taking $b = e^w$ and then $b = e^{-w}$, we get

$$\int \phi_j^* \phi_j \, d\tau = -\frac{1}{2n_C + 2}\left[\frac{e^w - e^{w(n_C+1)}}{1-e^w} - 2n_C + \frac{e^{-w} - e^{-w(n_C+1)}}{1-e^{-w}}\right]$$

The definition of w gives $w(n_C + 1) = 2ij\pi$, so

$e^{w(n_C+1)} = e^{2ij\pi} = \cos(2j\pi) + i\sin(2j\pi) = 1 + 0 = 1$. Similarly, $e^{-w(n_C+1)} = 1$. So

$$\int \phi_j^* \phi_j \, d\tau = -\frac{1}{2n_C + 2}\left[\frac{e^w - 1}{1-e^w} - 2n_C + \frac{e^{-w} - 1}{1-e^{-w}}\right] = -\frac{1}{2n_C + 2}(-1 - 2n_C - 1) = 1$$

17.6 From Fig. 17.1, the first excited state has two electrons in ϕ_1, one electron in ϕ_2, and one electron in ϕ_3. From (17.53) and (17.26), $q_1 = 2(0.372)^2 + 1(0.602)^2 + 1(0.602)^2 = 1.00$; $q_2 = 2(0.602)^2 + 1(0.372)^2 + 1(0.372)^2 = 1$; $q_3 = 1$; $q_4 = 1$. From (17.54) and (17.26), $p_{12} = 2(0.372)0.602 + 1(0.602)(0.372) + 1(0.602)(-0.372) = 0.448$; $p_{12}^{\text{tot}} = 1.448$; $p_{23} = 2(0.602)0.602 + 1(0.372)(-0.372) + 1(-0.372)(-0.372) = 0.725$; $p_{23}^{\text{tot}} = 1.725$; $p_{34}^{\text{tot}} = 1.448$.

17.7 **(a)** We have $\hat{C}_2^2 = \hat{E}$ and the symmetry species are

	$\hat{E}$	$\hat{C}_2$
A	1	1
B	1	–1

(b) The $\hat{C}_2$ symmetry rotation interchanges C_1 and C_4 and interchanges C_2 and C_3, so the normalized symmetry orbitals and their symmetry species are

$g_1 = 2^{-1/2}(f_1 + f_4)$ (A), $\quad g_3 = 2^{-1/2}(f_1 - f_4)$ (B),

$g_2 = 2^{-1/2}(f_2 + f_3)$ (A), $\quad g_4 = 2^{-1/2}(f_2 - f_3)$ (B)

As on p. 612, the secular equation is $\det[\langle g_p | \hat{H}^{\text{eff}} | g_q\rangle - \langle g_p | g_q\rangle e_k] = 0$. We have

$\langle g_1 | \hat{H}^{\text{eff}} | g_1\rangle = \tfrac{1}{2}\langle f_1 + f_4 | \hat{H}^{\text{eff}} | f_1 + f_4\rangle = \tfrac{1}{2}(\alpha + \alpha) = \alpha$;

$\langle g_1 | \hat{H}^{\text{eff}} | g_2\rangle = \tfrac{1}{2}\langle f_1 + f_4 | \hat{H}^{\text{eff}} | f_2 + f_3\rangle = \tfrac{1}{2}(\beta + \beta) = \beta$;

$\langle g_2 | \hat{H}^{\text{eff}} | g_2\rangle = \tfrac{1}{2}\langle f_2 + f_3 | \hat{H}^{\text{eff}} | f_2 + f_3\rangle = \tfrac{1}{2}(\alpha + \beta + \beta + \alpha) = \alpha + \beta$;

$\langle g_3 | \hat{H}^{\text{eff}} | g_3\rangle = \tfrac{1}{2}\langle f_1 - f_4 | \hat{H}^{\text{eff}} | f_1 - f_4\rangle = \tfrac{1}{2}(\alpha + \alpha) = \alpha$;

$\langle g_3 | \hat{H}^{\text{eff}} | g_4\rangle = \tfrac{1}{2}\langle f_1 - f_4 | \hat{H}^{\text{eff}} | f_2 - f_3\rangle = \tfrac{1}{2}(\beta + \beta) = \beta$;

$\langle g_4 | \hat{H}^{\text{eff}} | g_4\rangle = \tfrac{1}{2}\langle f_2 - f_3 | \hat{H}^{\text{eff}} | f_2 - f_3\rangle = \tfrac{1}{2}(\alpha - \beta - \beta + \alpha) = \alpha - \beta$;

$\langle g_1 | g_2\rangle = \tfrac{1}{2}\langle f_1 + f_4 | f_2 + f_3\rangle = 0$; $\quad \langle g_3 | g_4\rangle = \tfrac{1}{2}\langle f_1 - f_4 | f_2 - f_3\rangle = 0$.

The secular determinant for the A symmetry orbitals is

$$\begin{vmatrix} \langle g_1 | \hat{H}^{\text{eff}} | g_1 \rangle - e_k & \langle g_1 | \hat{H}^{\text{eff}} | g_2 \rangle \\ \langle g_1 | \hat{H}^{\text{eff}} | g_2 \rangle & \langle g_2 | \hat{H}^{\text{eff}} | g_2 \rangle - e_k \end{vmatrix} = 0 = \begin{vmatrix} \alpha - e_k & \beta \\ \beta & \alpha + \beta - e_k \end{vmatrix}$$

$$\begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0 = x^2 + x - 1 \quad \text{and} \quad x = -1.618,\ 0.618$$

For the first root, the equations for the coefficients are
$-1.618c_1 + c_2 = 0$ and $c_1 - 0.618c_2 = 0$, so $c_2 = 1.618c_1$. Normalization gives
$1 = c_1^2 + c_2^2 = c_1^2 + (1.618)^2 c_1^2 = 3.618c_1^2$ and $c_1 = 0.526$, $c_2 = 0.851$. So the HMO is
$c_1 g_1 + c_2 g_2 = 0.526(2^{-1/2})(f_1 + f_4) + 0.851(2^{-1/2})(f_2 + f_3) =$
$0.372 f_1 + 0.602 f_2 + 0.602 f_3 + 0.372 f_4$.

For the second root, the equations for the coefficients are
$0.618c_1 + c_2 = 0$ and $c_1 + 1.618c_2 = 0$, so $c_2 = -0.618c_1$. Normalization gives
$1 = c_1^2 + c_2^2 = c_1^2 + (0.618)^2 c_1^2 = 1.382c_1^2$ and $c_1 = 0.851$, $c_2 = -0.526$. So the HMO is
$c_1 g_1 + c_2 g_2 = 0.851(2^{-1/2})(f_1 + f_4) - 0.526(2^{-1/2})(f_2 + f_3) =$
$0.602 f_1 - 0.372 f_2 - 0.372 f_3 + 0.602 f_4$.

The secular determinant for the *B* symmetry orbitals is

$$\begin{vmatrix} \langle g_3 | \hat{H}^{\text{eff}} | g_3 \rangle - e_k & \langle g_3 | \hat{H}^{\text{eff}} | g_4 \rangle \\ \langle g_3 | \hat{H}^{\text{eff}} | g_4 \rangle & \langle g_4 | \hat{H}^{\text{eff}} | g_4 \rangle - e_k \end{vmatrix} = 0 = \begin{vmatrix} \alpha - e_k & \beta \\ \beta & \alpha - \beta - e_k \end{vmatrix}$$

$$\begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 = x^2 - x - 1 \quad \text{and} \quad x = 1.618,\ -0.618$$

For the first root, the equations for the coefficients are
$1.618c_3 + c_4 = 0$ and $c_3 + 0.618c_4 = 0$, so $c_4 = -1.618c_3$. Normalization gives
$1 = c_3^2 + c_4^2 = c_3^2 + (1.618)^2 c_3^2 = 3.618c_3^2$ and $c_3 = 0.526$, $c_4 = -0.851$. So the HMO is
$c_3 g_3 + c_4 g_4 = 0.526(2^{-1/2})(f_1 - f_4) - 0.851(2^{-1/2})(f_2 - f_3) =$
$0.372 f_1 - 0.602 f_2 + 0.602 f_3 - 0.372 f_4$.

For the second root, the equations for the coefficients are
$-0.618c_3 + c_4 = 0$ and $c_3 - 1.618c_4 = 0$, so $c_4 = 0.618c_3$. Normalization gives
$1 = c_3^2 + c_4^2 = c_3^2 + (0.618)^2 c_3^2 = 1.382c_3^2$ and $c_3 = 0.851$, $c_4 = 0.526$. So the HMO is
$c_3 g_3 + c_4 g_4 = 0.851(2^{-1/2})(f_1 - f_4) + 0.526(2^{-1/2})(f_2 - f_3) =$
$0.602 f_1 + 0.372 f_2 - 0.372 f_3 - 0.602 f_4$.

17.8 Imagine that we set up an *xy* coordinate system with origin at the center of each circle in Fig. 17.5, with the positive direction of the *x* axis pointing downward (going through the lowest apex, which lies at $\alpha - 2|\beta|$), and with the positive *y* axis pointing to the right. Let points in this plane represent the complex numbers $z = x + iy$ (as in Fig. 1.3). If each circle had a radius of 1, then, as noted in Prob. 1.28b, the *z* values of the points at each apex (the dots) would be the *n* *n*th roots of 1, where *n*, the number of apexes, is the number of carbons, n_C. Since the radius of each circle is $2|\beta|$, rather than 1, the x and y coordinates are multiplied by $2|\beta|$, and the z values of the apex points are $2|\beta|$ times the n_Cth roots of unity. Use of (1.36) for these roots gives $z = 2|\beta|\exp(i2\pi k/n_C)$, $k = 0, 1, \ldots, n_C - 1$, as the z values of the apexes. The energy scale in Fig. 17.5 is in the vertical direction with energy increasing going upwards. Thus the energy scale is in the $-x$ direction (as we have defined the x axis), and because the energy scale is set up with energy α occurring at the level of our coordinate origin, the energy of each apex point is α minus the x value of the apex point. The x value of a number in the complex plane is the real part of the number. Hence the energy of each apex point is $e_k = \alpha - \mathrm{Re}[2|\beta|\exp(i2\pi k/n_C)]$, where Re denotes the real part of a complex number. The real part of $e^{i\theta} = \cos\theta + i\sin\theta$ equals $\cos\theta$, so $e_k = \alpha - 2|\beta|\cos(2\pi k/n_C)$. Since $\beta < 0$, we have $|\beta| = -\beta$, and $e_k = \alpha + 2\beta\cos(2\pi k/n_C)$ as in (17.43).

17.9 **(a)** The harmonic-oscillator potential-energy function is $\frac{1}{2}k(R - R_e)^2$. The energy to compress three single bonds is $\frac{3}{2}(500\text{ N/m})(1.397 - 1.53)^2(10^{-10}\text{ m})^2 = 1.3\times 10^{-19}\text{ J}$. The energy to stretch three double bonds is $\frac{3}{2}(950\text{ N/m})(1.397 - 1.335)^2(10^{-10}\text{ m})^2 =$ $= 5.5\times 10^{-20}\text{ J}$. The sum of these energies is $1.8_5\times 10^{-19}\text{ J}$, and multiplication by the Avogadro constant gives 111 kJ/mol = 27 kcal/mol.

(b) Consider the gas-phase processes

$$\begin{tikzcd}
\text{benzene} \arrow[r, "1"] \arrow[d, "2"] & \text{cyclohexane} \\
\begin{array}{l}\text{nonconjugated benzene}\\ \text{with equal bond lengths}\end{array} \arrow[r, "3"] & \begin{array}{l}\text{nonconjugated benzene}\\ \text{with unequal bond lengths}\end{array} \arrow[u, "4"]
\end{tikzcd}$$

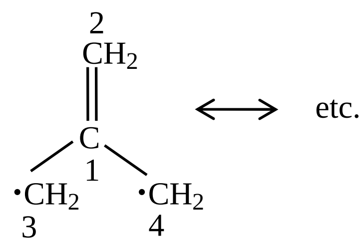
We have $\Delta E_1 = -49.8\text{ kcal/mol}$, $\Delta E_2 = 2|\beta|$, $\Delta E_3 = -27\text{ kcal/mol}$, $\Delta E_4 = 3(-28.6\text{ kcal/mol}) = -85.8\text{ kcal/mol}$. Substitution in $\Delta E_1 = \Delta E_2 + \Delta E_3 + \Delta E_4$ gives $2|\beta| = (-49.8 + 27 + 85.8)\text{ kcal/mol} = 63\text{ kcal/mol}$ and $|\beta| = 31\frac{1}{2}\text{ kcal/mol}$, which corresponds to 1.3_7 eV per molecule.

17.10 Consider the following gas-phase processes:

$$\begin{tikzcd} \text{benzene} \arrow[r, "1"] \arrow[d, "2"] & 6\text{C}(g) + 6\text{H}(g) \\ \begin{array}{l}\text{nonconjugated benzene}\\ \text{with equal bond lengths}\end{array} \arrow[r, "3"] & \begin{array}{l}\text{nonconjugated benzene}\\ \text{with unequal bond lengths}\end{array} \arrow[u, "4"] \end{tikzcd}$$

We have $\Delta E_1 = 1323\text{ kcal/mol}$, $\Delta E_2 = 2|\beta|$, $\Delta E_3 = -27\text{ kcal/mol}$ (see Prob. 17.9), $\Delta E_4 \approx 6(99\text{ kcal/mol}) + 3(83\text{ kcal/mol}) + 3(146\text{ kcal/mol}) = 1281\text{ kcal/mol}$. Substitution in $\Delta E_1 = \Delta E_2 + \Delta E_3 + \Delta E_4$ gives $2|\beta| = (1323 + 27 - 1281)\text{ kcal/mol} = 69\text{ kcal/mol}$ as the "experimental" delocalization energy with allowance for strain energy. (This gives $|\beta| = 34\frac{1}{2}\text{ kcal/mol}$, which corresponds to 1.5 eV per molecule.) If the strain energy is omitted, then ΔE_3 is taken as zero and we get the delocalization energy as $2|\beta| = (1323 - 1281)\text{ kcal/mol} = 42\text{ kcal/mol}$.

17.11 **(a)** The Lewis structure is

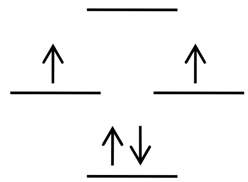


where "etc." denotes two resonance structures with the double-bond position changed. With carbon 1 bonded to carbons 2, 3, and 4, the HMO secular equation in the notation of Eqs. (17.19) and (17.20) is

$$\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 0 & 0 \\ 1 & 0 & x & 0 \\ 1 & 0 & 0 & x \end{vmatrix} = 0 = -1\begin{vmatrix} 1 & x & 0 \\ 1 & 0 & x \\ 1 & 0 & 0 \end{vmatrix} + x\begin{vmatrix} x & 1 & 1 \\ 1 & x & 0 \\ 1 & 0 & x \end{vmatrix} = -\begin{vmatrix} x & 0 \\ 0 & x \end{vmatrix} + x\left(1\begin{vmatrix} 1 & 1 \\ x & 0 \end{vmatrix} + x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}\right) =$$

$$-x^2 + x(-x) + x^2(x^2 - 1) = x^4 - 3x^2 = xx(x^2 - 3) = 0$$

where the first determinant was expanded using the elements of the fourth column. The secular equation has two $x = 0$ roots. The other two roots are found from $x^2 - 3 = 0$, so $x = 0,\ 0,\ 3^{1/2},\ -3^{1/2}$ and $e_k = \alpha + 3^{1/2}\beta,\ \alpha,\ \alpha,\ \alpha - 3^{1/2}\beta$. The HMO-energy-level pattern and ground-state orbital occupancy are



For the lowest MO, which has $x = -3^{1/2}$, the equations for the coefficients are

$$-3^{1/2}c_1 + c_2 + c_3 + c_4 = 0$$
$$c_1 - 3^{1/2}c_2 = 0$$
$$c_1 - 3^{1/2}c_3 = 0$$
$$c_1 - 3^{1/2}c_4 = 0$$

so $c_2 = c_3 = c_4 = 3^{-1/2}c_1$. Normalization gives $1 = c_1^2 + c_2^2 + c_3^2 + c_4^2 = c_1^2(1 + \frac{1}{3} + \frac{1}{3} + \frac{1}{3})$ and $c_1 = 2^{-1/2}$. Then $c_2 = c_3 = c_4 = 6^{-1/2}$.

Similarly, for the highest MO (with $x = 3^{1/2}$), we get $c_1 = 2^{-1/2}$, $c_2 = c_3 = c_4 = -6^{-1/2}$.

For the MOs with $x = 0$, the coefficients satisfy

$$c_2 + c_3 + c_4 = 0$$
$$c_1 = 0$$
$$c_1 = 0$$
$$c_1 = 0$$

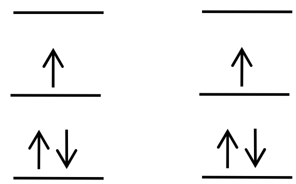
Normalization gives $|c_2|^2 + |c_3|^2 + |c_4|^2 = 1$. Because of the degeneracy, there are infinitely many possibilities that satisfy the two equations for $c_2,\ c_3,\ c_4$. Since this diradical has a C_3 symmetry axis, we can, if we like, take the degenerate HMOs to be eigenfunctions of the operator $\hat{O}_{C_3}$. The eigenvalues of $\hat{O}_{C_3}$ are the cube roots of 1, namely $e^{2\pi ik/3}$, where $k = 0, 1, 2$. Proceeding as was done for benzene, we can use the equations (17.37) and (17.38), except that $e^{2\pi ik/6}$ is replaced by $e^{2\pi ik/3}$, $\hat{O}_{C_6}$ is replaced by $\hat{O}_{C_3}$, and the sums go from $r = 2$ to $r = 4$. Thus (17.38) becomes $c_{r+1,j} = e^{2\pi ik/3}c_{rj}$. This equation shows that $|c_2| = |c_3| = |c_4|$, so the normalization condition becomes $3|c_2|^2 = 1$ and $|c_2| = 3^{-1/2}$. We shall take $c_2 = 3^{-1/2}$. In the equation $c_{r+1,j} = e^{2\pi ik/3}c_{rj}$, k cannot be zero, because this would give $c_4 = c_3 = c_2$, and these coefficients would not satisfy $c_2 + c_3 + c_4 = 0$. With $k = 1$, use of $c_{r+1,j} = e^{2\pi ik/3}c_{rj}$ gives $c_2 = 3^{-1/2}$, $c_3 = 3^{-1/2}e^{2\pi i/3}$, $c_4 = 3^{-1/2}e^{4\pi i/3}$. Use of $e^{i\theta} = \cos\theta + i\sin\theta$ shows that these coefficients satisfy $c_2 + c_3 + c_4 = 0$. With $k = 2$, use of $c_{r+1,j} = e^{2\pi ik/3}c_{rj}$ gives $c_2 = 3^{-1/2}$, $c_3 = 3^{-1/2}e^{4\pi i/3}, c_4 = 3^{-1/2}e^{8\pi i/3}$. Use of $e^{i\theta} = \cos\theta + i\sin\theta$ shows that these coefficients satisfy $c_2 + c_3 + c_4 = 0$. We thus can use these two sets of coefficients to get two complex HMOs $\phi_{2,\text{complex}}$ and $\phi_{3,\text{complex}}$ for the two HMOs with energy α.

To avoid dealing with complex MOs, we can (as was done for benzene) take the two linear combinations $2^{-1/2}(\phi_{2,\text{complex}} + \phi_{3,\text{complex}})$ and $2^{-1/2}(1/i)(\phi_{2,\text{complex}} - \phi_{3,\text{complex}})$ to get real MOs with the coefficients
$c_2 = (2/3)^{1/2}$, $c_3 = 6^{-1/2} \cdot 2\cos(2\pi/3) = -6^{-1/2}$, $c_4 = 6^{-1/2} \cdot 2\cos(4\pi/3) = -6^{-1/2}$ and
$c_2 = 0$, $c_3 = 6^{-1/2} \cdot 2\sin(2\pi/3) = 2^{-1/2}$, $c_4 = 6^{-1/2} \cdot 2\sin(4\pi/3) = -2^{-1/2}$. This gives
$\phi_{2,\text{real}} = (2/3)^{1/2} f_2 - 6^{-1/2} f_3 - 6^{-1/2} f_4$ and $\phi_{3,\text{real}} = 2^{-1/2} f_3 - 2^{-1/2} f_4$.
We use (17.54) to get the bond orders, and to avoid any ambiguities due to the partial occupation of the degenerate MOs, we shall use the complex coefficients. We have
$p_{12} = 2(2^{-1/2})6^{-1/2} + 1 \cdot \frac{1}{2}(0 \cdot 3^{-1/2} + 3^{-1/2} \cdot 0) + 1 \cdot \frac{1}{2}(0 \cdot 3^{-1/2} + 3^{-1/2} \cdot 0) = 3^{-1/2} = 0.577$.
Also, $p_{13} = 0.577 = p_{14}$.
From (17.53), $q_1 = 2(2^{-1/2})^2 + 1(0)^2 + 1(0)^2 = 1$,
$q_2 = 2(6^{-1/2})^2 + 1(3^{-1/2})^2 + 1(3^{-1/2})^2 = 1 = q_3 = q_4$.
From Prob. 17.19, $F_1 = 3^{1/2} - p_{21} - p_{31} - p_{41} = 3^{1/2} - 3^{-1/2} - 3^{-1/2} - 3^{-1/2} = 0$.
$F_2 = 3^{1/2} - p_{21} = 3^{1/2} - 3^{-1/2} = 1.155 = p_{31} = p_{41}$.

The orbital occupancies and energies give
$E_\pi = 2(\alpha + 3^{1/2}\beta) + 1(\alpha) + 1(\alpha) = 4\alpha + (12)^{1/2}\beta$. The energies of two π electrons in an isolated double bond and two π electrons each localized on a C add to
$E_{\text{localized}} = 2(\alpha + \beta) + \alpha + \alpha = 4\alpha + 2\beta$, so the delocalization energy is
$4\alpha + (12)^{1/2}\beta - (4\alpha + 2\beta) = 1.464\beta$.

(b) This diradical is linear with the Lewis structure $\mathrm{H{-}\underset{1}{\dot{C}}{=}\underset{2}{C}{=}\underset{3}{\dot{C}}{-}H}$. If the molecular axis is the z axis, then the π bond between carbons 1 and 2 is formed by overlap of $2p_x$ AOs and the π bond between carbons 2 and 3 is formed by overlap of $2p_y$ AOs. The unpaired electron on carbon 3 is in a $2p_x$ AO and interacts with the electrons of the π bond between carbons 1 and 2. The unpaired electron on carbon 1 is in a $2p_y$ AO and interacts with the electrons of the π bond between carbons 2 and 3. Thus we have two sets of π electrons; one set consists of three π_x electrons and one set consists of three π_y electrons. The conjugated carbon framework is linear with three carbons, and is the same framework as for the allyl radical of Prob. 17.1, so the HMO secular equation, the HMO energies, and the HMO coefficients are the same as for allyl. Thus the energies (lowest first) are $e_k = \alpha + 1.414\beta,\ \alpha,\ \alpha - 1.414\beta$; the HMOs from lowest to highest are
$\phi_1 = 0.5 f_1 + 0.707 f_2 + 0.5 f_3$
$\phi_2 = 0.707 f_1 - 0.707 f_3$
$\phi_3 = 0.5 f_1 - 0.707 f_2 + 0.5 f_3$

With three electrons in each set of π MOs, the orbital occupancy is



In using (17.54), we sum over all four of the occupied π MOs, so
$p_{12} = \sum_i n_i c_{1i} c_{2i} = 2(0.5)0.707 + 2(0.5)0.707 + 1(0.707)0 + 1(0.707)0 = 1.414 = p_{23}$.
From (17.53), $q_1 = 2(0.5)^2 + 2(0.5)^2 + 1(0.707)^2 + 1(0.707)^2 = 2 = q_3$;
$q_2 = 2(0.707)^2 + 2(0.707)^2 + 1(0) + 1(0) = 2$.
From Prob. 17.19, $F_1 = 3^{1/2} - p_{12} = 1.732 - 1.414 = 0.318$;
$F_2 = 3^{1/2} - p_{12} - p_{23} = 1.732 - 1.414 - 1.414 = -1.096$.
The orbital occupancies and energies give
$E_\pi = 2(\alpha + 2^{1/2}\beta) + 2(\alpha + 2^{1/2}\beta) + 1(\alpha) + 1(\alpha) = 6\alpha + (32)^{1/2}\beta$. The energies of four π electrons in two isolated double bonds and two π electrons each localized on a C add to $E_{\text{localized}} = 4(\alpha + \beta) + \alpha + \alpha = 6\alpha + 4\beta$, so the delocalization energy is
$6\alpha + (32)^{1/2}\beta - (6\alpha + 4\beta) = 1.657\beta$.

17.12 To ionize the molecule by removing an electron from the HOMO of energy $\alpha - \beta x$ requires an energy input of $\beta x - \alpha$, the ionization energy. The x values are known, and we have four pieces of data to be fit by varying two parameters α and β. We use the Excel Solver (with the constraint that β is negative) to minimize the sums of the squares of the deviations of the calculated values $\beta x - \alpha$ from the experimental values. With the initial guesses $\alpha = 0$ and $\beta = -1$ eV, the Solver converges to the values $\alpha = -6.146$ eV, $\beta = -3.316$ eV. The fit is pretty good, with the predicted ionization energies of the first four molecules being 9.46, 8.20, 7.52, and 7.12 eV. The predicted ionization energy for pentacene with $x = -0.220$ is (–3.316)(–0.220) eV + 6.146 eV = 6.88 eV.

17.13 **(a)** In $CH_2{=}CH{-}CH{=}CH_2$, there are two $CH_2{=}CH$ bonds and one $CH{-}CH$ bond, so $\sum_b n_b E_{\pi,b} = 2(2.0000\beta) + 0.4660\beta = 4.466\beta$.

(b) Benzene has three $CH{=}CH$ bonds and three $CH{-}CH$ bonds, so $\sum_b n_b E_{\pi,b} = 3(2.0699\beta) + 3(0.4660\beta) = 7.6077\beta$. The Hückel E_π of benzene is given by (17.51) as $6\alpha + 8\beta$, and is 8β with α omitted. Hence the Hess–Schaad resonance energy of benzene is $(7.6077 - 8)\beta = -0.3923\beta = 0.3923|\beta|$. The REPE is $0.3923|\beta|/6 = 0.065|\beta|$.
(c) In cyclobutadiene, there are two $CH{=}CH$ bonds and two $CH{-}CH$ bonds, so $\sum_b n_b E_{\pi,b} = 2(2.0699\beta) + 2(0.4660\beta) = 5.0718\beta$. The Hückel E_π of cyclobutadiene is given by Fig. 17.5 as $2(\alpha + 2\beta) + 2\alpha = 4\alpha + 4\beta$, and is 4β with α omitted. Hence the

Hess–Schaad resonance energy of cyclobutadiene is $(5.0718 - 4)\beta = 1.0718\beta = -1.0718|\beta|$. The REPE is $-1.0718|\beta|/4 = -0.268|\beta|$ (antiaromatic).

Planar [8]annulene has four $\mathrm{CH{=\!=}CH}$ bonds and four $\mathrm{CH{-\!-}CH}$ bonds, so $\sum_b n_b E_{\pi,b} = 4(2.0699\beta) + 4(0.4660\beta) = 10.1436\beta$. The HMO energies with α omitted are given by (17.43) as $2\beta,\ 2^{1/2}\beta,\ 2^{1/2}\beta,\ 0,\ 0,\ -2^{1/2}\beta,\ -2^{1/2}\beta,\ 2\beta$ and the Hückel E_π of [8]annulene is $2(2\beta) + 2(2^{1/2}\beta) + 2(2^{1/2}\beta) + 1(0) + 1(0) = 9.6569\beta$. The Hess–Schaad resonance energy of [8]annulene is $(10.1436 - 9.6569)\beta = 0.4867\beta = -0.4867|\beta|$. The REPE is $-0.4867|\beta|/8 = -0.061|\beta|$ (antiaromatic).

Planar [18]annulene has 9 $\mathrm{CH{=\!=}CH}$ bonds and 9 $\mathrm{CH{-\!-}CH}$ bonds, so $\sum_b n_b E_{\pi,b} = 9(2.0699\beta) + 9(0.4660\beta) = 22.8231\beta$. The HMO energies with α omitted are given by (17.43) as
$2\beta,\ 1.8794\beta,\ 1.8794\beta,\ 1.5321\beta,\ 1.5321\beta,\ \beta,\ \beta,\ 0.3473\beta,\ 0.3473\beta,$
$-0.3473\beta,\ -0.3473\beta,\ -\beta,\ -\beta,\ -1.5321\beta,\ -1.5321\beta,\ -1.8794\beta,\ -1.8794\beta,\ -2\beta$
and the Hückel E_π of [18]annulene is $2(2\beta) + 2(1.8794\beta) + 2(1.8794\beta) +$
$2(1.5321\beta) + 2(1.5321\beta) + 2\beta + 2\beta + 2(0.3473\beta) + 2(0.3473\beta) = 23.0352\beta$. The Hess–Schaad resonance energy of [18]annulene is $(22.8231 - 23.0352)\beta = -0.2121\beta = 0.2121|\beta|$. The REPE is $0.2121|\beta|/18 = 0.0118|\beta|$ (aromatic).

Azulene has 3 $\mathrm{CH{=\!=}CH}$ bonds, 2 $\mathrm{CH{=\!=}C}$ bonds, 3 $\mathrm{CH{-\!-}CH}$ bonds, 2 $\mathrm{CH{-\!-}C}$ bonds, and one $\mathrm{C{-\!-}C}$ bond, so
$\sum_b n_b E_{\pi,b} = 3(2.0699\beta) + 2(2.1083\beta) + 3(0.4660\beta) + 2(0.4362\beta) + 0.4358\beta = 13.1325\beta$.
There are 10 π electrons and the Hückel E_π with α omitted is $2(2.3103\beta) + 2(1.6516\beta) + 2(1.3557\beta) + 2(0.8870\beta) + 2(0.4773\beta) = 13.3638\beta$. The Hess–Schaad resonance energy of azulene is $(13.1325 - 13.3638)\beta = -0.2313\beta = 0.2313|\beta|$. The REPE is $0.2313|\beta|/10 = 0.0231|\beta|$ (aromatic).

17.14 **(a)** The conjugated carbon framework and the HMOs of $C_5H_5^-$ are the same as for C_5H_5. The Lewis structure of $C_5H_5^-$ has four π electrons in double bonds and two π electrons as a lone pair on the C that has no double bonds. The six π electrons in $C_5H_5^-$ fill the lowest three HMOs in the middle figure in Fig. 17.5. The HMO energies are given by (17.43) as $\alpha + 2\beta\ (k = 0),\ \alpha + 0.618\beta\ (k = 1),\ \alpha + 0.618\beta\ (k = 4),\ \alpha - 1.618\beta,\ (k = 2),$ $\alpha - 1.618\beta,\ (k = 3)$. Thus the $k = 0,\ 1,\ 4$ HMOs are occupied. (See also the comment after Eq. (17.45).] For each of these three HMOs, we use (17.44) to calculate the coefficients c_{1k} and c_{2k}. We get $c_{1,0} = c_{2,0} = 5^{-1/2}$; $c_{1,1} = 5^{-1/2}$, $c_{2,1} = 5^{-1/2}e^{2\pi i/5}$; $c_{1,4} = 5^{-1/2}$, $c_{2,4} = 5^{-1/2}e^{8\pi i/5}$. From (17.54),
$$p_{12} = 2(\tfrac{1}{2})(5^{-1/2}5^{-1/2} + 5^{-1/2}5^{-1/2}) + 2(\tfrac{1}{2})(5^{-1/2}5^{-1/2}e^{2\pi i/5} + 5^{-1/2}e^{-2\pi i/5}5^{-1/2}) +$$
$$2(\tfrac{1}{2})(5^{-1/2}5^{-1/2}e^{8\pi i/5} + 5^{-1/2}e^{-8\pi i/5}5^{-1/2}) = 0.4 + 0.2[2\cos(2\pi/5) + 2\cos(8\pi/5)] = 0.6472.$$

By symmetry, this is the mobile bond order for all the C-C bonds. From (17.57), $R_{12} = (1.521 - 0.186 \cdot 0.6472)$ Å $= 1.401$ Å .

(b) The conjugated carbon framework and the HMOs of $C_7H_7^+$ are the same as for C_7H_7. The Lewis structure of $C_7H_7^+$ has six π electrons in three double bonds and a C that has no double bonds. The six π electrons in $C_7H_7^+$ fill the lowest three HMOs. From the comment after Eq. (17.45), the lowest three HMOs have $k = 0,\ 1,\ 6$. For each of these three HMOs, we use (17.44) to calculate the coefficients c_{1k} and c_{2k}. We get $c_{1,0} = c_{2,0} = 7^{-1/2}$; $c_{1,1} = 7^{-1/2}$, $c_{2,1} = 7^{-1/2}e^{2\pi i/7}$; $c_{1,6} = 7^{-1/2}$, $c_{2,6} = 7^{-1/2}e^{12\pi i/7}$. From (17.54), $p_{12} = 2(\frac{1}{2})(7^{-1/2}7^{-1/2} + 7^{-1/2}7^{-1/2}) + 2(\frac{1}{2})(7^{-1/2}7^{-1/2}e^{2\pi i/7} + 7^{-1/2}e^{-2\pi i/7}7^{-1/2}) +$
$2(\frac{1}{2})(7^{-1/2}7^{-1/2}e^{12\pi i/7} + 7^{-1/2}e^{-12\pi i/7}7^{-1/2}) = \frac{2}{7} + \frac{1}{7}[2\cos(2\pi/7) + 2\cos(12\pi/7)] = 0.6420.$
By symmetry, this is the mobile bond order for all the C-C bonds. From (17.57), $R_{12} = (1.521 - 0.186 \cdot 0.6420)$ Å $= 1.402$ Å .

(c) The conjugated carbon framework and the HMOs of $C_8H_8^{2-}$ are the same as for C_8H_8. The ten π electrons in $C_8H_8^{2-}$ fill the lowest five HMOs. From the comment after Eq. (17.45), the lowest five HMOs have $k = 0,\ 1,\ 7,\ 2,\ 6$. For each of these five HMOs, we use (17.44) to calculate the coefficients c_{1k} and c_{2k}. We get
$c_{1,0} = c_{2,0} = 8^{-1/2}$; $c_{1,1} = 8^{-1/2}$, $c_{2,1} = 8^{-1/2}e^{2\pi i/8}$; $c_{1,7} = 8^{-1/2}$, $c_{2,7} = 8^{-1/2}e^{14\pi i/8}$, $c_{1,2} = 8^{-1/2}$, $c_{2,2} = 8^{-1/2}e^{4\pi i/8}$, $c_{1,6} = 8^{-1/2}$, $c_{2,6} = 8^{-1/2}e^{12\pi i/8}$. From (17.54),
$p_{12} = 2(\frac{1}{2})(8^{-1/2}8^{-1/2} + 8^{-1/2}8^{-1/2}) + 2(\frac{1}{2})(8^{-1/2}8^{-1/2}e^{2\pi i/8} + 8^{-1/2}e^{-2\pi i/8}8^{-1/2}) +$
$2(\frac{1}{2})(8^{-1/2}8^{-1/2}e^{14\pi i/8} + 8^{-1/2}e^{-14\pi i/8}8^{-1/2}) + 2(\frac{1}{2})(8^{-1/2}8^{-1/2}e^{4\pi i/8} + 8^{-1/2}e^{-4\pi i/8}8^{-1/2}) +$
$2(\frac{1}{2})(8^{-1/2}8^{-1/2}e^{12\pi i/8} + 8^{-1/2}e^{-12\pi i/8}8^{-1/2})$
$= 0.25 + \frac{1}{8}[2\cos(\pi/4) + 2\cos(14\pi/8) + 2\cos(\pi/2) + 2\cos(12\pi/8)] = 0.6036.$
By symmetry, this is the mobile bond order for all the C-C bonds. From (17.57), $R_{12} = (1.521 - 0.186 \cdot 0.6036)$ Å $= 1.409$ Å .

17.15 **(a)** For the a_u HMOs,

$$\langle g_4 | \hat{H}^{\text{eff}} | g_4 \rangle = \tfrac{1}{4}\langle f_1 - f_4 + f_5 - f_8 | \hat{H}^{\text{eff}} | f_1 - f_4 + f_5 - f_8 \rangle = \tfrac{1}{4}(\alpha + \alpha + \alpha + \alpha) = \alpha,$$

$$\langle g_4 | \hat{H}^{\text{eff}} | g_5 \rangle = \tfrac{1}{4}\langle f_1 - f_4 + f_5 - f_8 | \hat{H}^{\text{eff}} | f_2 - f_3 + f_6 - f_7 \rangle = \tfrac{1}{4}(\beta + \beta + \beta + \beta) = \beta,$$

$$\langle g_5 | \hat{H}^{\text{eff}} | g_5 \rangle = \tfrac{1}{4}\langle f_2 - f_3 + f_6 - f_7 | \hat{H}^{\text{eff}} | f_2 - f_3 + f_6 - f_7 \rangle$$
$$= \tfrac{1}{4}(\alpha - \beta - \beta + \alpha + \alpha - \beta - \beta + \alpha) = \alpha - \beta .$$

The symmetry orbitals are orthonormal, and the a_u secular equation is

$$\begin{vmatrix} \alpha - e_k & \beta \\ \beta & \alpha - \beta - e_k \end{vmatrix} = 0, \quad \begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 = x^2 - x - 1, \quad x = -0.618,\ 1.618$$

For the b_{2g} HMOs,

$\langle g_6|\hat{H}^{\text{eff}}|g_6\rangle = \frac{1}{4}\langle f_1 - f_4 - f_5 + f_8|\hat{H}^{\text{eff}}|f_1 - f_4 - f_5 + f_8\rangle = \frac{1}{4}(\alpha+\alpha+\alpha+\alpha) = \alpha$

$\langle g_6|\hat{H}^{\text{eff}}|g_7\rangle = \frac{1}{4}\langle f_1 - f_4 - f_5 + f_8|\hat{H}^{\text{eff}}|f_2 - f_3 - f_6 + f_7\rangle = \frac{1}{4}(\beta+\beta+\beta+\beta) = \beta$

$\langle g_6|\hat{H}^{\text{eff}}|g_8\rangle = 2^{-3/2}\langle f_1 - f_4 - f_5 + f_8|\hat{H}^{\text{eff}}|f_9 - f_{10}\rangle = 2^{-3/2}(\beta+\beta+\beta+\beta) = 2^{1/2}\beta$

$\langle g_7|\hat{H}^{\text{eff}}|g_7\rangle = \frac{1}{4}\langle f_2 - f_3 - f_6 + f_7|\hat{H}^{\text{eff}}|f_2 - f_3 - f_6 + f_7\rangle =$

$\frac{1}{4}(\alpha-\beta-\beta+\alpha+\alpha-\beta-\beta+\alpha) = \alpha-\beta$

$\langle g_7|\hat{H}^{\text{eff}}|g_8\rangle = 2^{-3/2}\langle f_2 - f_3 - f_6 + f_7|\hat{H}^{\text{eff}}|f_9 - f_{10}\rangle = 0$

$\langle g_8|\hat{H}^{\text{eff}}|g_8\rangle = \frac{1}{2}\langle f_9 - f_{10}|\hat{H}^{\text{eff}}|f_9 - f_{10}\rangle = \frac{1}{2}(\alpha-\beta-\beta+\alpha) = \alpha-\beta$

The secular equation is $\begin{vmatrix} \alpha - e_k & \beta & 2^{1/2}\beta \\ \beta & \alpha-\beta-e_k & 0 \\ 2^{1/2}\beta & 0 & \alpha-\beta-e_k \end{vmatrix} = 0, \quad \begin{vmatrix} x & 1 & 2^{1/2} \\ 1 & x-1 & 0 \\ 2^{1/2} & 0 & x-1 \end{vmatrix} = 0$

Expansion using the last row gives $(x-1)(x^2 - x - 3) = 0$ with the roots $x = 1,\ 2.303,\ -1.303$.

For the b_{1g} HMOs,

$\langle g_9|\hat{H}^{\text{eff}}|g_9\rangle = \frac{1}{4}\langle f_1 + f_4 - f_5 - f_8|\hat{H}^{\text{eff}}|f_1 + f_4 - f_5 - f_8\rangle = \frac{1}{4}(\alpha+\alpha+\alpha+\alpha) = \alpha$

$\langle g_9|\hat{H}^{\text{eff}}|g_{10}\rangle = \frac{1}{4}\langle f_1 + f_4 - f_5 - f_8|\hat{H}^{\text{eff}}|f_2 + f_3 - f_6 - f_7\rangle = \frac{1}{4}(\beta+\beta+\beta+\beta) = \beta$

$\langle g_{10}|\hat{H}^{\text{eff}}|g_{10}\rangle = \frac{1}{4}\langle f_2 + f_3 - f_6 - f_7|\hat{H}^{\text{eff}}|f_2 + f_3 - f_6 - f_7\rangle =$

$\frac{1}{4}(\alpha+\beta+\beta+\alpha+\alpha+\beta+\beta+\alpha) = \alpha+\beta$

The secular equation is

$\begin{vmatrix} \alpha - e_k & \beta \\ \beta & \alpha+\beta-e_k \end{vmatrix} = 0, \quad \begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0, \quad x^2 + x - 1 = 0, \quad x = 0.618,\ -1.618$

The HMO energies $\alpha - \beta x$ (including those found on pages 612–613) are
$\alpha + 2.303\beta,\ \alpha + 1.618\beta,\ \alpha + 1.303\beta,\ \alpha + \beta,\ \alpha + 0.618\beta,$
$\alpha - 0.618\beta,\ \alpha - \beta,\ \alpha - 1.303\beta,\ \alpha - 1.618\beta,\ \alpha - 2.303\beta$

(b) The lowest HMO energy $\alpha + 2.303\beta$ corresponds to the b_{3u} root $x = -2.303$. Use of this x value and the elements of the secular determinant on p. 612 gives as the equation for the coefficients of the symmetry orbitals g_1, g_2, g_3

$$
\begin{aligned}
-2.303c_1 + c_2 + 2^{1/2}c_3 &= 0 \\
c_1 - 1.303c_2 \qquad &= 0 \\
2^{1/2}c_1 \qquad - 1.303c_3 &= 0
\end{aligned}
$$

So $c_2 = 0.7675c_1$, $c_3 = 1.085c_1$. Normalization gives $1 = c_1^2 + c_2^2 + c_3^2 = c_1^2(1 + 0.5891 + 1.177)$ and $c_1 = 0.601_3$, $c_2 = 0.461_5$, $c_3 = 0.652_6$. So
$\phi_1 = c_1g_1 + c_2g_2 + c_3g_3 =$
$0.301(f_1 + f_4 + f_5 + f_8) + 0.231(f_2 + f_3 + f_6 + f_7) + 0.461(f_9 + f_{10})$.

17.16 We have $E_\pi = \sum_i n_i e_i$, where the sum goes over the HMOs and n_i is the number of electrons in the ith HMO. Use of (17.8) gives

$e_i = \langle \phi_i \,|\, \hat{H}^{\text{eff}} \,|\, \phi_i \rangle = \langle \sum_r c_{ri} f_r \,|\, \hat{H}^{\text{eff}} \,|\, \sum_s c_{si} f_s \rangle = \sum_r \sum_s c_{ri}^* c_{si} \langle f_r \,|\, \hat{H}^{\text{eff}} \,|\, f_s \rangle$ (Eq. 1)

In the sums in Eq. 1, the following kinds of terms occur. For those terms with $s = r$, we have $\langle f_r \,|\, \hat{H}^{\text{eff}} \,|\, f_s \rangle = \alpha$, and these terms contribute $\alpha \sum_r |c_{ri}|^2$ to the double sum. For those terms with atom s not bonded to atom r, we have $\langle f_r \,|\, \hat{H}^{\text{eff}} \,|\, f_s \rangle = 0$, and these terms contribute zero. For those terms with atom s bonded to r, we have $\langle f_r \,|\, \hat{H}^{\text{eff}} \,|\, f_s \rangle = \beta$. There are two terms in the double sum in Eq. 1 for each pair of bonded atoms. For example, if carbons 2 and 3 are bonded, then Eq. 1 has the terms $c_{2i}^* c_{3i} \beta$ and $c_{3i}^* c_{2i} \beta$. Thus, the contribution of terms from pairs of bonded atoms to the double sum in Eq. 1 is $\beta \sum_{s-r} (c_{ri}^* c_{si} + c_{si}^* c_{ri})$. Adding the contributions from the various kinds of terms, we have $e_i = \alpha \sum_r |c_{ri}|^2 + \beta \sum_{s-r} (c_{ri}^* c_{si} + c_{si}^* c_{ri})$. Substitution into $E_\pi = \sum_i n_i e_i$ gives $E_\pi = \sum_i n_i \left[\alpha \sum_r |c_{ri}|^2 + \beta \sum_{s-r} (c_{ri}^* c_{si} + c_{si}^* c_{ri}) \right] =$
$\alpha \sum_r \sum_i n_i |c_{ri}|^2 + \beta \sum_{s-r} \sum_i n_i (c_{ri}^* c_{si} + c_{si}^* c_{ri}) = \alpha \sum_r q_r + 2\beta \sum_{s-r} p_{rs}$, where (17.53) and (17.54) were used and $\sum_{s-r}$ denotes a sum over carbon–carbon bonds.

17.17 **(a)** For p_{rs}^{tot} equal to 1 and to 3, Eq. (17.57) gives 1.521 Å and 1.149 Å, respectively. The typical carbon–carbon single-bond length is 1.53 to 1.54 Å, and the typical carbon–carbon triple-bond length is 1.20 Å.

(b) We use the numbering in the figure in Prob. 17.20 part (c). The HMO bond orders, the bond lengths found from (17.57), and the experimental lengths [given as the averages of three determinations of azulene bond lengths listed in J. M. L. Martin et al., *J. Phys. Chem.*, **100**, 15358 (1996)] are

r–s	1–2	1–9	9–10	8–9	7–8	6–7
p_{rs}^{tot}	1.656	1.596	1.401	1.586	1.664	1.639
$R_{rs,(16.63)}$/Å	1.399	1.410	1.446	1.412	1.397	1.402
$R_{rs,\text{exper}}$/Å	1.39_5	1.41_0	1.49_4	1.38_6	1.40_2	1.39_3

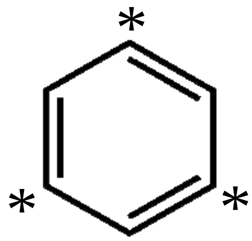
An online HMO calculator is at www.chem.ucalgary.ca/SHMO/

17.18 Equation (17.58) gives $E_\pi = \alpha(q_1 + q_2 + q_3 + q_4) + 2\beta(p_{12} + p_{23} + p_{34}) =$
$\alpha(1+1+1+1) + 2\beta(0.894 + 0.447 + 0.894) = 4\alpha + 4.47\beta$.
From (17.27) and Fig. 17.1, $E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta$.

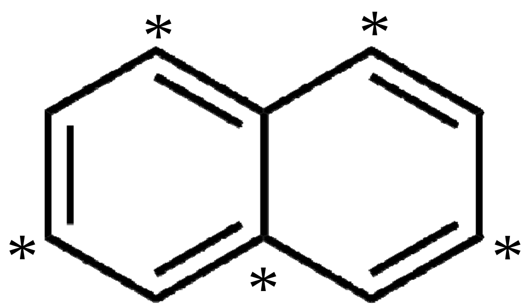
17.19 $F_1 = 3^{1/2} - p_{12} = 1.732 - 0.894 = 0.838 = F_4$.

$F_2 = 3^{1/2} - (p_{12} + p_{23}) = 1.732 - 0.894 - 0.447 = 0.391 = F_3$. The larger value for carbon 1 indicates that an end carbon is preferentially attacked by free radicals.

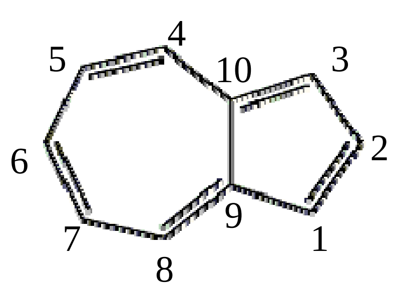
17.20 **(a)**



(b)



(c) It is impossible to do this for azulene:



For example, if we star carbons 1, 3, 4, 6, and 8, this leaves the unstarred atoms 9 and 10 bonded to each other

17.21 Equations (17.9) and (17.14) give $\sum_s [(H_{rs}^{\text{eff}} - \delta_{rs} e_i) c_{si}] = 0,\ r = 1, 2, \ldots, n_{\text{C}}$. From (17.11) to (17.13): when $s = r$, the sum has the term $(\alpha - e_i) c_{ri}$; atoms s that are bonded to r contribute the terms $\sum_{s \to r} \beta c_{si}$; atoms s not bonded to r contribute 0. Thus (17.9) becomes $(\alpha - e_i) c_{ri} + \sum_{s \to r} \beta c_{si} = 0$. Division by β and use of (17.20) gives $x_i c_{ri} + \sum_{s \to r} c_{si} = 0,\ r = 1, 2, \ldots, n_{\text{C}}$.

(b) Let the two sets of carbons (starred and unstarred) be called A and B. Let the carbon atoms in set A be numbered 1, 2,…, h and those in set B be numbered h + 1, h + 2,…, n_{C}. Then the set of equations in part (a) consists of the two sets

$x_i c_{ri} + \sum_{s\to r} c_{si} = 0,\ r = 1, 2, \ldots, h$ (set 1) and $x_i c_{ri} + \sum_{s\to r} c_{si} = 0,\ r = h+1, h+2, \ldots, n_{\mathrm{C}}$ (set 2). Since the atoms *r* in the equations of set 1 belong to set A, the atoms *s* bonded to each *r* in the set 1 equations belong to set B. In the equations of set 2, the atoms *r* belong to B and the atoms *s* belong to A. We now make the following changes in all the equations of sets 1 and 2. We replace x_i by $-x_i$ and replace the coefficients of the atoms of set A by their negatives. The set A atoms are the *r* atoms in set 1 and are the *s* atoms in set 2. Hence the set 1 equations become $(-x_i)(-c_{ri}) + \sum_{s\to r} c_{si} = 0,\ r = 1, 2, \ldots, h$. These equations are unchanged from their previous forms and so are satisfied. The set 2 equations become $(-x_i)c_{ri} + \sum_{s\to r}(-c_{si}) = 0,\ r = h+1, h+2, \ldots, n_{\mathrm{C}}$. The left side of each equation has been multiplied by –1, and since the right side is zero, these equations are still satisfied.

17.22 **(a)** From Fig. 17.5, the HMO energies are $\alpha + 2\beta,\ \alpha,\ \alpha,\ \alpha - 2\beta$. The molecule has four π electrons and $E_\pi = \sum_i n_i e_i = 2(\alpha + 2\beta) + 1(\alpha) + 1(\alpha) = 4\alpha + 4\beta$. The energy of the four π electrons in two isolated double bonds is [as noted after E. (17.50)] $4\alpha + 4\beta$. Subtraction gives the delocalization energy as 0.

(b) As noted after Eq. (17.45), the lowest MO has $k = 0$ and the next two MOs have $k = 1$ and $k = 3$. From (17.44), the coefficients of the carbon 1 and 2 AOs in the occupied MOs are $c_{1,0} = \frac{1}{2}$, $c_{2,0} = \frac{1}{2}$; $c_{1,1} = \frac{1}{2}$, $c_{2,1} = \frac{1}{2}e^{2\pi i/4} = \frac{1}{2}i$; $c_{1,3} = \frac{1}{2}$, $c_{2,3} = \frac{1}{2}e^{6\pi i/4} = -\frac{1}{2}i$. Then (17.54) gives $p_{12} = \frac{1}{2}(2)(\frac{1}{2}\frac{1}{2} + \frac{1}{2}\frac{1}{2}) + \frac{1}{2}(1)(\frac{1}{2}\frac{1}{2}i - \frac{1}{2}i\frac{1}{2}) + \frac{1}{2}(1)[\frac{1}{2}(-\frac{1}{2}i) + \frac{1}{2}i\frac{1}{2}] = 0.5$ and $p_{12}^{\mathrm{tot}} = 1.5$. By symmetry, $p_{23}^{\mathrm{tot}} = p_{34}^{\mathrm{tot}} = p_{41}^{\mathrm{tot}} = 1.5$.

17.23 From (17.53), $\sum_r q_r = \sum_r \sum_i n_i |c_{ri}|^2 = \sum_i n_i \sum_r |c_{ri}|^2 = \sum_i n_i = n_\pi$, where we used the normalization condition (17.16) and the fact that the sum of the numbers of π electrons in the various HMOs gives the total number of π electrons.

17.24 **(a)** With the overlap integral for each pair of bonded carbons taken as *S* and the assumptions (17.11) to (17.13) used, the HMO secular equation (17.9) for benzene is

$$\begin{vmatrix} \alpha - e_i & \beta - Se_i & 0 & 0 & 0 & \beta - Se_i \\ \beta - Se_i & \alpha - e_i & \beta - Se_i & 0 & 0 & 0 \\ 0 & \beta - Se_i & \alpha - e_i & \beta - Se_i & 0 & 0 \\ 0 & 0 & \beta - Se_i & \alpha - e_i & \beta - Se_i & 0 \\ 0 & 0 & 0 & \beta - Se_i & \alpha - e_i & \beta - Se_i \\ \beta - Se_i & 0 & 0 & 0 & \beta - Se_i & \alpha - e_i \end{vmatrix} = 0,$$

$\begin{vmatrix} w & 1 & 0 & 0 & 0 & 1 \\ 1 & w & 1 & 0 & 0 & 0 \\ 0 & 1 & w & 1 & 0 & 0 \\ 0 & 0 & 1 & w & 1 & 0 \\ 0 & 0 & 0 & 1 & w & 1 \\ 1 & 0 & 0 & 0 & 1 & w \end{vmatrix} = 0$ where each row of the first determinant was divided by $\beta - Se_i$, so $w \equiv (\alpha - e_i)/(\beta - Se_i)$.

(b) Solving the definition of w in part (a), we get

$$e_i = \frac{\alpha - w\beta}{1 - Sw} = \frac{\alpha - w\beta + Sw\alpha - Sw\alpha}{1 - Sw} = \frac{\alpha(1 - Sw)}{1 - Sw} - \frac{w(\beta - S\alpha)}{1 - Sw} = \alpha - \frac{w\gamma}{1 - Sw}$$

where $\gamma \equiv \beta - S\alpha$.

(c) As noted in part (a), the w values are the same as the x values found without overlap. Hence from (17.35), w = –2, –1, –1, 1, 1, 2. The formula in (b) with S = 0.25 gives $e_i =$ $\alpha - (-2)\gamma/[1 - 0.25(-2)] = \alpha + 1.33\gamma,\ \alpha + 0.80\gamma,\ \alpha + 0.80\gamma,\ \alpha - 1.33\gamma,\ \alpha - 1.33\gamma,\ \alpha - 4\gamma$.

(d) Use of the orbital-energy formula of part (b) gives

$$h\nu = \frac{hc}{\lambda} = e_{\text{LUMO}} - e_{\text{HOMO}} = \alpha - \frac{w_{\text{LU}}\gamma}{1 - Sw_{\text{LU}}} - \left(\alpha - \frac{w_{\text{HO}}\gamma}{1 - Sw_{\text{HO}}}\right)$$

$$\frac{1}{\lambda} = \frac{\gamma}{hc}\frac{w_{\text{HO}}(1 - Sw_{\text{LU}}) - w_{\text{LU}}(1 - Sw_{\text{HO}})}{(1 - Sw_{\text{LU}})(1 - Sw_{\text{HO}})} = \frac{\gamma}{hc}\frac{w_{\text{HO}} - w_{\text{LU}}}{1 + S^2 w_{\text{LU}} w_{\text{HO}} - S(w_{\text{LU}} + w_{\text{HO}})}$$

The w values are the same as the x values found without overlap, and for an alternant hydrocarbon, $x_{\text{LU}} = -x_{\text{HO}}$. so $w_{\text{LU}} = -w_{\text{HO}}$ with overlap included. Hence $w_{\text{LU}} + w_{\text{HO}} = 0$. Also, $w_{\text{LU}} w_{\text{HO}} = -w_{\text{LU}} w_{\text{LU}} = -w_{\text{LU}}^2$. Note that $\Delta w \equiv |w_{\text{LU}} - w_{\text{HO}}| = |w_{\text{LU}} + w_{\text{LU}}| = 2|w_{\text{LU}}|$ and $(\Delta w)^2 = 4w_{\text{LU}}^2$, so $w_{\text{LU}} w_{\text{HO}} = -w_{\text{LU}}^2 = -\frac{1}{4}(\Delta w)^2$. The equation for $1/\lambda$ becomes

$$\frac{1}{\lambda} = \frac{|\gamma|}{hc}\frac{\Delta w}{1 - \frac{1}{4}S^2(\Delta w)^2}.$$

17.25 From (17.60) and (17.63) with $r = s$, $F_{\pi,rr} = H_{\pi,rr}^{\text{core}} + \sum_{t=1}^{b}\sum_{u=1}^{b} P_{tu}[(rr|tu) - \frac{1}{2}(ru|tr)] =$ $F_{\pi,rr} = H_{\pi,rr}^{\text{core}} + \sum_{t=1}^{b}\sum_{u=1}^{b} P_{tu}(\delta_{tu}\gamma_{rt} - \frac{1}{2}\delta_{ru}\delta_{tr}\gamma_{rt}) = H_{\pi,rr}^{\text{core}} + \sum_{t=1}^{b}(P_{tt}\gamma_{rt} - \frac{1}{2}P_{tr}\delta_{tr}\gamma_{rt}) =$ $H_{\pi,rr}^{\text{core}} + \sum_{t=1}^{b} P_{tt}\gamma_{rt} - \frac{1}{2}P_{rr}\gamma_{rr}$.

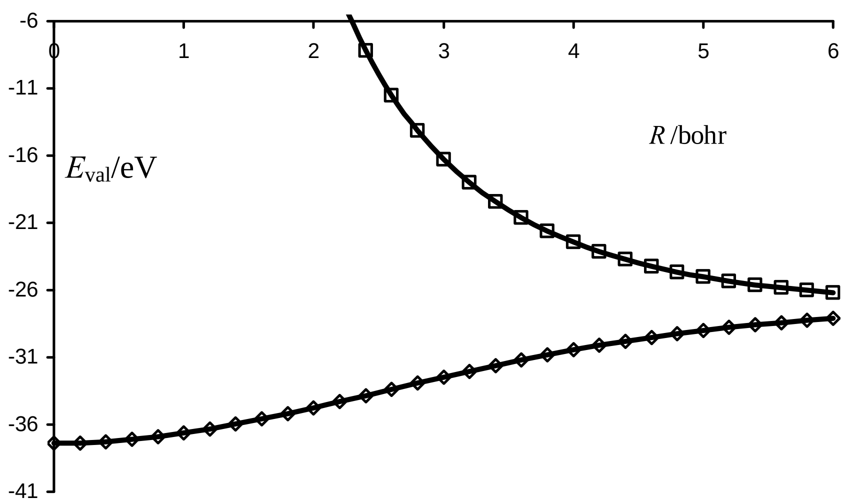
From (17.60) and (17.63) with $r \neq s$, $F_{\pi,rs} = H_{\pi,rs}^{\text{core}} + \sum_{t=1}^{b} \sum_{u=1}^{b} P_{tu}[(rs|tu) - \frac{1}{2}(ru|ts)] =$
$H_{\pi,rs}^{\text{core}} + \sum_{t=1}^{b} \sum_{u=1}^{b} P_{tu}(\delta_{rs}\delta_{tu}\gamma_{rt} - \frac{1}{2}\delta_{ru}\delta_{ts}\gamma_{rt}) = H_{\pi,rs}^{\text{core}} + \sum_{t=1}^{b}[P_{tt}(0)\gamma_{rt} - \frac{1}{2}P_{tr}\delta_{ts}\gamma_{rt}] =$
$H_{\pi,rs}^{\text{core}} - \frac{1}{2}P_{sr}\gamma_{rs}$, where δ_{rs} was replaced by 0, since $r \neq s$.

17.26 There are two valence AOs, $1s_A$ and $1s_B$, so the sum in (17.66) contains two terms and the secular determinant in (17.68) has order 2. From (17.70), $H_{11}^{\text{eff}} = H_{22}^{\text{eff}} = -13.6 \text{ eV}$. From (17.71), $H_{12}^{\text{eff}} = \frac{1}{2}(1.75)(H_{11}^{\text{eff}} + H_{22}^{\text{eff}})S_{12} = -1.75(0.5)(13.6+13.6)S_{12} \text{ eV} = -23.8S_{12} \text{ eV}$.
The secular equation (17.68) is

$$\begin{vmatrix} H_{11}^{\text{eff}} - e_i & H_{12}^{\text{eff}} - e_i S_{12} \\ H_{12}^{\text{eff}} - e_i S_{12} & H_{11}^{\text{eff}} - e_i \end{vmatrix} = 0, \ (H_{11}^{\text{eff}} - e_i)^2 - (H_{12}^{\text{eff}} - e_i S_{12})^2 = 0, \ H_{11}^{\text{eff}} - e_i = \pm(H_{12}^{\text{eff}} - e_i S_{12})$$

$$e_i = \frac{H_{11}^{\text{eff}} \pm H_{12}^{\text{eff}}}{1 \pm S_{12}} = \frac{(-13.6 \mp 23.8S_{12}) \text{ eV}}{1 \pm S_{12}} \qquad \text{where } S_{12} = e^{-R}(1 + R + \tfrac{1}{3}R^2)$$

where R is in atomic units (bohrs). From (17.67), $E_{\text{val}} = 2e_i$. We set up a spreadsheet with R values in column A, S_{12} values in column B, one E_{val} value in column C and the second E_{val} in column D. The results are



For all values of R, the E_{val} found using the lower signs in the formula lies above the other E_{val}. The ground state E_{val} continually decreases as R decreases and the excited-state E_{val} continually increases as R decreases. The EHT method (which omits internuclear repulsion) fails completely, predicting a bond distance of 0.

If symmetry orbitals are used, then the unnormalized symmetry orbitals are $g_1 = \text{H}_1 1s + \text{H}_2 1s$ and $g_2 = \text{H}_1 1s - \text{H}_2 1s$. We have
$\langle g_1 | \hat{H}_{\text{eff}} | g_1 \rangle = \langle \text{H}_1 1s + \text{H}_2 1s | \hat{H}_{\text{eff}} | \text{H}_1 1s + \text{H}_2 1s \rangle = H_{11}^{\text{eff}} + H_{22}^{\text{eff}} + 2H_{12}^{\text{eff}} = 2(H_{11}^{\text{eff}} + H_{12}^{\text{eff}})$
and $\langle g_1 | g_1 \rangle = \langle \text{H}_1 1s + \text{H}_2 1s | \text{H}_1 1s + \text{H}_2 1s \rangle = 2 + 2S_{12}$. The symmetry orbitals g_1 and g_2 belong to different symmetry species, so the secular equation for the ground electronic

state is $\left|\langle g_1|\hat{H}_{\text{eff}}\,|\,g_1\rangle - e_i\langle g_1|g_1\rangle\right| = 0$. So
$e_i = \langle g_1|\hat{H}_{\text{eff}}\,|\,g_1\rangle/\langle g_1|g_1\rangle = (H_{11}^{\text{eff}} + H_{12}^{\text{eff}})/(1+S_{12})$ = as above.

17.27 (a) We number the valence AOs as follows:

1	2	3	4	5	6	7	8
$H_1 1s$	$H_2 1s$	$H_3 1s$	$H_4 1s$	C2s	C2p_x	C2p_y	C2p_z

From (17.70), $H_{11}^{\text{eff}} = H_{22}^{\text{eff}} = H_{33}^{\text{eff}} = H_{44}^{\text{eff}} = -13.6\text{ eV}$; $H_{55}^{\text{eff}} = -20.8\text{ eV}$, $H_{66}^{\text{eff}} = H_{77}^{\text{eff}} = H_{88}^{\text{eff}} = -11.3\text{ eV}$. The molecule is tetrahedral with $R_{\text{CH}} = 1.09_4$ Å = 2.06_7 bohr. The distance between two H's is given by the law of cosines as
$R_{\text{HH}}/\text{Å} = [(1.094)^2 + (1.094)^2 - 2(1.094)(1.094)\cos 109.47°]^{1/2} = 1.094(8/3)^{1/2} = 1.786$ and $R_{\text{HH}} = 3.376$ bohr. Equation (13.60) with $k = 1$ gives $S_{12} = S_{13} = \cdots = S_{34} = 0.2795$. Orthogonality gives $S_{56} = S_{57} = S_{58} = S_{67} = S_{68} = S_{78} = 0$. Slater's rules give the orbital exponents as 1.625 for C2s and C2p and 1 for H1s.

For $S_{15} = \langle H_1 1s|\,\text{C}2s\rangle$, the parameters defined in the Prob. 15.24 solution have the values $p = \frac{1}{2}(1+1.625)2.067 = 2.713$, $t = (1-1.625)/(1+1.625) = -0.238$. Interpolation in the MROO reference of Prob. 15.29 gives $S_{15} = 0.568 = S_{25} = S_{35} = S_{45}$.

To evaluate $S_{16} = \langle H_1 1s|\,\text{C}2p_x\rangle$, we express C$2p_x$ as a linear combination of a 2p AO on an axis that points to H_1 (a $2p\sigma$ AO) and a 2p AO on an axis perpendicular to the C-H_1 line (a $2p\pi$ AO), as was done in Prob. 15.24. The x axis and the C-H_1 line in Fig. 15.9 are in the directions (1, 0, 0) and (1, 1, 1), respectively. Use of the vector dot product shows that the angle α between these directions satisfies $1(1) + 0(1) + 0(1) = 1(3^{1/2})\cos\alpha$, so $\cos\alpha = 3^{-1/2}$ and $\alpha = 54.736°$. We use modified versions of Fig. 15.6 and Eq. (15.40) in which z and z' are changed to x and x', respectively. The $2p_x$ and $2p_y$ AOs are proportional to x and y, respectively, and multiplication of the modified equations in (15.40) by the exponential part of a 2p AO gives
$2p_{x'} = 2p\sigma = 2p_x\cos\alpha + 2p_y\sin\alpha$ and $2p_{y'} = 2p\pi = -2p_x\sin\alpha + 2p_y\cos\alpha$.
(Note that the y direction in these equations is not the same as the y direction in Fig. 15.9.) From these two equations, we get (using Cramer's rule)
$2p_x = 2p\sigma\cos\alpha - 2p\pi\sin\alpha = 0.5773(2p\sigma) - 0.8165(2p\pi)$
Then $\langle H_1 1s|\,\text{C}2p_x\rangle = 0.5773\langle H_1 1s|\,\text{C}2p\sigma\rangle - 0.8165\langle H_1 1s|\,\text{C}2p\pi\rangle$. The overlap of the negative half of C2$p\pi$ with $H_1 1s$ cancels the overlap of the positive half of C2$p\pi$ with $H_1 1s$, so $\langle H_1 1s|\,\text{C}2p\pi\rangle$ = 0. For $\langle H_1 1s|\,\text{C}2p\sigma\rangle$, p = 2.713 and t = –0.238. Interpolation in the MROO tables gives $\langle H_1 1s|\,\text{C}2p\sigma\rangle$ = 0.464, so $\langle H_1 1s|\,\text{C}2p_x\rangle$ = 0.5773(0.464) = 0.268 = S_{16}.

The angle between the C-H_1 line and the y axis (or the z axis) in Fig. 15.9 is the same as that between C-H$_1$ and the x axis, so $\langle \mathrm{H}_1 1s | \mathrm{C}2p_x \rangle = \langle \mathrm{H}_1 1s | \mathrm{C}2p_y \rangle = \langle \mathrm{H}_1 1s | \mathrm{C}2p_z \rangle =$ $0.268 = S_{17} = S_{18}$.

The angle β between the C-H$_2$ line and the positive side of the y axis in Fig. 15.9 is found (using the dot product) to have cos $\beta = -3^{-1/2}$, and the same procedure used for $\langle \mathrm{H}_1 1s | \mathrm{C}2p_x \rangle$ gives $\langle \mathrm{H}_2 1s | \mathrm{C}2p_y \rangle = -0.268 = S_{27}$. (This is clear from Fig. 15.9, where we see that whereas H$_1$1s overlaps mainly the positive half of $\mathrm{C}2p_x$, H$_2$1s overlaps mainly the negative half of $\mathrm{C}2p_y$.) Similarly, $\langle \mathrm{H}_2 1s | \mathrm{C}2p_z \rangle = -0.268 = S_{28}$. Also, $S_{26} = 0.268$, $S_{36} = -0.268$, $S_{37} = 0.268$, $S_{38} = -0.268$, $S_{46} = -0.268$, $S_{47} = -0.268$, $S_{48} = 0.268$.

Equation (17.71) gives $H_{12}^{\mathrm{eff}} = 0.5(1.75)(-13.6 \text{ eV} - 13.6 \text{ eV})0.2795 = -6.65 \text{ eV} =$ $H_{13}^{\mathrm{eff}} = H_{14}^{\mathrm{eff}} = \cdots H_{34}^{\mathrm{eff}}$; $H_{15}^{\mathrm{eff}} = 0.5(1.75)(-13.6 \text{ eV} - 20.3 \text{ eV})0.568 = -16.8 \text{ eV} =$ $H_{25} = H_{35} = H_{45}$;
$H_{16}^{\mathrm{eff}} = H_{17}^{\mathrm{eff}} = H_{18}^{\mathrm{eff}} = 0.5(1.75)(-13.6 \text{ eV} - 11.3 \text{ eV})0.268 = -5.84 \text{ eV}$;
$H_{27}^{\mathrm{eff}} = H_{28}^{\mathrm{eff}} = 5.84 \text{ eV}$, etc.

The secular equation $\det(H_{rs}^{\mathrm{eff}} - e_i S_{rs}) = 0$ is

$$\begin{vmatrix} a-e_i & d-S_{12}e_i & d-S_{12}e_i & d-S_{12}e_i & f-S_{15}e_i & k-S_{16}e_i & k-S_{16}e_i & k-S_{16}e_i \\ d-S_{12}e_i & a-e_i & d-S_{12}e_i & d-S_{12}e_i & f-S_{15}e_i & k-S_{16}e_i & -k+S_{16}e_i & -k+S_{16}e_i \\ d-S_{12}e_i & d-S_{12}e_i & a-e_i & d-S_{12}e_i & f-S_{15}e_i & -k+S_{16}e_i & k-S_{16}e_i & -k+S_{16}e_i \\ d-S_{12}e_i & d-S_{12}e_i & d-S_{12}e_i & a-e_i & f-S_{15}e_i & -k+S_{16}e_i & -k+S_{16}e_i & k-S_{16}e_i \\ f-S_{15}e_i & f-S_{15}e_i & f-S_{15}e_i & f-S_{15}e_i & b-e_i & 0 & 0 & 0 \\ k-S_{16}e_i & k-S_{16}e_i & -k+S_{16}e_i & -k+S_{16}e_i & 0 & c-e_i & 0 & 0 \\ k-S_{16}e_i & -k+S_{16}e_i & k-S_{16}e_i & -k+S_{16}e_i & 0 & 0 & c-e_i & 0 \\ k-S_{16}e_i & -k+S_{16}e_i & -k+S_{16}e_i & k-S_{16}e_i & 0 & 0 & 0 & c-e_i \end{vmatrix} = 0$$

where $a \equiv -13.6 \text{ eV}$, $b \equiv -20.8 \text{ eV}$, $c \equiv -11.3 \text{ eV}$, $d \equiv -6.65 \text{ eV}$, $f \equiv -16.8 \text{ eV}$, $k \equiv -5.84 \text{ eV}$, and the S values are given earlier in this solution.

(b) The unnormalized symmetry orbitals for the hydrogens are given by (15.42) to (15.45). The C2s, C2p_x, C2p_y, C2p_z AOs are symmetry orbitals. Let the symmetry orbitals (15.42) and C2s, which belong to symmetry species a_1, be numbered 1 and 2. Let the t_2 symmetry orbitals be numbered as follows:

(15.43)	$\mathrm{C}2p_x$	(15.44)	$\mathrm{C}2p_y$	(15.45)	$\mathrm{C}2p_z$
g_3	g_4	g_5	g_6	g_7	g_8

The matrix elements for the a_1 orbitals are
$\langle g_1 | \hat{H}_{\mathrm{eff}} | g_1 \rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s + \mathrm{H}_3 1s + \mathrm{H}_4 1s | \hat{H}_{\mathrm{eff}} | \mathrm{H}_1 1s + \mathrm{H}_2 1s + \mathrm{H}_3 1s + \mathrm{H}_4 1s \rangle =$
$H_{11}^{\mathrm{eff}} + H_{22}^{\mathrm{eff}} + H_{33}^{\mathrm{eff}} + H_{44}^{\mathrm{eff}} + 2H_{12}^{\mathrm{eff}} + 2H_{13}^{\mathrm{eff}} + 2H_{14}^{\mathrm{eff}} + 2H_{23}^{\mathrm{eff}} + 2H_{24}^{\mathrm{eff}} + 2H_{34}^{\mathrm{eff}} =$
$4H_{11}^{\mathrm{eff}} + 12H_{12}^{\mathrm{eff}} = 4a + 12d$ (where the notation and AO numbering of part (a) are used);
$\langle g_1 | \hat{H}_{\mathrm{eff}} | g_2 \rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s + \mathrm{H}_3 1s + \mathrm{H}_4 1s | \hat{H}_{\mathrm{eff}} | \mathrm{C}2s \rangle = 4H_{15}^{\mathrm{eff}} = 4f$;

$\langle g_2|\hat{H}_{\text{eff}}\,|\,g_2\rangle = \langle \text{C}2s|\hat{H}_{\text{eff}}\,|\text{C}2s\rangle = H_{55}^{\text{eff}} = b$;
$\langle g_1|g_1\rangle = \langle \text{H}_1 1s + \text{H}_2 1s + \text{H}_3 1s + \text{H}_4 1s|\text{H}_1 1s + \text{H}_2 1s + \text{H}_3 1s + \text{H}_4 1s\rangle = 4 + 12S_{12}$;
$\langle g_1|g_2\rangle = \langle \text{H}_1 1s + \text{H}_2 1s + \text{H}_3 1s + \text{H}_4 1s|\text{C}2s\rangle = 4S_{15}$; $\langle g_2|g_2\rangle = \langle \text{C}2s|\text{C}2s\rangle = 1$.
The a_1 secular equation is

$$\begin{vmatrix} 4a + 12d - (4 + 12S_{12})e_i & 4f - 4S_{15}e_i \\ 4f - 4S_{15}e_i & b - e_i \end{vmatrix} = 0$$

The matrix elements for the t_2 orbitals are

$$\begin{aligned}\langle g_3|\hat{H}_{\text{eff}}\,|\,g_3\rangle &= \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s\rangle \\ &= H_{11}^{\text{eff}} + H_{22}^{\text{eff}} + H_{33}^{\text{eff}} + H_{44}^{\text{eff}} + 2H_{12}^{\text{eff}} - 2H_{13}^{\text{eff}} - 2H_{14}^{\text{eff}} - 2H_{23}^{\text{eff}} - 2H_{24}^{\text{eff}} + 2H_{34}^{\text{eff}} \\ &= 4H_{11}^{\text{eff}} - 4H_{12}^{\text{eff}} = 4a - 4d;\end{aligned}$$

$\langle g_3|\hat{H}_{\text{eff}}\,|\,g_4\rangle = \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_x\rangle = H_{16}^{\text{eff}} + H_{26}^{\text{eff}} - H_{36}^{\text{eff}} - H_{46}^{\text{eff}} = 4k$

$$\begin{aligned}\langle g_3|\hat{H}_{\text{eff}}\,|\,g_5\rangle &= \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s\rangle \\ &= H_{11}^{\text{eff}} - H_{22}^{\text{eff}} - H_{33}^{\text{eff}} + H_{44}^{\text{eff}} + \cdots = 0;\end{aligned}$$

$\langle g_3|\hat{H}_{\text{eff}}\,|\,g_6\rangle = \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_y\rangle = H_{17}^{\text{eff}} + H_{27}^{\text{eff}} - H_{37}^{\text{eff}} - H_{47}^{\text{eff}} = 0$;
$\langle g_3|\hat{H}_{\text{eff}}\,|\,g_7\rangle = \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s\rangle = 0$;
$\langle g_3|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{H}_1 1s + \text{H}_2 1s - \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = H_{18}^{\text{eff}} + H_{28}^{\text{eff}} - H_{38}^{\text{eff}} - H_{48}^{\text{eff}} = 0$;
$\langle g_4|\hat{H}_{\text{eff}}\,|\,g_4\rangle = \langle \text{C}2p_x|\hat{H}_{\text{eff}}\,|\text{C}2p_x\rangle = c$;
$\langle g_4|\hat{H}_{\text{eff}}\,|\,g_5\rangle = \langle \text{C}2p_x|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s\rangle = H_{16}^{\text{eff}} - H_{26}^{\text{eff}} + H_{36}^{\text{eff}} - H_{46}^{\text{eff}} = 0$
$\langle g_4|\hat{H}_{\text{eff}}\,|\,g_6\rangle = \langle \text{C}2p_x|\hat{H}_{\text{eff}}\,|\text{C}2p_y\rangle = 0$;
$\langle g_4|\hat{H}_{\text{eff}}\,|\,g_7\rangle = \langle \text{C}2p_x|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s\rangle = H_{16}^{\text{eff}} - H_{26}^{\text{eff}} - H_{36}^{\text{eff}} + H_{46}^{\text{eff}} = 0$;
$\langle g_4|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{C}2p_x|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = 0$;

$$\begin{aligned}\langle g_5|\hat{H}_{\text{eff}}\,|\,g_5\rangle &= \langle \text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s\rangle \\ &= 4H_{11}^{\text{eff}} - 4H_{12}^{\text{eff}} = 4a - 4d;\end{aligned}$$

$\langle g_5|\hat{H}_{\text{eff}}\,|\,g_6\rangle = \langle \text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_y\rangle = H_{17}^{\text{eff}} - H_{27}^{\text{eff}} + H_{37}^{\text{eff}} - H_{47}^{\text{eff}} = 4k$
$\langle g_5|\hat{H}_{\text{eff}}\,|\,g_7\rangle = \langle \text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s\rangle = 0$;
$\langle g_5|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{H}_1 1s - \text{H}_2 1s + \text{H}_3 1s - \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = H_{18}^{\text{eff}} - H_{28}^{\text{eff}} + H_{38}^{\text{eff}} - H_{48}^{\text{eff}} = 0$;
$\langle g_6|\hat{H}_{\text{eff}}\,|\,g_6\rangle = \langle \text{C}2p_y|\hat{H}_{\text{eff}}\,|\text{C}2p_y\rangle = c$;
$\langle g_6|\hat{H}_{\text{eff}}\,|\,g_7\rangle = \langle \text{C}2p_y|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s\rangle = H_{17}^{\text{eff}} - H_{27}^{\text{eff}} - H_{37}^{\text{eff}} + H_{47}^{\text{eff}} = 0$;
$\langle g_6|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{C}2p_y|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = 0$;

$$\begin{aligned}\langle g_7|\hat{H}_{\text{eff}}\,|\,g_7\rangle &= \langle \text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s\rangle \\ &= 4H_{11}^{\text{eff}} - 4H_{12}^{\text{eff}} = 4a - 4d;\end{aligned}$$

$\langle g_7|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{H}_1 1s - \text{H}_2 1s - \text{H}_3 1s + \text{H}_4 1s|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = H_{18}^{\text{eff}} - H_{28}^{\text{eff}} - H_{38}^{\text{eff}} + H_{48}^{\text{eff}} = 4k$
$\langle g_8|\hat{H}_{\text{eff}}\,|\,g_8\rangle = \langle \text{C}2p_z|\hat{H}_{\text{eff}}\,|\text{C}2p_z\rangle = c$

$\langle g_3|g_3\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s\rangle = 4 - 4S_{12}$;
$\langle g_3|g_4\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{C}2p_x\rangle = S_{16} + S_{26} - S_{36} - S_{46} = 4S_{16}$;
$\langle g_3|g_5\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s\rangle = 0$;
$\langle g_3|g_6\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{C}2p_y\rangle = S_{17} + S_{27} - S_{37} - S_{47} = 0$;
$\langle g_3|g_7\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s\rangle = 0$;
$\langle g_3|g_8\rangle = \langle \mathrm{H}_1 1s + \mathrm{H}_2 1s - \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{C}2p_z\rangle = S_{18} + S_{28} - S_{38} - S_{48} = 0$;
$\langle g_4|g_4\rangle = \langle \mathrm{C}2p_x|\mathrm{C}2p_x\rangle = 1$;
$\langle g_4|g_5\rangle = \langle \mathrm{C}2p_x|\mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s\rangle = S_{16} - S_{26} + S_{36} - S_{46} = 0$;
$\langle g_4|g_6\rangle = \langle \mathrm{C}2p_x|\mathrm{C}2p_y\rangle = 0$
$\langle g_4|g_7\rangle = \langle \mathrm{C}2p_x|\mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s\rangle = S_{16} - S_{26} - S_{36} + S_{46} = 0$;
$\langle g_4|g_8\rangle = \langle \mathrm{C}2p_x|\mathrm{C}2p_z\rangle = 0$;
$\langle g_5|g_5\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s\rangle = 4 - 4S_{12}$;
$\langle g_5|g_6\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{C}2p_y\rangle = S_{17} - S_{27} + S_{37} - S_{47} = 4S_{16}$;
$\langle g_5|g_7\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s\rangle = 0$;
$\langle g_5|g_8\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s + \mathrm{H}_3 1s - \mathrm{H}_4 1s|\mathrm{C}2p_z\rangle = S_{18} - S_{28} + S_{38} - S_{48} = 0$;
$\langle g_6|g_6\rangle = \langle \mathrm{C}2p_y|\mathrm{C}2p_y\rangle = 1$;
$\langle g_6|g_7\rangle = \langle \mathrm{C}2p_y|\mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s\rangle = S_{17} - S_{27} - S_{37} + S_{47} = 0$;
$\langle g_6|g_8\rangle = \langle \mathrm{C}2p_y|\mathrm{C}2p_z\rangle = 0$;
$\langle g_7|g_7\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s|\mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s\rangle = 4 - 4S_{12}$;
$\langle g_7|g_8\rangle = \langle \mathrm{H}_1 1s - \mathrm{H}_2 1s - \mathrm{H}_3 1s + \mathrm{H}_4 1s|\mathrm{C}2p_z\rangle = S_{18} - S_{28} - S_{38} + S_{48} = 4S_{16}$;
$\langle g_8|g_8\rangle = \langle \mathrm{C}2p_z|\mathrm{C}2p_z\rangle = 1$.

The secular equation is

$$\begin{vmatrix} A & B & 0 & 0 & 0 & 0 \\ B & c-e_i & 0 & 0 & 0 & 0 \\ 0 & 0 & A & B & 0 & 0 \\ 0 & 0 & B & c-e_i & 0 & 0 \\ 0 & 0 & 0 & 0 & A & B \\ 0 & 0 & 0 & 0 & B & c-e_i \end{vmatrix} = 0$$

where $A \equiv 4a - 4d - (4 - 4S_{12})e_i$, $B \equiv 4k - 4S_{16}e_i$, and the notation is as in part (a).

17.28 In the ZDO approximation (17.62) and (17.63), $(rs|tu)$ equals $\delta_{rs}\delta_{tu}\gamma_{rt}$ and is zero unless $r = s$ and $t = u$. The CNDO method uses the ZDO approximation for all electron-repulsion integrals, and so neglects all integrals with $r \neq s$ and/or with $t \neq u$. Thus CNDO neglects integrals b, d, e, f, and g. INDO neglects fewer integral than CNDO, in that the ZDO approximation is not applied when r, s, t, and u are all centered on the same atom. The AOs in integral b are all on the same atom, so INDO does not neglect b but still neglects d, e, f, and g. MNDO uses the NDDO approximation, in which the ZDO approximation $f_r^*(1) f_s(1)\, dv_1 = 0$ is used only when f_r and f_s are on different atoms. Hence in NDDO, $(rs|tu)$ in (14.39) is zero only if either r and s are on different atoms or t and u are on different atoms. Hence MNDO does not neglect integrals b and f, but neglects d, e, and g. AM1 neglects the same integrals as MNDO, namely, d, e, and g.

17.29 Substitution in the equation on p. 627 gives $\Delta H^\circ_{f,298,\mathrm{H_2O}(g)} =$

$(6.02214\times10^{23}\ \mathrm{mol}^{-1})(-493.358+144.796+2\cdot11.396+316.100)\,\mathrm{eV}\ +$

$[2(52.102) + 59.559]$ kcal/mol =

$-(5.82341\times10^{24}\ \mathrm{eV})(1.602177\times10^{-19}\ \mathrm{J/eV})+163.763\ \mathrm{kcal/mol}\ =$

–933.013 kJ/mol + 163.763 kcal/mol = –59.232 kcal/mol

17.30 **(a)** The results are (where C_1 is an end carbon)

propane	μ/D	$\Delta H^\circ_{f,298,g}$	R_{CC}/Å	R_{C_1H}/Å	R_{C_2H}/Å	∠CCC	∠HC_1H	∠HC_2H
AM1	0.004	–24.3 kcal/mol	1.507	1.117	1.122	111.8°	108.4°	107.1°
PM3	0.005	–23.6 kcal/mol	1.512	1.098	1.108	111.8°	107.4°	105.6°
exper.	0.083	–25.0 kcal/mol	1.526	1.09_1	1.096	112.4°	$107._7$°	106.1°

(b)

H_2S	μ/D	$\Delta H^\circ_{f,298,g}$	R_{HS}/Å	∠HSH
AM1	1.98	4.0 kcal/mol	1.317	98.8°
PM3	1.77	–0.9 kcal/mol	1.290	93.5°
exper.	0.97	–4.9 kcal/mol	1.328	92.2°

(c)

benzene	$\Delta H^\circ_{f,298,g}$	R_{CC}/Å	R_{CH}/Å
AM1	22.0 kcal/mol	1.395	1.110
PM3	23.5 kcal/mol	1.391	1.095
exper.	19.8 kcal/mol	1.397	1.084

17.31 The differences between $\Delta H^\circ_{f,298,g}$ for the geometry-optimized eclipsed and staggered forms give a barrier of 1.25 kcal/mol in AM1 and 1.4 kcal/mol in PM3. These results are in poor agreement with the experimental value 2.9 kcal/mol.

17.32 The results are

CH_2O	μ/D	R_{CH}/Å	R_{CO}/Å	∠HCH

AM1	2.32	1.110	1.227	115.6°
exper.	2.33	1.111	1.205	116.1

wavenumbers/cm^{-1}	b_1	b_2	a_1	a_1	a_1	b_2
AM1	1155*	1162*	1443	2053	3121	3083
experimental	1167	1249	1500	1746	2783	2843

where the symmetry species of the vibrations are listed. (*One finds that different programs running AM1 give somewhat different wavenumbers for the two lowest frequencies.)

17.33 Partial results are (where the carbons are numbered 1, 2, 3, 4 starting at one end)

butane AM1	μ/D	$\Delta H^\circ_{f,298}$	R_{12}/Å	R_{23}/Å	D(4321)	∠123
gauche	0.005	–30.5 kcal/mol	1.507	1.515	74.7°	112.7°
anti	0	–31.2 kcal/mol	1.507	1.514	180°	111.6°

17.34 Results are (where the conformers I and II are shown in the Prob. 15.57 solution)

AM1	μ	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	1.48 D	130.1°	117.6°	110.6°	1.103 Å	1.230 Å	1.357 Å	0.971 Å
II	4.02 D	127.3°	114.1	109.6°	1.105 Å	1.227 Å	1.366 Å	0.966 Å

The predicted $\Delta H^\circ_{f,298}$ values are –97.4 kcal/mol for I and –90.0 kcal/mol for II.

17.35 **(a)** Use of MOPAC in WebMO to first optimize the geometry and then find the vibrational wavenumbers gives the following PM6 results: 249, 1003, 1074, 1137.5, 1250.3, 1250.6, 1321, 1354.5, 2556, 2674, 2683, 2759 cm^{-1}.

(b) With anharmonicity neglected, the zero-point energy (ZPE) per molecule is $\frac{1}{2}hc\sum_i \tilde{\nu}_i = 0.5(6.6261\times10^{-34}$ J s$)(2.9979\times10^8$ m/s)(19311 cm^{-1})(100 cm)/(1 m) = 1.918×10^{-19} J. The ZPE per mole is $(1.918\times10^{-19}$ J$)(6.0221\times10^{23}$ mol$^{-1}) = 115.5$ kJ/mol = 27.6 kcal/mol.

(c) 1138 cm^{-1} for CO stretching; 2556 cm^{-1} for OH stretching; 249 cm^{-1} for CO torsion; 1355 cm^{-1} for COH bending; 2759 cm^{-1} for symmetric CH stretching.

(d) The Tables of Molecular Vibrational Frequencies Consolidated Volume I, T. Shimanouchi, at www.nist.gov/data/nsrds/NSRDS-NBS-39.pdf gives the following fundamental wavenumbers in cm^{-1}: 1033 for CO stretching, 1060 for CH_3 rocking, 1165 for CH_3 rocking, 1345 for OH bending, 1455 for CH_3 symmetric deformation, 1477 for

CH_3 deformation, 1477 for CH_3 deformation, 2844 for symmetric CH_3 stretching, 2960 for CH_3 stretching, 3000 for CH_3 stretching, 3681 for OH stretching. Because of interaction between torsion (internal rotation) and molecular rotation, the torsional frequency is not well defined, but this reference lists two related quantities as 200 and 295 cm^{-1}. The PM6 OH stretching shows a huge error.

Use of MOPAC in WebMO to first optimize the geometry and then find the vibrational wavenumbers gives the following RM1 results in cm^{-1}: 308 (CO torsion), 1011, 1094, 1257, 1260, 1280, 1381 (COH bending), 1461 (CO stretching), 2957, 2977, 3018 (symmetric CH stretching), 3332 (OH stretching).

17.36 Results are

AM1	R_{HC}/Å	R_{CN}/Å	R_{HN}/Å	∠HCN
HCN	1.069	1.160		180°
transition state	1.298	1.216	1.398	67.5°
HNC		1.178	0.967	180°

17.37 **(a)** F_3COH has 5 bonds and so has 5 bond-stretching terms. There are $\frac{1}{2}(4)3 = 6$ different ways to select two of the four atoms bonded to C, so there are 6 bond angles centered at C. There is one bond angle at O. Thus there are 7 bond-bending terms. There are three 1,4 atom pairs, namely, F_a-H, F_b-H, F_c-H, where the subscripts label the F atoms bonded to C. Hence there are 3 torsion terms. With three 1,4 atoms and no 1,5 atoms, there are 3 van der Waals terms and 3 electrostatic terms.

(b) Cl_3CCCl_2OH has 8 bonds and so has 8 bond-stretching terms. There are 6 bond angles centered at the end C, 6 centered at the second C, and one at the O, giving 13 bond-bending terms. There are 9 pairs of 1,4 atoms that have the two carbon atoms as atoms 2 and 3 (as in ethane), and 3 pairs of 1,4 atoms that have C and O as atoms 2 and 3, so we have 12 torsion terms. Besides these twelve 1,4 atom pairs, there are three 1,5 atom pairs, each such pair consisting of an H and one of the Cl atoms on the end C. Thus there are 15 van der Waals terms and 15 electrostatic terms.

17.38 **(a)** Setting $V = 0$ at $R = \sigma$, we have $0 = a/\sigma^{12} - b/\sigma^6$ and $a = b\sigma^6$. Substitution of this expression for a into V gives $V = b\sigma^6/R^{12} - b/R^6$.

(b) At the minimum, we have $dV/dR = 0 = -12b\sigma^6/R^{13} + 6b/R^7$. Solving this equation for R, and calling the result R^*, we get $R^* = 2^{1/6}\sigma$.

(c) Use of the V expression found in part (a) gives $V(\infty) = 0$ and $V(R^*) = b\sigma^6/(2^{1/6}\sigma)^{12} - b/(2^{1/6}\sigma)^6 = -b/4\sigma^6$. So $\varepsilon = V(\infty) - V(R^*) = b/4\sigma^6$ and $b = 4\sigma^6\varepsilon$.

(d) Substitution of $b = 4\sigma^6\varepsilon$ into $V = b\sigma^6/R^{12} - b/R^6$ gives $V = 4\varepsilon[\sigma^{12}/R^{12} - \sigma^6/R^6]$. Substitution of $\sigma = 2^{-1/6}R*$ into the last expression for V gives $V = \varepsilon[(R*)^{12}/R^{12} - 2(R*)^6/R^6]$.

17.39 Spartan Student Version 5.0 (which has the MMFF94s force field) gives these results for the two planar conformers shown in the Prob. 16.46a solution:

	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	126.7°	121.8°	104.3°	1.100 Å	1.217 Å	1.342 Å	0.980 Å
II	124.6°	124.3	112.0°	1.101 Å	1.217 Å	1.346 Å	0.976 Å

The steric energies are –0.040756 hartrees or –107.005 kJ/mol for I and –0.0329555 hartrees or –86.525 kJ/mol for II, so $E_{II} - E_I =$ 20.48 kJ/mol = 4.89 kcal/mol.

If we choose Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO Version 13.0 (www.webmo.net), we get (to view a bond length or angle, click on the Adjust arrow icon and then click and shift-click on the relevant atoms to select them)

	∠HC=O	∠OCO	∠COH	R_{CH}	$R_{C=O}$	R_{CO}	R_{OH}
I	127.1°	121.8°	102.3°	1.116 Å	1.206 Å	1.344 Å	0.972 Å
II	124.9°	125.7	108.4°	1.115 Å	1.209 Å	1.348 Å	0.971 Å

The steric energies are –3.348 kcal/mol for I and 3.608 kcal/mol for II, so $E_{II} - E_I =$ 6.96 kcal/mol.

17.40 Spartan Student 5.0 (which has the MMFF94s force field) gives the steric energy as –19.809 kJ/mol for the staggered conformation and –6.358 kJ/mol for the eclipsed conformation, for a barrier of 13.45 kJ/mol = 3.21 kcal/mol. Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO Version 13.0 (www.webmo.net) gives 0.816 kcal/mol for the eclipsed and 3.548 kcal/mol for the staggered, for a barrier of 2.73 kcal/mol. (See the online manual for how to adjust a dihedral angle.)

17.41 Spartan Student 5.0 gives the steric energy as –21.24 kJ/mol for the anti conformer and –17.97 kJ/mol for the higher-energy gauche conformer, for an energy difference of 3.27 kJ/mol = 0.78 kcal/mol. The CCCC dihedral angle in the gauche conformer is predicted to be 65.3°. The predicted CC bond distances are C1C2 = 1.520 Å, C2C3 = 1.527 Å in the anti conformer and C1C2 = 1.521 Å, C2C3 = 1.529 Å in the gauche conformer.

Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO (www.webmo.net) gives 2.172 kcal/mol for the anti conformer and 3.035 kcal/mol for the gauche conformer, for an energy difference of 0.86 kcal/mol. The gauche CCCC dihedral angle is predicted to be 65.2°. The CC bond distances are predicted to be C1C2 = 1.534 Å, C2C3 = 1.537 Å in the anti conformer and C1C2 = 1.534 Å, C2C3 = 1.538 Å in the gauche conformer. (To view a bond length or angle or dihedral angle, click on the Adjust arrow icon and then click and shift-click on the relevant atoms to select them.)

17.42 Use of Tinker in WebMO to first optimize the geometry and then find the vibrational wavenumbers gives the following MM3 wavenumbers in cm^{-1}: 263 (torsion), 1053 (CO stretching), 1087, 1107, 1288 (COH bending), 1432, 1447, 1485, 2874 (symmetric CH stretching), 2972, 2977, 3680 (OH stretching). These are in much better agreement with experiment than the semiempirical results. (These is also a 10 cm^{-1} wavenumber listed, but when viewed this is seen to involve rotational, not vibrational, motion.) The ZPE is found to be 2.152×10^{-19} J per molecule and 129.6 kJ/mol.

17.43 Spartan Student 5.0 (which has the MMFF94s force field) gives the following geometries for the two conformers shown in the Prob. 16.46 solution:

	$\angle$H5C=C	$\angle$HCH	$\angle$CCO	$\angle$HCO	$\angle$COH	R_{CH4}/ Å	R_{CH5}/Å	$R_{C=C}$/Å
I	120.7°	118.2°	121.7°	114.5°	108.2°	1.084	1.085	1.331
II	122.4°	117.5	124.5°	111.5°	108.7°	1.086	1.084	1.333

	R_{CH6}/Å	R_{CO}/Å	R_{OH}/Å	D(CCOH)
I	1.082	1.365	0.973	180°
II	1.084	1.365	0.973	0°

The steric energies are 6.337 kJ/mol for I and 0.343 kJ/mol for II, for an energy difference of 5.99 kJ/mol = 1.43 kcal/mol with II more stable at 0 K.

Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO gives 2.113 kcal/mol for conformer I and –0.516 kcal/mol for conformer II, for an energy difference of 2.63 kcal/mol. Bond lengths are 1.340 Å for CC and 1.357 Å for CO in conformer I, and 1.339 Å for CC and 1.357 Å for CO in conformer II.

17.44 **(a)** Spartan Student 5.0 (which has the MMFF94s force field) gives these results

	$\angle$FCC	$\angle$HCC	R_{CF}/Å	R_{CH}/Å	$R_{C=C}$/Å	E_{steric}
cis CHFCHF	121.9°	126.6°	1.345	1.079	1.327	8.73 kJ/mol
trans CHFCHF	121.7°	126.4°	1.345	1.079	1.326	2.12 kJ/mol

The trans isomer is predicted to be more stable by 6.61 kJ/mol = 1.6 kcal/mol.

Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO Version 13.0 (www.webmo.net) gives

	∠FCC	∠HCC	R_{CF}/Å	R_{CH}/Å	$R_{C=C}$/Å	E_{steric}
cis CHFCHF	121.8°	119.9°	1.323	1.102	1.343	1.552 kcal/mol
trans CHFCHF	121.0°	120.2°	1.323	1.102	1.342	2.509 kcal/mol

The cis isomer is predicted to be more stable by 0.96 kcal/mol. (For the experimental results, see part (c) below.)

(b) Comprehensive-Mechanics in the Clean-Up menu in the Editor in WebMO gives

	∠ClCC	∠HCC	R_{CCl}/Å	R_{CH}/Å	$R_{C=C}$/Å	E_{steric}
cis CHClCHCl	124.9°	122.0°	1.722	1.102	1.340	2.661 kcal/mol
trans CHClCHCl	122.0°	124.1°	1.721	1.102	1.339	2.716 kcal/mol

The cis isomer is predicted to be more stable by 0.06 kcal/mol.

(c) Comprehensive-Mechanics in the Editor in WebMO gives

	∠ICC	∠HCC	R_{CI}/Å	R_{CH}/Å	$R_{C=C}$/Å	E_{steric}
cis CHICHI	127.4°	120.7°	2.079	1.102	1.339	–0.19 kcal/mol
trans CHICHI	122.9°	123.7°	2.077	1.102	1.339	–0.19 kcal/mol

The isomers are predicted to be of equal stability.

Experimental data show that for CHFCHF, the cis isomer is more stable than the trans by 1.1 kcal/mol and for CHClCHCl, the cis isomer is more stable by 0.7 kcal/mol [N. C. Craig et al., *J. Phys. Chem.*, **75**, 1453 (1971)]. For CHICHI, the cis–trans energy difference is 0.0 kcal/mol [S. Furuyama et al., *J. Phys. Chem.*, **72**, 3204 (1968)].

In view of electrostatic and steric repulsions between the cis halogens, the greater stability of many of the cis isomers is surprising and not yet fully explained.

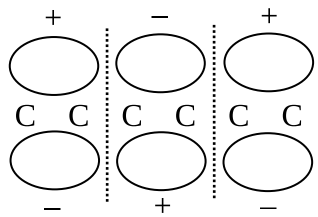
17.45 **(a)** For $CH_3CH_2CH_3$, $\Delta H^\circ_{f,298}$ = 2.05 kcal/mol + 8(–4.590 kcal/mol) + 2(2.447 kcal/mol) + 4(0.001987 kcal/mol-K)(298.1 K) + 2(1.045 kcal/mol) = –25.32 kcal/mol.

(b) For $(CH_3)_3CH$, $\Delta H^\circ_{f,298}$/(kcal/mol) = 3.18 + 10(–4.590) + 3(2.447) + 4(0.001987)(298.1) + 3(1.045) – 2.627 = –32.50.

(c) For C_4H_8, $\Delta H^\circ_{f,298}$/(kcal/mol) = 32.63 + 8(–4.590) + 4(2.447) + 4(0.001987)(298.1) – 1.780 = 6.29.

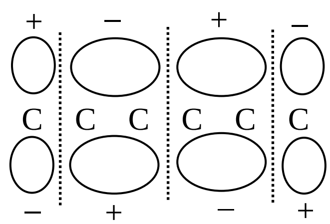
(d) Three; two gauche conformers that are mirror images of each other and one anti conformer.

17.46 **(a)** $CH_2{=\!=}CHCH{=\!=}CHCH{=\!=}CH_2$ has 6 π electrons, so the HOMO is the third lowest and has two nodes (not counting the node in the plane of the carbons), as follows:



The π AOs on the two end carbons have the same signs for their upper lobes, so a figure like Fig. 17.12 but with the signs reversed for one of the end AOs shows that a disrotatory path produces a bonding interaction. The reaction path is predicted to be disrotatory.

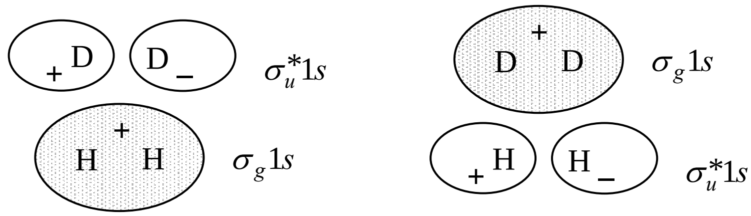
(b) For the photochemical reaction, a photon excites an electron from the HOMO shown in part (a) to an MO with three nodes, and the HOMO is now



[The signs of the AOs can be found from Eq. (17.30).] The π AOs on the two end carbons have opposite signs for their upper lobes, so the reaction path is predicted to be conrotatory.

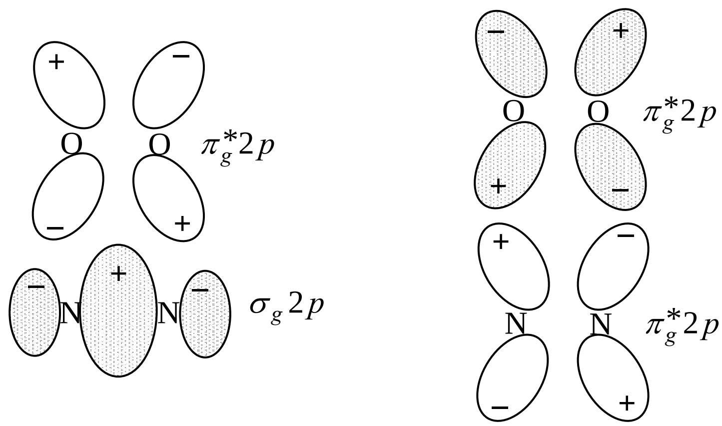
(c) The polyene (17.28) has $2s + 2$ carbons and has $n_\pi = 2s + 2$ π electrons. These electrons fill the lowest $s + 1$ MOs. The highest-occupied π MO has s nodes. As we go from one end of the molecule to the other, each node produces a sign change. If s is an even number, then an even number of sign changes gives the sign of the upper lobe on the last carbon as the same as the upper lobe on the first carbon. Hence, as in parts (a) and (b), if s is even, the thermal reaction proceeds by a disrotatory path and the photochemical reaction goes by a conrotatory path. If s is an odd number, an odd number of sign changes gives the sign of the upper lobe on the last carbon as the opposite of the upper lobe on the first carbon. Hence, if s is odd, the thermal reaction proceeds by a conrotatory path and the photochemical reaction goes by a disrotatory path.

17.47 **(a)** The HOMOs (shaded) and LUMOs are



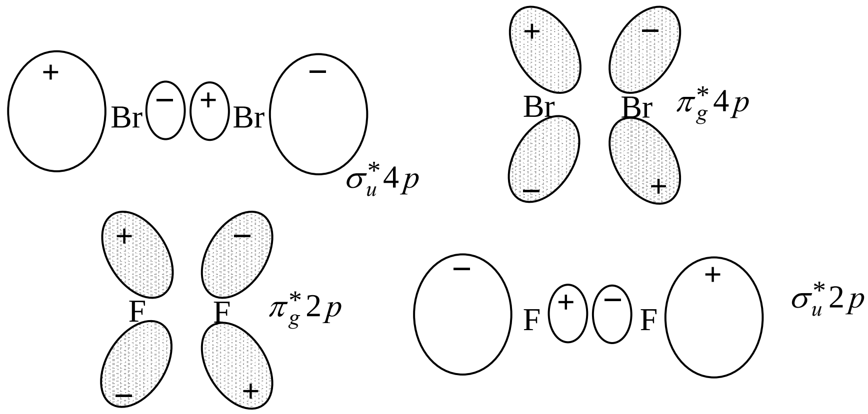
The overlap is not positive and a high activation energy is predicted for a broadside path.

(b) From Sec. 13.7, the N_2 HOMO is $\sigma_g 2p$ and the N_2 LUMO is $\pi_g^* 2p$. The O_2 HOMO is $\pi_g^* 2p$ and the O_2 LUMO is also $\pi_g^* 2p$. (Each of the two $\pi_g^* 2p$ MOs in O_2 is half-filled.)



The overlap between the N_2 HOMO and the O_2 LUMO is not positive. The overlap between the O_2 HOMO and the N_2 LUMO is positive, but flow of electrons out of the O_2 HOMO, which is antibonding, would strengthen the oxygen–oxygen bond. Hence a high activation energy is predicted for a broadside path. (The phase of a wave function is arbitrary, and in the figure, the O_2 HOMO and the N_2 LUMO have been given opposite phases.)

(c) Although the following figures show some positive overlap, flow of electrons out of antibonding HOMOs would strengthen a bond that needs to be broken, so a high activation energy is predicted. [Since the HOMOs are antibonding, one should also consider electron flow out the highest-occupied *bonding* MO (whose shape is shown by the $\sigma_g 2p$ MO in Fig. 13.11) of one species into the LUMO of the other. These MO pairs do not have positive overlap.]



(d) The ethylene HOMO is a π_u MO and the LUMO is a π_g^* MO (see Sec. 15.9). In the following figures, the plane of the ethylene molecule is perpendicular to the plane of the paper. A high activation energy is predicted.