Solutions manual for *Modern Quantum Chemistry*

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1 Chapter 1

Exercise 1.1 a) Show that $O_{ij} = \vec{e}_i \cdot \mathscr{O}\vec{e}_j$. b) If $\mathscr{O}\vec{a} = \vec{b}$ show that $b_i = \sum_j O_{ij} a_j$.

Solution:
a) We already know:

$$\mathscr{O}\vec{e}_j = \sum_{k=1}^{n} \vec{e}_k O_{kj}$$

Hence:

$$\vec{e}_i \cdot \mathscr{O}\vec{e}_j = \vec{e}_i \cdot \sum_{k=1}^{n} \vec{e}_k O_{kj} = \sum_{k=1}^{n} \vec{e}_i \vec{e}_k O_{kj} = \sum_{k=1}^{n} \delta_{ik} O_{kj} = O_{ij}$$

b) $b_i = \vec{e}_i \cdot \vec{b} = \vec{e}_i \cdot \mathscr{O}\vec{a}$
Hence:

$$b_i = \vec{e}_i \cdot \sum_{j=1}^{n} \mathscr{O} a_j \vec{e}_j = \sum_{j=1}^{n} a_j \vec{e}_i \cdot \mathscr{O}\vec{e}_j$$

From the last problem, we know:

$$\vec{e}_i \cdot \mathscr{O}\vec{e}_j = O_{ij}$$

Therefore:

$$b_i = \sum_{j=1}^{n} a_j O_{ij}$$

Exercise 1.2 Calculate $[\mathbf{A}, \mathbf{B}]$ and $\{\mathbf{A}, \mathbf{B}\}$ when

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 2 & 2 \\ 0 & 2 & -1 \end{pmatrix} \quad \mathbf{B} = \begin{pmatrix} 1 & -1 & 1 \\ -1 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$

Solution:

$$\begin{aligned}
[\mathbf{A}, \mathbf{B}] &= \mathbf{AB} - \mathbf{BA} \\
&= \begin{pmatrix} 1 & 1 & 0 \\ 1 & 2 & 2 \\ 0 & 2 & -1 \end{pmatrix} \cdot \begin{pmatrix} 1 & -1 & 1 \\ -1 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & -1 & 1 \\ -1 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 1 & 0 \\ 1 & 2 & 2 \\ 0 & 2 & -1 \end{pmatrix} \\
&= \begin{pmatrix} 0 & -2 & 4 \\ 2 & 0 & 3 \\ -4 & -3 & 0 \end{pmatrix}
\end{aligned}$$

$$
\begin{aligned}
\{\mathbf{A},\mathbf{B}\} &= \mathbf{AB}+\mathbf{BA}\\
&= \begin{pmatrix} 1 & 1 & 0\\ 1 & 2 & 2\\ 0 & 2 & -1\end{pmatrix}\cdot\begin{pmatrix} 1 & -1 & 1\\ -1 & 0 & 0\\ 1 & 0 & 1\end{pmatrix}+\begin{pmatrix} 1 & -1 & 1\\ -1 & 0 & 0\\ 1 & 0 & 1\end{pmatrix}\cdot\begin{pmatrix} 1 & 1 & 0\\ 1 & 2 & 2\\ 0 & 2 & -1\end{pmatrix}\\
&= \begin{pmatrix} 0 & 0 & -2\\ 0 & -2 & 3\\ -2 & 3 & -2\end{pmatrix}
\end{aligned}
$$

Exercise 1.3 If $\mathbf{A}$ is an $N\times M$ matrix and $\mathbf{B}$ is a $M\times K$ matrix show that $(\mathbf{AB})^\dagger=\mathbf{B}^\dagger\mathbf{A}^\dagger$.

Solution:
We set $\mathbf{C}=\mathbf{AB}$, hence:

$$C_{ij}=\sum_k A_{ik}B_{kj}$$

$$C_{ij}^\dagger=C_{ji}^*=\sum_k A_{jk}^*B_{ki}^*$$

Because $A_{kj}^\dagger=A_{kj}^*\quad B_{ik}^\dagger=B_{ki}^*$,

$$C_{ij}^\dagger=\sum_k B_{ik}^\dagger A_{kj}^\dagger$$

$$\mathbf{C}^\dagger=\mathbf{B}^\dagger\mathbf{A}^\dagger$$

Exercise 1.4 Show that
a. tr$\mathbf{AB}$=tr$\mathbf{BA}$.
b. $(\mathbf{AB})^{-1}=\mathbf{B}^{-1}\mathbf{A}^{-1}$.
c. If $\mathbf{U}$ is unitary and $\mathbf{B}=\mathbf{U}^\dagger\mathbf{AU}$, then $\mathbf{A}=\mathbf{UBU}^\dagger$.
d. If the product $\mathbf{C}=\mathbf{AB}$ of two Hermitian matrices is also Hermitian, then $\mathbf{A}$ and $\mathbf{B}$ commute.
e. If $\mathbf{A}$ is Hermitian then $\mathbf{A}^{-1}$, if it exists, is also Hermitian.
f. If $\mathbf{A}=\begin{pmatrix} A_{11} & A_{12}\\ A_{21} & A_{22}\end{pmatrix}$, the $\mathbf{A}^{-1}=\dfrac{1}{(A_{11}A_{22}-A_{12}A_{21})}\begin{pmatrix} A_{22} & -A_{12}\\ -A_{21} & A_{11}\end{pmatrix}$.

Solution:
a. We set $\mathbf{C}=\mathbf{AB}\quad\mathbf{D}=\mathbf{BA}$, hence:

$$
\begin{aligned}
\mathrm{tr}\mathbf{C} &= \sum_{n=1}^{N} C_{nn}\\
&= \sum_{n=1}^{N}\sum_{k=1}^{N} A_{nk}B_{kn}
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{tr}\mathbf{D} &= \sum_{n=1}^{N} D_{nn}\\
&= \sum_{n=1}^{N}\sum_{k=1}^{N} B_{nk}A_{kn}
\end{aligned}
$$

Replace n with k and k with n in tr$\mathbf{D}=\sum\limits_{n=1}^{N}\sum\limits_{k=1}^{N}B_{nk}A_{kn}$ respectively(n and k are dummy variables and have same value range):

$$\begin{aligned}\mathrm{tr}\mathbf{D} &= \sum_{k=1}^{N}\sum_{n=1}^{N} B_{kn}A_{nk} \\ &= \sum_{n=1}^{N}\sum_{k=1}^{N} A_{nk}B_{kn}\end{aligned}$$

Thus:

$$\mathrm{tr}\mathbf{AB} = \mathrm{tr}\mathbf{BA}$$

b. Because $\mathbf{AA}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{1}$, therefore:

$$(\mathbf{AB})^{-1}(\mathbf{AB}) = \mathbf{1}$$

$$(\mathbf{AB})^{-1}\mathbf{AB} = \mathbf{1}$$

$$(\mathbf{AB})^{-1}\mathbf{ABB}^{-1} = \mathbf{B}^{-1}$$

$$(\mathbf{AB})^{-1}\mathbf{A} = \mathbf{B}^{-1}$$

$$(\mathbf{AB})^{-1}\mathbf{AA}^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1}$$

$$(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1}$$

c. From the definition of unitary matrix:

$$\mathbf{U}^\dagger = \mathbf{U}^{-1}$$

Therefore:

$$\begin{aligned}\mathbf{UBU}^\dagger &= \mathbf{UU}^\dagger\mathbf{AUU}^\dagger \\ &= \mathbf{UU}^{-1}\mathbf{AUU}^{-1} \\ &= \mathbf{A}\end{aligned}$$

c.

$$A_{ik}B_{kj} = C_{ij}$$

$$B_{jk}A_{ki} = C_{ji}$$

$$(B_{jk}A_{ki})^* = C_{ji}^*$$

$$B_{jk}^*A_{ki}^* = C_{ji}^*$$

Because $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are Hermitian matrices, hence:

$$B_{ij}A_{ki}^* = C_{ji}^*$$

d.

$$\mathbf{AB} = \mathbf{C}$$

$$(\mathbf{AB})^\dagger = \mathbf{C}^\dagger$$

$$\mathbf{B}^\dagger\mathbf{A}^\dagger = \mathbf{C}^\dagger$$

$$\mathbf{BA} = \mathbf{C}$$

Therefore:

$$\mathbf{AB} = \mathbf{BA}$$

$$[\mathbf{A}, \mathbf{B}] = 0$$

e. We already know that:

$$\mathbf{AA}^{-1} = \mathbf{1}$$

$$(\mathbf{AA}^{-1})^\dagger = \mathbf{1}^\dagger$$

$$(\mathbf{A}^{-1})^\dagger\mathbf{A}^\dagger = \mathbf{1}^\dagger$$

And therefore:

$$(\mathbf{A}^{-1})^\dagger \mathbf{A} = \mathbf{1}$$
$$(\mathbf{A}^{-1})^\dagger = \mathbf{A}^{-1}$$

Thus $\mathbf{A}^{-1}$ is Hermitian.

f. We suppose $\mathbf{A}^{-1} = \begin{pmatrix} x & y \\ z & w \end{pmatrix}$. Because $\mathbf{A}\mathbf{A}^{-1} = \mathbf{1}$, hence:

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} x & y \\ z & w \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

And we have simultaneous equations:

$$\begin{cases} A_{11}x + A_{12}z = 1 \\ A_{21}x + A_{22}z = 0 \\ A_{11}y + A_{12}w = 0 \\ A_{21}y + A_{22}w = 1 \end{cases}$$

The solution is:

$$\begin{cases} x = \dfrac{A_{22}}{A_{11}A_{22} - A_{12}A_{21}} \\ y = \dfrac{-A_{12}}{A_{11}A_{22} - A_{12}A_{21}} \\ z = \dfrac{-A_{21}}{A_{11}A_{22} - A_{12}A_{21}} \\ w = \dfrac{A_{11}}{A_{11}A_{22} - A_{12}A_{21}} \end{cases}$$

At last, we have:

$$\mathbf{A}^{-1} = \frac{1}{(A_{11}A_{22} - A_{12}A_{21})} \begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix}$$

Exercise 1.5 Verify the above properties for 2×2 determinants.

Solution:

1. Take the determinant $\begin{vmatrix} 0 & a \\ 0 & b \end{vmatrix}$ as example:

$$\begin{vmatrix} 0 & a \\ 0 & b \end{vmatrix} = 0 \times b - 0 \times a = 0$$

2. For determinant $\begin{vmatrix} a & 0 \\ 0 & b \end{vmatrix}$:

$$\begin{vmatrix} a & 0 \\ 0 & b \end{vmatrix} = ab - 0 = ab$$

3. If $\mathbf{A} = \begin{vmatrix} a & b \\ c & d \end{vmatrix}$, and $\mathbf{B} = \begin{vmatrix} c & d \\ a & b \end{vmatrix}$, then:

$$\det(\mathbf{B}) = bc - ad = -(ad - bc) = -\det(\mathbf{A})$$

4. Suppose $\mathbf{A} = \begin{vmatrix} a & b \\ c & d \end{vmatrix}$, so $\mathbf{A}^\dagger = \begin{vmatrix} a^* & c^* \\ b^* & d^* \end{vmatrix}$:

$$|\mathbf{A}| = ad - bc$$
$$\left|\mathbf{A}^\dagger\right| = a^*d^* - b^*c^*$$

So it is obviously that $|\mathbf{A}| = \left(\left|\mathbf{A}^\dagger\right|\right)^*$

5.

$$\mathbf{A} = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix}$$
$$\mathbf{B} = \begin{vmatrix} 4 & 3 \\ 2 & 1 \end{vmatrix}$$
$$\mathbf{AB} = \begin{vmatrix} 8 & 5 \\ 20 & 13 \end{vmatrix}$$
$$|\mathbf{A}| = -2 \quad |\mathbf{B}| = -2$$
$$|\mathbf{AB}| = 4$$
$$|\mathbf{A}|\,|\mathbf{B}| = |\mathbf{AB}|$$

Exercise 1.6 Using properties (1)-(5) prove that in general

Solution:
6. Suppose the ith and jth columns in the determinant $\mathbf{A}$ are equal:

$$\mathbf{A} = \begin{vmatrix} a_{11} & a_{12} & \dots & a_{1i} & \dots & a_{1j} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2i} & \dots & a_{2j} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{ni} & \dots & a_{nj} & \dots & a_{nn} \end{vmatrix} = x$$

Now exchange the ith and jth columns and have:

$$\mathbf{A}' = \begin{vmatrix} a_{11} & a_{12} & \dots & a_{1j} & \dots & a_{1i} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2j} & \dots & a_{2i} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nj} & \dots & a_{ni} & \dots & a_{nn} \end{vmatrix} = x'$$

Because $\mathbf{A}$ and $\mathbf{A}'$ are same, $x = x'$. And from the property (3), we know that $x = -x'$. Finally, $x = x' = 0$.

7.

$$\mathbf{AA}^{-1} = \mathbf{1}$$

Hence:

$$\left|\mathbf{AA}^{-1}\right| = |\mathbf{1}|$$
$$|\mathbf{A}|\left|\mathbf{A}^{-1}\right| = 1$$
$$\left|\mathbf{A}^{-1}\right| = (|\mathbf{A}|)^{-1}$$

8. Because $|\mathbf{A}| = \left(\left|\mathbf{A}^\dagger\right|\right)^*$, therefore:

$$(|\mathbf{A}|)^* = \left|\mathbf{A}^\dagger\right|$$

Since $\mathbf{A}\mathbf{A}^\dagger = \mathbf{1}$,

$$|\mathbf{A}| \left|\mathbf{A}^\dagger\right| = 1$$

So:

$$|\mathbf{A}| (|\mathbf{A}|)^* = 1$$

9. From $\mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{1}$, we know

$$\mathbf{U}^\dagger = \mathbf{U}^{-1}$$

And therefore:

$$\left|\mathbf{U}^\dagger\right| = \left|\mathbf{U}^{-1}\right| = (|\mathbf{U}|)^{-1}$$

Because

$$\mathbf{U}^\dagger\mathbf{O}\mathbf{U} = \mathbf{\Omega}$$

$$\left|\mathbf{U}^\dagger\right| |\mathbf{O}| |\mathbf{U}| = |\mathbf{\Omega}|$$

$$|\mathbf{U}| \left|\mathbf{U}^\dagger\right| |\mathbf{O}| |\mathbf{U}| (|\mathbf{U}|)^{-1} = |\mathbf{U}| |\mathbf{\Omega}| (|\mathbf{U}|)^{-1}$$

Hence:

$$|\mathbf{O}| = |\mathbf{\Omega}|$$

Exercise 1.7 Using Eq.(1.39), note that the inverse of a 2×2 matrix $\mathbf{A}$ obtained in Exercise 1.4f can be written as

$$\mathbf{A}^{-1} = \frac{1}{|\mathbf{A}|}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix}$$

Show that the equation

$$\mathbf{A}\mathbf{c} = \mathbf{0}$$

where $\mathbf{A}$ is an $N \times N$ matrix and $\mathbf{c}$ is a column matrix with elements $c_i, i = 1, 2, \ldots, N$ can have a nontrivial solution($\mathbf{c} \neq \mathbf{0}$) only when $|\mathbf{A}| = 0$.

Solution:
From Exercise 1.4f we know

$$\mathbf{A}^{-1} = \frac{1}{(A_{11}A_{22} - A_{12}A_{21})}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix}$$

Because:

$$|\mathbf{A}| = A_{11}A_{22} - A_{12}A_{21}$$

Thus

$$\mathbf{A}^{-1} = \frac{1}{|\mathbf{A}|}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11f} \end{pmatrix}$$

If $|\mathbf{A}| \neq 0$, then $\mathbf{A}^{-1}$ exists.

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{c} = \mathbf{0}$$

$$\mathbf{c} = \mathbf{0}$$

Exercise 1.8 Show that the trace of a matrix is invariant under a unitary transformation, i.e., if

$$\mathbf{\Omega} = \mathbf{U}^\dagger\mathbf{O}\mathbf{U}$$

then show that $\mathrm{tr}\mathbf{\Omega} = \mathrm{tr}\mathbf{O}$.

Solution:
Because $\mathrm{tr}\mathbf{AB} = \mathrm{tr}\mathbf{BA}$,

$$\mathrm{tr}\boldsymbol{\Omega} = \mathrm{tr}\mathbf{U}^\dagger\mathbf{O}\mathbf{U} = \mathrm{tr}\mathbf{O}\mathbf{U}\mathbf{U}^\dagger$$

Since

$$\mathbf{U}\mathbf{U}^\dagger = \mathbf{1}$$

$$\mathrm{tr}\boldsymbol{\Omega} = \mathrm{tr}\mathbf{O}\mathbf{1} = \mathrm{tr}\mathbf{O}$$

Exercise 1.9 Show that Eq.(1.90) contains Eq.(1.87) for all $\alpha = 1, 2, \ldots, N$.

Solution:

$$\mathbf{U}\omega = \begin{pmatrix} c_1^1 & c_1^2 & \ldots & c_1^N \\ c_2^1 & c_2^2 & \ldots & c_2^N \\ \vdots & \vdots & & \vdots \\ c_N^1 & c_N^2 & \ldots & c_N^N \end{pmatrix} \begin{pmatrix} \omega_1 & & & \\ & \omega_2 & & \\ & & \ddots & \\ & & & \omega_N \end{pmatrix}$$

$$= \begin{pmatrix} \omega_1 c_1^1 & \omega_2 c_1^2 & \ldots & \omega_N c_1^N \\ \omega_1 c_2^1 & \omega_2 c_2^2 & \ldots & \omega_N c_2^N \\ \vdots & \vdots & & \ldots \\ \omega_1 c_N^1 & \omega_2 c_N^2 & \ldots & \omega_N c_N^N \end{pmatrix} = \mathbf{OU}$$

Since

$$\mathbf{c}^\alpha = \begin{pmatrix} c_1^\alpha \\ c_2^\alpha \\ \vdots \\ c_N^\alpha \end{pmatrix}$$

$$\mathbf{U}\omega = \left(\omega_1 c^1, \omega_2 c^2, \ldots, \omega_N c^N\right)$$

It is obviously that

$$\mathbf{O}\mathbf{c}^\alpha = \omega \mathbf{c}^\alpha \quad \alpha = 1, 2, \ldots, N$$

Exercise 1.9 & **Exercise 1.10**
Just have a try. And I don't think approach (b) is friendly to human. It is convenient when works as a computer program.

Exercise 1.12 Given that $\mathbf{U}^\dagger\mathbf{A}\mathbf{U} = \mathbf{a} = \begin{pmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_N \end{pmatrix}$ or $\mathbf{A}\mathbf{c}^\alpha = a_\alpha \mathbf{c}^\alpha \quad \alpha = 1, 2, \ldots, N$. Show that

a. $\det\left(\mathbf{A}^n\right) = a_1^n a_2^n \cdots a_N^n$.
b. $\mathrm{tr}\mathbf{A}^n = \sum\limits_{\alpha=1}^{N} a_\alpha^n$.
c. If $\mathbf{G}(\omega) = (\omega\mathbf{1} - \mathbf{A})^{-1}$, then

$$(\mathbf{G}(\omega))_{ij} = \sum_{\alpha=1}^{N} \frac{U_{i\alpha}U_{j\alpha}^*}{\omega - a_\alpha} = \sum_{\alpha=1}^{N} \frac{c_i^\alpha c_j^{\alpha *}}{\omega - a_\alpha}$$

Show that using Dirac notation this can be rewritten as

$$(\mathbf{G}(\omega))_{ij} \equiv \langle i \,|\, \mathscr{G}(\omega) \,|\, j \rangle = \sum_\alpha \frac{\langle i \,|\, \alpha \rangle \langle \alpha \,|\, j \rangle}{\omega - a_\alpha}$$

Solution:
a. Since $\mathbf{A}^n = \mathbf{U}\mathbf{a}^n\mathbf{U}^\dagger$, thus

$$\det\left(\mathbf{A}^n\right) = \det\left(\mathbf{U}\right)\det\left(\mathbf{a}^n\right)\det\left(\mathbf{U}^\dagger\right)$$

Because $\mathbf{U}^{-1} = \mathbf{U}^\dagger$,

$$\begin{aligned}\det\left(\mathbf{A}^n\right) &= \det\left(\mathbf{U}\right)\det\left(\mathbf{a}^n\right)\det\left(\mathbf{U}^{-1}\right)\\ &= \left(\det\left(\mathbf{a}\right)\right)^n\\ &= a_1^n a_2^n \cdots a_N^n\end{aligned}$$

b. Because $\operatorname{tr}\left(\mathbf{U}^\dagger\mathbf{A}^n\mathbf{U}\right) = \operatorname{tr}\left(\mathbf{A}^n\mathbf{U}\mathbf{U}^\dagger\right) = \operatorname{tr}\left(\mathbf{A}^n\right)$, hence

$$\operatorname{tr}\left(\mathbf{A}^n\right) = \operatorname{tr}\left(\mathbf{a}^n\right) = \sum_{\alpha=1}^{N} a_\alpha^n$$

c.

$$\begin{aligned}\mathbf{X} &= \mathbf{U}^\dagger(\omega\mathbf{1} - \mathbf{A})\mathbf{U}\\ &= \omega\mathbf{U}^\dagger\mathbf{1}\mathbf{U} - \mathbf{U}^\dagger\mathbf{A}\mathbf{U} = \omega\mathbf{1} - \mathbf{a}\\ &= \begin{pmatrix}\omega - a_1 & & & \\ & \omega - a_2 & & \\ & & \ddots & \\ & & & \omega - a_N\end{pmatrix}\end{aligned}$$

It is diagonal matrix, therefore

$$\mathbf{G}(\omega) = \mathbf{U}\begin{pmatrix}\omega - a_1 & & & \\ & \omega - a_2 & & \\ & & \ddots & \\ & & & \omega - a_N\end{pmatrix}\mathbf{U}^\dagger$$

$$(\mathbf{G}(\omega))_{ij} = \sum_\alpha\sum_\beta U_{i\alpha}X_{\alpha\beta}\left(U^\dagger\right)_{\beta j}$$

Because $X_{\alpha\beta} = \delta_{\alpha\beta}(\omega - a_\alpha)^{-1}$,

$$(\mathbf{G}(\omega))_{ij} = \sum_\alpha \frac{U_{i\alpha}U_{j\alpha}^*}{\omega - a_\alpha} = \sum_\alpha \frac{c_i^\alpha c_j^{\alpha *}}{\omega - a_\alpha}$$

Because

$$U_{i\alpha} = \langle i \,|\, \alpha \rangle \quad U_{j\alpha}^* = \langle \alpha \,|\, j \rangle$$

$$(\mathbf{G}(\omega))_{ij} = \sum_\alpha \frac{U_{i\alpha}U_{j\alpha}^*}{\omega - a_\alpha} = \sum_\alpha \frac{\langle i \,|\, \alpha \rangle \langle \alpha \,|\, j \rangle}{\omega - a_\alpha}$$

Exercise 1.13 If

$$\mathbf{A} = \begin{pmatrix} a & b \\ b & a \end{pmatrix}$$

show that

$$f(\mathbf{A}) = \begin{pmatrix} \dfrac{f(a+b)+f(a-b)}{2} & \dfrac{f(a+b)-f(a-b)}{2} \\ \dfrac{f(a+b)-f(a-b)}{2} & \dfrac{f(a+b)+f(a-b)}{2} \end{pmatrix}$$

Solution:
First of all, we should diagonalize $\mathbf{A}$.

$$\begin{vmatrix} a-\omega & b \\ b & a-\omega \end{vmatrix} = 0$$

We have

$$\omega_1 = a+b \quad \omega_2 = a-b$$

So the diagonal matrix

$$\mathbf{a} = \begin{pmatrix} a+b & 0 \\ 0 & a-b \end{pmatrix}$$

When $\omega = a+b$,

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = (a+b) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Solve the equations, and we have

$$\begin{pmatrix} c_1^1 \\ c_2^1 \end{pmatrix} = \begin{pmatrix} \dfrac{1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} \end{pmatrix}$$

Similarly, when $\omega = a-b$, we get

$$\begin{pmatrix} c_1^2 \\ c_2^2 \end{pmatrix} = \begin{pmatrix} \dfrac{1}{\sqrt{2}} \\ -\dfrac{1}{\sqrt{2}} \end{pmatrix}$$

And therefore

$$\mathbf{U} = \begin{pmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \end{pmatrix}$$

Hence

$$\begin{aligned} f(\mathbf{A}) &= \mathbf{U} f(\mathbf{a}) \mathbf{U}^\dagger \\ &= \begin{pmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} f(a+b) & 0 \\ 0 & f(a-b) \end{pmatrix} \begin{pmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \end{pmatrix} \\ &= \begin{pmatrix} \dfrac{f(a+b)+f(a-b)}{2} & \dfrac{f(a+b)-f(a-b)}{2} \\ \dfrac{f(a+b)-f(a-b)}{2} & \dfrac{f(a+b)+f(a-b)}{2} \end{pmatrix} \end{aligned}$$

Exercise 1.14 Using the above representation of $\delta(x)$, show that

$$a(0) = \int_{-\infty}^{\infty} \mathrm{d}x \; a(x)\delta(x)$$

Solution:

$$\begin{aligned}
\lim_{\varepsilon\to 0} a(x) &= \lim_{\varepsilon\to 0}\left(\int_{-\infty}^{\infty} \mathrm{d}x\ a(x)\delta(x)\right)\\
&= \lim_{\varepsilon\to 0}\left(\int_{-\infty}^{-\varepsilon} \mathrm{d}x\ a(x)\delta(x) + \int_{+\varepsilon}^{-\varepsilon} \mathrm{d}x\ a(x)\delta(x) + \int_{+\varepsilon}^{\infty} \mathrm{d}x\ a(x)\delta(x)\right)\\
&= \lim_{\varepsilon\to 0}\int_{+\varepsilon}^{-\varepsilon} \mathrm{d}x\ a(x)\delta(x)\\
&= a(0)
\end{aligned}$$

Exercise 1.15 As a further illustration of the consistency of our notation, consider the matrix representation of an operator $\mathscr{O}$ in the basis $\{\psi_i(x)\}$. Starting with

$$\mathscr{O}\psi_i(x) = \sum_j \psi_j(x) O_{ji}$$

Show that

$$O_{ji} = \int \mathrm{d}x\ \psi_j^*(x)\mathscr{O}\psi_i(x)$$

Then using Eqs.(1.127a) and (1.138) rewrite (1) in bra-ket notation and show that it is identical to Eq.(1.55).
Solution:

$$\begin{aligned}
\mathscr{O}\psi_i(x) &= \sum_j \psi_j(x) O_{ji}\\
\psi_k^*(x)\mathscr{O}\psi_i(x) &= \sum_j \psi_k^*(x)\psi_j(x) O_{ji}\\
\int \mathrm{d}x\ \psi_k^*(x)\mathscr{O}\psi_i(x) &= \int \mathrm{d}x\ \sum_j \psi_k^*(x)\psi_j(x) O_{ji}\\
&= O_{ji}\sum_j\left(\int \mathrm{d}x\ \sum_j \psi_k^*(x)\psi_j(x)\right)\\
&= O_{ji}\sum_j \delta_{kj} = O_{ki}
\end{aligned}$$

Therefore

$$O_{ji} = \int \mathrm{d}x\ \psi_j^*(x)\mathscr{O}\psi_i(x)$$

Exercise 1.16

Solution:

$$\begin{aligned}
\mathscr{O}\phi(x) &= \omega\phi(x)\\
\sum_{j=1}^{\infty}\mathscr{O}c_j\psi_j(x) &= \sum_{j=1}^{\infty}\omega c_j\psi_j(x)
\end{aligned}$$

Multiply $\psi_i^*(x)$ on both side:

$$\begin{aligned}
\sum_{j=1}^{\infty}\psi_i^*(x)\mathscr{O}c_j\psi_j(x) &= \sum_{j=1}^{\infty}\omega c_j\psi_i^*(x)\psi_j(x)\\
\sum_{j=1}^{\infty}O_{ij}c_j &= \omega\sum_{j=1}^{\infty}c_j\delta_{ij}\\
&= \omega c_i
\end{aligned}$$

Assume

$$\mathbf{O} = \begin{pmatrix} o_1 \\ o_2 \\ \vdots \\ o_n \end{pmatrix} \qquad o_n = (o_{n1}, o_{n2}, \ldots, o_{nj})$$

Therefore:

$$o_i c = \omega c_i$$

Generalize i from n to ∞:

$$O_{ij} c = \omega c$$

Exercise 1.17

Solution:

a.

$$\int \mathrm{d}x \;\; \langle i \,|\, x \rangle \, \langle x \,|\, j \rangle = \langle i \,|\, j \rangle = \delta_{ij}$$

$$\int \mathrm{d}x \;\, \psi_i^*(x) \psi_j(x) = \delta_{ij}$$

b.

$$\sum_{i=1}^{\infty} \langle x' \,|\, i \rangle \, \langle i \,|\, x \rangle = \langle x' \,|\, x \rangle = \delta(x' - x) = \delta(x - x')$$

$$\sum_i \psi_i^*(x') \psi_i(x) = \delta(x - x')$$

c.

$$\int \mathrm{d}x \;\; \langle x' \,|\, x \rangle \, \langle x \,|\, a \rangle = \langle x' \,|\, a \rangle$$

Because $\langle x' \,|\, x \rangle = \delta(x - x')$,

$$\int \mathrm{d}x \;\, \delta(x - x') a(x) = a(x')$$

d.

$$\mathscr{O} \,|a\rangle = |b\rangle$$

Multiply $\langle x|$ on the left side and insert unity:

$$\begin{aligned} \langle x \,|\, b \rangle &= \langle x \,|\, \mathscr{O} \,|\, a \rangle \\ &= \int \mathrm{d}x' \;\; \langle x \,|\, \mathscr{O} \,|\, x' \rangle \, \langle x' \,|\, a \rangle \end{aligned}$$

$$b(x) = \int \mathrm{d}x' \;\, O(x, x') a(x')$$

e.

$$\begin{aligned} O(x, x') &= \langle x \,|\, \mathscr{O} \,|\, x' \rangle \\ &= \sum_i \sum_j \langle x \,|\, i \rangle \, \langle i \,|\, \mathscr{O} \,|\, j \rangle \, \langle j \,|\, x' \rangle \\ &= \sum_{ij} \psi_i(x) O_{ij} \psi_j^*(x') \end{aligned}$$

Exercise 1.18

Solution:
Since $|\tilde{\Phi}\rangle$ is normalized:

$$\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle = 1$$
$$\int_{-\infty}^{\infty} \left(N\mathrm{e}^{-\alpha x^2}\right)^* N\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = 1$$
$$N^2 \int_{-\infty}^{\infty} \mathrm{e}^{-2\alpha x^2}\,\mathrm{d}x = 1$$
$$N^2 \cdot \sqrt{\frac{\pi}{2\alpha}} = 1$$
$$N^2 = \sqrt{\frac{2\alpha}{\pi}}$$

Therefore,

$$\begin{aligned}
\left\langle \tilde{\Phi} \middle| \mathscr{H} \middle| \tilde{\Phi} \right\rangle &= \int_{-\infty}^{\infty} N\mathrm{e}^{-\alpha x^2} \left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \delta(x)\right) N\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x \\
&= N^2 \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2} \left(-2\alpha^2 x^2 \mathrm{e}^{-\alpha x^2} + \alpha\mathrm{e}^{-\alpha x^2} - \delta(x)\mathrm{e}^{-\alpha x^2}\right)\,\mathrm{d}x \\
&= N^2 \int_{-\infty}^{\infty} \left(-2\alpha^2 x^2 \mathrm{e}^{-2\alpha x^2} + \alpha\mathrm{e}^{-2\alpha x^2} - \delta(x)\mathrm{e}^{-2\alpha x^2}\right)\,\mathrm{d}x \\
&= N^2 \cdot \left(-\frac{\alpha}{2}\sqrt{\frac{\pi}{2\alpha}} + \alpha\sqrt{\frac{\pi}{2\alpha}} - 1\right) \\
&= \sqrt{\frac{2\alpha}{\pi}} \left(\frac{\alpha}{2}\sqrt{\frac{\pi}{2\alpha}} - 1\right) \\
&= \frac{\alpha}{2} - \sqrt{\frac{2\alpha}{\pi}}
\end{aligned}$$

To minimize variation integral,

$$\frac{\partial\mathscr{E}}{\partial\alpha} = \frac{1}{2} - \sqrt{\frac{1}{2\pi\alpha}} = 0$$
$$\alpha = \frac{2}{\pi}$$

So we get the result

$$\mathscr{E} = -\frac{1}{\pi}$$

Exercise 1.19

Solution:

$$\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle = \int_0^{\infty} N^2 \mathrm{e}^{-2\alpha r^2} \cdot r^2\,\mathrm{d}r = 1$$
$$N^2 \cdot \frac{2\cdot\pi^{1/2}}{8\cdot(2\alpha)^{1/2}} = 1$$
$$N^2 = 8\sqrt{\frac{2\alpha^3}{\pi}}$$

$$
\begin{aligned}
\mathscr{E} = \left\langle \tilde{\Phi} \middle| \mathscr{H} \middle| \tilde{\Phi} \right\rangle &= \int_0^\infty N\mathrm{e}^{-\alpha r^2} \left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right) N\mathrm{e}^{-\alpha r^2} r^2 \,\mathrm{d}r \\
&= N^2 \int_0^\infty \left(3\alpha r^2 \mathrm{e}^{-2\alpha r^2} - 2\alpha^2 r^4 \mathrm{e}^{-2\alpha r^2} - r\mathrm{e}^{-2\alpha r^2}\right) \mathrm{d}r \\
&= N^2 \left(3\alpha \cdot \frac{2 \cdot \pi^{1/2}}{8 \cdot (2\alpha)^{3/2}} - 2\alpha^2 \cdot \frac{24 \cdot \pi^{1/2}}{32 \cdot 2 \cdot (2\alpha)^{5/2}} - \frac{1}{4\alpha}\right) \\
&= 8\sqrt{\frac{2\alpha^3}{\pi}} \left(\frac{3}{16}\sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}\right) \\
&= \frac{3}{2}\alpha - 2\sqrt{\frac{2\alpha}{\pi}}
\end{aligned}
$$

To minimize variation integral,

$$
\frac{\partial \mathscr{E}}{\partial \alpha} = \frac{3}{2} - \sqrt{\frac{2}{\pi\alpha}} = 0
$$

$$
\alpha = \frac{8}{9\pi}
$$

So the result is:

$$
\mathscr{E} = -\frac{4}{3\pi} = -0.4244
$$

Exercise 1.21

Solution:

a.

$$
\begin{aligned}
\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle &= \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \langle \Phi_\alpha \,|\, \Phi_\beta \rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \\
&= \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \delta_{\alpha\beta} \\
&= \sum_{\alpha} \left| \left\langle \Phi_\alpha \middle| \tilde{\Phi}' \right\rangle \right|^2 = 1
\end{aligned}
$$

Because $\left\langle \Phi_0 \middle| \tilde{\Phi}' \right\rangle = 0$:

$$
\sum_{\alpha=1}^{\infty} \left| \left\langle \Phi_\alpha \middle| \tilde{\Phi}' \right\rangle \right|^2 = 1
$$

Therefore:

$$
\begin{aligned}
\left\langle \tilde{\Phi} \middle| \mathscr{H} \middle| \tilde{\Phi} \right\rangle &= \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \langle \Phi_\alpha \,|\, \mathscr{H} \,|\, \Phi_\beta \rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \\
&= \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \mathscr{E}_\alpha \cdot \delta_{\alpha\beta} \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \\
&= \sum_{\alpha=1}^{\infty} \mathscr{E}_\alpha \cdot \left| \left\langle \Phi_\alpha \middle| \tilde{\Phi}' \right\rangle \right|^2
\end{aligned}
$$

Because $\alpha = 1, 2, \ldots$, $\mathscr{E}_\alpha \geq \mathscr{E}_1$:

$$
\left\langle \tilde{\Phi} \middle| \mathscr{H} \middle| \tilde{\Phi} \right\rangle \geq \mathscr{E}_1
$$

b.

$$
\begin{aligned}
\left\langle \tilde{\Phi}' \middle| \tilde{\Phi}' \right\rangle = 1 &= \left(x\,|\tilde{\Phi}_0\rangle + y\,|\tilde{\Phi}_1\rangle\right)^* \left(x\,|\tilde{\Phi}_0\rangle + y\,|\tilde{\Phi}_1\rangle\right) \\
&= \left(x^*\,\langle\tilde{\Phi}_0| + y^*\,\langle\tilde{\Phi}_1|\right)^* \left(x\,|\tilde{\Phi}_0\rangle + y\,|\tilde{\Phi}_1\rangle\right) \\
&= |x|^2 \left\langle \tilde{\Phi}_0 \middle| \tilde{\Phi}_0 \right\rangle + |y|^2 \left\langle \tilde{\Phi}_1 \middle| \tilde{\Phi}_1 \right\rangle + xy \left(\left\langle \tilde{\Phi}_0 \middle| \tilde{\Phi}_1 \right\rangle + \left\langle \tilde{\Phi}_1 \middle| \tilde{\Phi}_0 \right\rangle\right)
\end{aligned}
$$

Because $|\tilde{\Phi}_\alpha\rangle$ is orthogonal,

$$\left\langle \tilde{\Phi}' \middle| \tilde{\Phi}' \right\rangle = x^2 + y^2 = 1$$

c.

$$\begin{aligned}
\left\langle \tilde{\Phi}' \middle| \mathscr{H} \middle| \tilde{\Phi}' \right\rangle &= \left(x\,|\tilde{\Phi}_0\rangle + y\,|\tilde{\Phi}_1\rangle \right)^* \mathscr{H} \left(x\,|\tilde{\Phi}_0\rangle + y\,|\tilde{\Phi}_1\rangle \right) \\
&= |x|^2 \left\langle \tilde{\Phi}_0 \middle| \mathscr{H} \middle| \tilde{\Phi}_0 \right\rangle + |y|^2 \left\langle \tilde{\Phi}_1 \middle| \mathscr{H} \middle| \tilde{\Phi}_1 \right\rangle \\
&= |x|^2 E_0 + \left(1 - |x|^2\right) E_1 \\
&= E_1 - |x|^2 (E_1 - E_0)
\end{aligned}$$

Because $E_1 \geq E_0$,

$$\begin{aligned}
\left\langle \tilde{\Phi}' \middle| \mathscr{H} \middle| \tilde{\Phi}' \right\rangle = E_1 - |x|^2 (E_1 - E_0) &\geq \mathscr{E}_1 \\
E_1 &\geq \mathscr{E}_1
\end{aligned}$$

Exercise 1.22

Solution:
Firstly, we form the matrix representation of operator $\mathscr{H}$ in the basis:

$$\begin{aligned}
(\mathbf{H})_{11} &= \langle 1s \,|\, \mathscr{H} \,|\, 1s \rangle = \langle 1s \,|\, \mathscr{H}_0 \,|\, 1s \rangle + \langle 1s \,|\, Fr\cos\theta \,|\, 1s \rangle \\
&= -\frac{1}{2} + \langle 1s \,|\, Fr\cos\theta \,|\, 1s \rangle \\
(\mathbf{H})_{22} &= \langle 2p_z \,|\, \mathscr{H} \,|\, 2p_z \rangle = \langle 2p_z \,|\, \mathscr{H}_0 \,|\, 2p_z \rangle + \langle 2p_z \,|\, Fr\cos\theta \,|\, 2p_z \rangle \\
&= -\frac{1}{8} + \langle 2p_z \,|\, Fr\cos\theta \,|\, 2p_z \rangle \\
(\mathbf{H})_{12} &= \langle 1s \,|\, \mathscr{H} \,|\, 2p_z \rangle = \langle 1s \,|\, \mathscr{H}_0 \,|\, 2p_z \rangle + \langle 1s \,|\, Fr\cos\theta \,|\, 2p_z \rangle \\
&= \langle 1s \,|\, Fr\cos\theta \,|\, 2p_z \rangle \\
(\mathbf{H})_{21} &= \langle 2p_z \,|\, \mathscr{H} \,|\, 1s \rangle = \langle 2p_z \,|\, \mathscr{H}_0 \,|\, 1s \rangle + \langle 2p_z \,|\, Fr\cos\theta \,|\, 1s \rangle \\
&= \langle 2p_z \,|\, Fr\cos\theta \,|\, 1s \rangle
\end{aligned}$$

($2p_z$ is centrosymmetric, so $\langle 1s \,|\, \mathscr{H} \,|\, 2p_z \rangle = 0$.)

$$\begin{aligned}
\langle 1s \,|\, Fr\cos\theta \,|\, 1s \rangle &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \pi^{-1/2}\mathrm{e}^{-r} \cdot Fr\cos\theta \cdot \pi^{-1/2}\mathrm{e}^{-r} \cdot r^2 \sin\theta \,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{F}{r}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \sin\theta\cos\theta \cdot r^3\mathrm{e}^{-2r}\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{3F}{8r}\int_0^{2\pi}\int_0^{\pi} \sin\theta\cos\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\langle 2p_z \,|\, Fr\cos\theta \,|\, 2p_z \rangle &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} (32\pi)^{-1/2} r\mathrm{e}^{-r/2}\cos\theta \cdot Fr\cos\theta \cdot (32\pi)^{-1/2} r\mathrm{e}^{-r/2}\cos\theta \cdot r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{F}{32\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \cos^3\theta\sin\theta\,\mathrm{d}\theta \cdot r^5\mathrm{e}^{-r}\,\mathrm{d}r\,\mathrm{d}\phi = 0 \\
\langle 1s \,|\, Fr\cos\theta \,|\, 2p_z \rangle &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \pi^{-1/2}\mathrm{e}^{-r} \cdot Fr\cos\theta \cdot (32\pi)^{-1/2} r\mathrm{e}^{-r/2}\cos\theta \cdot r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{F}{\sqrt{32}\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \cos^2\theta\sin\theta\,\mathrm{d}\theta \cdot r^4\mathrm{e}^{-3/2r}\,\mathrm{d}r\,\mathrm{d}\phi \\
&= \frac{F}{\sqrt{32}\pi}\int_0^{2\pi}\int_0^{\infty} \frac{2}{3} r^4\mathrm{e}^{-3/2r}\,\mathrm{d}r\,\mathrm{d}\phi \\
&= \frac{256F}{243\sqrt{2}}
\end{aligned}$$

Then we can solve the eigenvalue equation:

$$\mathbf{Hc} = E\mathbf{c}$$

We have the determinant to be 0:

$$\begin{vmatrix} -\frac{1}{2} - E & \frac{256F}{243\sqrt{2}} \\ \frac{256F}{243\sqrt{2}} & -\frac{1}{8} - E \end{vmatrix} = 0$$

$$E^2 + \frac{5}{8}E + \frac{1}{6} - \frac{256^2F^2}{2\cdot 243^2} = 0$$

We solve the characteristic polynomial and the result is:

$$\begin{aligned} E &= \frac{1}{2}\left(-\frac{5}{8} \pm \sqrt{\frac{25}{64} - 4\left(\frac{1}{16} - \frac{256^2F^2}{2\cdot 243^2}\right)}\right) \\ &= -\frac{5}{16} \pm \frac{1}{2}\sqrt{\frac{9}{64} + \frac{256^2F^2}{2\cdot 243^2}} \\ &= -\frac{5}{16} \pm \frac{3}{16}\sqrt{1 + \frac{128\cdot 256^2F^2}{9\cdot 243^2}} \end{aligned}$$

We should talk about which sign be taken, but I'll skip it and just show the result:

$$E = -\frac{5}{16} - \frac{3}{16}\sqrt{1 + \frac{128\cdot 256^2F^2}{9\cdot 243^2}}$$

Using Taylor series expansion:

$$\begin{aligned} E &\approx -\frac{5}{16} - \frac{3}{16}\left(1 + \frac{1}{2}\frac{128\cdot 256^2F^2}{9\cdot 243^2}\right) \\ &= -\frac{1}{2} - \frac{1}{2}\cdot\frac{3}{16}\frac{128\cdot 256^2}{9\cdot 243^2}F^2 \end{aligned}$$

So $\alpha = 2.96$.

2 Chapter 2

Exercise 2.1

Solution:
Case 1. $m = 2i-1, n = 2j-1$

$$\begin{aligned} \langle \chi_m \,|\, \chi_n \rangle &= \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha*}(\mathbf{r})\psi_n^{\alpha}(\mathbf{r})\,\mathrm{d}\omega\ \alpha^*(\omega)\alpha(\omega) = \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha*}(\mathbf{r})\psi_n^{\alpha}(\mathbf{r})\cdot 1 \\ &= \delta_{mn} = 0 \end{aligned}$$

Case 2. $m = 2i, n = 2j$

$$\begin{aligned} \langle \chi_m \,|\, \chi_n \rangle &= \int \mathrm{d}\mathbf{r}\ \psi_m^{\beta*}(\mathbf{r})\psi_n^{\beta}(\mathbf{r})\,\mathrm{d}\omega\ \beta^*(\omega)\beta(\omega) = \int \mathrm{d}\mathbf{r}\ \psi_m^{\beta*}(\mathbf{r})\psi_n^{\beta}(\mathbf{r})\cdot 1 \\ &= \delta_{mn} = 0 \end{aligned}$$

Case 3. $m = n = 2i-1$

$$\begin{aligned} \langle \chi_m \,|\, \chi_n \rangle &= \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha*}(\mathbf{r})\psi_n^{\alpha}(\mathbf{r})\,\mathrm{d}\omega\ \alpha^*(\omega)\alpha(\omega) = \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha*}(\mathbf{r})\psi_n^{\alpha}(\mathbf{r})\cdot 1 \\ &= \delta_{mn} = 1 \end{aligned}$$

Case 4. $m = n = 2i$

$$\begin{aligned}\langle \chi_m \,|\, \chi_n \rangle &= \int \mathrm{d}\mathbf{r}\ \psi_m^{\beta *}(\mathbf{r})\psi_n^{\beta}(\mathbf{r})\,\mathrm{d}\omega\ \beta^*(\omega)\beta(\omega) = \int \mathrm{d}\mathbf{r}\ \psi_m^{\beta *}(\mathbf{r})\psi_n^{\beta}(\mathbf{r}) \cdot 1 \\ &= \delta_{mn} = 1\end{aligned}$$

Case 5. $m = 2i-1, n = 2j$

$$\begin{aligned}\langle \chi_m \,|\, \chi_n \rangle &= \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha *}(\mathbf{r})\psi_n^{\beta}(\mathbf{r})\,\mathrm{d}\omega\ \alpha^*(\omega)\beta(\omega) = \int \mathrm{d}\mathbf{r}\ \psi_m^{\alpha *}(\mathbf{r})\psi_n^{\beta}(\mathbf{r}) \cdot 0 \\ &= 0\end{aligned}$$

So we conclude that

$$\langle \chi_m \,|\, \chi_n \rangle = \delta_{mn}$$

Exercise 2.2

Solution:

$$\begin{aligned}\sum_{i=1}^{N} h(i)\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) &= h(1)\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) + h(2)\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) + \ldots \\ &\quad + h(N)\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) \\ &= \varepsilon_1\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) + \varepsilon_2\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) + \ldots \\ &\quad + \varepsilon_N\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) \\ &= \left(\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N\right)\left(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\ldots\chi_k(\mathbf{x}_N)\right) \\ &= E\Psi^{\mathrm{HP}}\end{aligned}$$

Where $E = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N$.

Exercise 2.3

Solution:

$$\begin{aligned}\langle \Psi \,|\, \Psi \rangle &= \int \frac{1}{\sqrt{2}}\big(\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) - \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\big)\frac{1}{\sqrt{2}}\big(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\big)\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \\ &= \frac{1}{2}\int \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \\ &\qquad - \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \\ &= \frac{1}{2}(1 - 0 - 0 + 1) \\ &= 1\end{aligned}$$

Exercise 2.4

Solution:

$$\begin{aligned}\mathscr{H}\Psi_{12}^{\mathrm{HP}} &= (h(1) + h(2))\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \\ &= \varepsilon_i\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + \varepsilon_j\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \\ &= (\varepsilon_i + \varepsilon_j)\Psi_{12}^{\mathrm{HP}} \\ \mathscr{H}\Psi_{21}^{\mathrm{HP}} &= (h(1) + h(2))\chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1) \\ &= \varepsilon_j\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + \varepsilon_i\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \\ &= (\varepsilon_i + \varepsilon_j)\Psi_{21}^{\mathrm{HP}}\end{aligned}$$

$$
\begin{aligned}
\mathscr{H}\Psi(\mathbf{x}_1,\mathbf{x}_2) &= (h(1)+h(2))\left[2^{-1/2}\big(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\big)\right] \\
&= 2^{-1/2}\big(h(1)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-h(1)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)+h(2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-h(2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\big) \\
&= 2^{-1/2}\big(\varepsilon_i\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-\varepsilon_j\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)+\varepsilon_j\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-\varepsilon_i\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\big) \\
&= (\varepsilon_i+\varepsilon_j)\left[2^{-1/2}\big(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)-\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\big)\right] \\
&= (\varepsilon_i+\varepsilon_j)\Psi(\mathbf{x}_1,\mathbf{x}_2)
\end{aligned}
$$

Exercise 2.5

Solution:

$$
\begin{aligned}
\langle K\,|\,L\rangle &= \int \frac{1}{\sqrt{2}}\big(\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)-\chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\big)\frac{1}{\sqrt{2}}\big(\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)-\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\big)\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \\
&= \frac{1}{2}\int \big(\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)-\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2) \\
&\qquad -\chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)+\chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\big)\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \\
&= \frac{1}{2}(\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}-\delta_{jk}\delta_{il}+\delta_{jl}\delta_{ik}) \\
&= \delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}
\end{aligned}
$$

Exercise 2.6

Solution:

$$
\begin{aligned}
\langle\psi_1\,|\,\psi_1\rangle &= \int \frac{1}{2\,(1+S_{12})}(\phi_1^*+\phi_2^*)(\phi_1+\phi_2)\,\mathrm{d}\tau \\
&= \int \frac{1}{2\,(1+S_{12})}(\phi_1^*\phi_1+\phi_2^*\phi_2+\phi_1^*\phi_2+\phi_2^*\phi_1)\,\mathrm{d}\tau \\
&= \int \frac{1}{2\,(1+S_{12})}(1+1+S_{12}+S_{12})\,\mathrm{d}\tau \\
&= 1 \\
\langle\psi_2\,|\,\psi_2\rangle &= \int \frac{1}{2\,(1-S_{12})}(\phi_1^*-\phi_2^*)(\phi_1-\phi_2)\,\mathrm{d}\tau \\
&= \int \frac{1}{2\,(1-S_{12})}(\phi_1^*\phi_1+\phi_2^*\phi_2-\phi_1^*\phi_2-\phi_2^*\phi_1)\,\mathrm{d}\tau \\
&= \int \frac{1}{2\,(1-S_{12})}(1+1-S_{12}-S_{12})\,\mathrm{d}\tau \\
&= 1
\end{aligned}
$$

$$
\begin{aligned}
\langle\psi_1\,|\,\psi_2\rangle &= \int [2\,(1+S_{12})]^{-1/2}\,[2\,(1-S_{12})]^{-1/2}\,(\phi_1^*+\phi_2^*)(\phi_1-\phi_2)\,\mathrm{d}\tau \\
&= \int \left[4\,\left(1-S_{12}^2\right)\right]^{-1/2}(\phi_1^*\phi_1-\phi_2^*\phi_2-\phi_1^*\phi_2+\phi_2^*\phi_1)\,\mathrm{d}\tau \\
&= \int \left[4\,\left(1-S_{12}^2\right)\right]^{-1/2}(1-1-S_{12}+S_{12})\,\mathrm{d}\tau \\
&= 0
\end{aligned}
$$

Exercise 2.7

Solution:
The system(Benzene) has 42 electrons. So the number of possible determinants is

$$\binom{72}{42} = \frac{72!}{42!30!} = 1.643 \times 10^{20}$$

The number of singly excited determinants is $42 \times 30 = 1260$. And there are $\binom{42}{2} \times \binom{30}{2} = 374535$ doubly excited determinants.

Exercise 2.8

Solution:

$$\begin{aligned}
\left\langle \Psi_{12}^{34} \,\middle|\, h_1 \,\middle|\, \Psi_{12}^{34} \right\rangle &= \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \left[2^{-1/2}(\chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2))\right]^* \\
&\qquad \times h(\mathbf{r}_1) \left[2^{-1/2}(\chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2))\right] \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \big[\chi_3(\mathbf{x}_1)^* \chi_4(\mathbf{x}_2)^* h(\mathbf{r}_1) \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) + \chi_4(\mathbf{x}_1)^* \chi_3(\mathbf{x}_2)^* h(\mathbf{r}_1) \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2) \\
&\qquad - \chi_4(\mathbf{x}_1)^* \chi_3(\mathbf{x}_2)^* h(\mathbf{r}_1) \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_1)^* \chi_4(\mathbf{x}_2)^* h(\mathbf{r}_1) \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2)\big] \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \big[\chi_3(\mathbf{x}_1)^* h(\mathbf{r}_1) \chi_3(\mathbf{x}_1) + \chi_4(\mathbf{x}_1)^* h(\mathbf{r}_1) \chi_4(\mathbf{x}_1)\big] \\
&= \frac{1}{2} \langle 3 \,|\, h(1) \,|\, 3 \rangle + \frac{1}{2} \langle 4 \,|\, h(1) \,|\, 4 \rangle
\end{aligned}$$

By exactly the same procedure, one finds that $\left\langle \Psi_{12}^{34} \middle| h_1 \middle| \Psi_{12}^{34} \right\rangle = \left\langle \Psi_{12}^{34} \middle| h_2 \middle| \Psi_{12}^{34} \right\rangle$ and thus

$$\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{O}_1 \,\middle|\, \Psi_{12}^{34} \right\rangle = \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle$$

$$\begin{aligned}
\left\langle \Psi_1^2 \,\middle|\, \mathscr{O}_1 \,\middle|\, \Psi_{12}^{34} \right\rangle &= \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \left[2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))\right]^* \\
&\qquad \times \mathscr{O}_1 \left[2^{-1/2}(\chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2))\right] \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \big[\chi_1(\mathbf{x}_1)^* \chi_2(\mathbf{x}_2)^* \mathscr{O}_1 \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) + \chi_2(\mathbf{x}_1)^* \chi_1(\mathbf{x}_2)^* \mathscr{O}_1 \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2) \\
&\qquad - \chi_1(\mathbf{x}_1)^* \chi_2(\mathbf{x}_2)^* \mathscr{O}_1 \chi_4(\mathbf{x}_1)\chi_3(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)^* \chi_1(\mathbf{x}_2)^* \mathscr{O}_1 \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2)\big] \\
&= 0
\end{aligned}$$

$$\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{O}_1 \,\middle|\, \Psi_1^2 \right\rangle = 0$$

Exercise 2.8

Solution:

$$\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_0 \rangle &= \langle \Psi_0 \,|\, \mathscr{O}_1 + \mathscr{O}_2 \,|\, \Psi_0 \rangle \\
&= \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,|\, 12 \rangle - \langle 12 \,|\, 21 \rangle \\
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \left\langle \Psi_0 \,\middle|\, \mathscr{O}_1 + \mathscr{O}_2 \,\middle|\, \Psi_{12}^{34} \right\rangle \\
&= \langle 12 \,|\, 34 \rangle - \langle 12 \,|\, 43 \rangle \\
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle &= \left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{O}_1 + \mathscr{O}_2 \,\middle|\, \Psi_0 \right\rangle \\
&= \langle 34 \,|\, 12 \rangle - \langle 34 \,|\, 21 \rangle \\
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{O}_1 + \mathscr{O}_2 \,\middle|\, \Psi_{12}^{34} \right\rangle \\
&= \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,|\, 34 \rangle - \langle 34 \,|\, 43 \rangle
\end{aligned}$$

Therefore:

$$\mathscr{H}=\begin{pmatrix}\langle 1\,|\,h\,|\,1\rangle+\langle 2\,|\,h\,|\,2\rangle+\langle 12\,|\,12\rangle-\langle 12\,|\,21\rangle & \langle 12\,|\,34\rangle-\langle 12\,|\,43\rangle\\ \langle 34\,|\,12\rangle-\langle 34\,|\,21\rangle & \langle 3\,|\,h\,|\,3\rangle+\langle 4\,|\,h\,|\,4\rangle+\langle 34\,|\,34\rangle-\langle 34\,|\,43\rangle\end{pmatrix}$$

Exercise 2.13

Solution:
Case 1. $a\neq b, r\neq s$:

$$|\Psi_a^r\rangle=|\chi_1\ldots\chi_r\chi_b\ldots\chi_N\rangle$$
$$|\Psi_b^s\rangle=|\chi_1\ldots\chi_a\chi_s\ldots\chi_N\rangle$$

There are no two columns correspondingly to be equal. So

$$\langle\Psi_a^r\,|\,\mathscr{O}_1\,|\,\Psi_b^s\rangle=0$$

Case 2. $a=b, r\neq s$:

$$|\Psi_a^r\rangle=|\chi_1\ldots\chi_r\ldots\chi_N\rangle$$
$$|\Psi_b^s\rangle=|\chi_1\ldots\chi_s\ldots\chi_N\rangle$$
$$\langle\Psi_a^r\,|\,\mathscr{O}_1\,|\,\Psi_b^s\rangle=\langle r\,|\,h\,|\,s\rangle$$

Case 3. $a\neq b, r=s$:

$$|\Psi_a^r\rangle=|\chi_1\ldots\chi_r\chi_b\ldots\chi_N\rangle$$
$$|\Psi_b^s\rangle=|\chi_1\ldots\chi_a\chi_r\ldots\chi_N\rangle=-\,|\chi_1\ldots\chi_r\chi_a\ldots\chi_N\rangle$$
$$\langle\Psi_a^r\,|\,\mathscr{O}_1\,|\,\Psi_b^s\rangle=-\,\langle b\,|\,h\,|\,a\rangle$$

Case 4. $a=b, r=s$:

$$|\Psi_a^r\rangle=|\chi_1\ldots\chi_r\chi_b\ldots\chi_N\rangle$$
$$|\Psi_b^s\rangle=|\chi_1\ldots\chi_r\chi_b\ldots\chi_N\rangle$$
$$\langle\Psi_a^r\,|\,\mathscr{O}_1\,|\,\Psi_b^s\rangle=\sum_c^N\langle c\,|\,h\,|\,c\rangle-\langle a\,|\,h\,|\,a\rangle+\langle r\,|\,h\,|\,r\rangle$$

Exercise 2.14

Solution:

$$|{}^N\Psi_0\rangle=|\chi_1\ldots\chi_a\chi_b\ldots\chi_N\rangle$$
$$|{}^{N-1}\Psi_a\rangle=|\chi_1\ldots\chi_{a-1}\chi_{a+1}\ldots\chi_N\rangle$$

So we have:

$$\begin{aligned}{}^NE_0&=\left\langle{}^N\Psi_0\,\middle|\,\mathscr{H}\,\middle|\,{}^N\Psi_0\right\rangle=\left\langle{}^N\Psi_0\,\middle|\,\mathscr{O}_1+\mathscr{O}_2\,\middle|\,{}^N\Psi_0\right\rangle\\&=\sum_m^N\langle\chi_m\,|\,h\,|\,\chi_m\rangle+\sum_m^N\sum_{n>m}^N\langle\chi_m\chi_n\,\|\,\chi_m\chi_n\rangle\end{aligned}$$

$$\begin{aligned}{}^{N-1}E_a&=\left\langle{}^{N-1}\Psi_a\,\middle|\,\mathscr{H}\,\middle|\,{}^{N-1}\Psi_a\right\rangle=\left\langle{}^{N-1}\Psi_a\,\middle|\,\mathscr{O}_1+\mathscr{O}_2\,\middle|\,{}^{N-1}\Psi_a\right\rangle\\&=\sum_{x(x\neq a)}^N\langle\chi_x\,|\,h\,|\,\chi_x\rangle+\sum_{x(x\neq a)}^N\sum_{y>x(y\neq a)}^N\langle\chi_x\chi_y\,\|\,\chi_x\chi_y\rangle\end{aligned}$$

Therefore

$${}^NE_0-{}^{N-1}E_a=\langle\chi_a\,|\,h\,|\,\chi_a\rangle+\sum_{m=1}^{a-1}\langle\chi_m\chi_a\,\|\,\chi_m\chi_a\rangle+\sum_{n=a+1}^N\langle\chi_a\chi_n\,\|\,\chi_a\chi_n\rangle$$

Because $\langle \chi_a \chi_n \| \chi_a \chi_n \rangle = \langle \chi_n \chi_a \| \chi_n \chi_a \rangle$ and $\langle \chi_a \chi_a \| \chi_a \chi_a \rangle = 0$.

$$ {}^{N}E_0 - {}^{N-1}E_a = \langle \chi_a \,|\, h \,|\, \chi_a \rangle + \sum_{m=1}^{N} \langle \chi_m \chi_a \| \chi_m \chi_a \rangle $$

Exercise 2.15

Solution:

$$ \mathscr{H} |\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} \mathscr{H} \mathscr{P}_i \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} $$

Because $\mathscr{H}$ and $\mathscr{P}$ commute with each other.

$$ \mathscr{H} |\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} \mathscr{P}_i \mathscr{H} \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} $$

Since

$$ \begin{aligned} \mathscr{H} \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} &= \sum_{i}^{N} h(i) \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \\ &= \sum_{i}^{N} \{\chi_i(1)\chi_j(2) \ldots h(i)\chi_s(i) \ldots \chi_k(N)\} \\ &= \sum_{i}^{N} \varepsilon_s(i) \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \\ &= (\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N) \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \end{aligned} $$

$$ \begin{aligned} \mathscr{H} |\Psi\rangle &= \frac{1}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} \mathscr{P}_i \mathscr{H} \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \\ &= \frac{1}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} \mathscr{P}_i (\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N) \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \\ &= \frac{\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N}{\sqrt{N!}} \sum_{i}^{N!} (-1)^{p_i} \mathscr{P}_i \{\chi_i(1)\chi_j(2) \ldots \chi_k(N)\} \\ &= (\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N) |\Psi\rangle \end{aligned} $$

Exercise 2.17

Solution:

$$ \left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle = \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,|\, 34 \rangle - \langle 34 \,|\, 43 \rangle $$

$$ \begin{aligned} \langle 3 \,|\, h \,|\, 3 \rangle &= \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\omega_1 \;\; \psi_2^*(\mathbf{r}_1)\alpha^*(\omega_1) h \psi_2(\mathbf{r}_1)\alpha(\omega_1) \\ &= \int \mathrm{d}\mathbf{r}_1 \;\; \psi_2^*(\mathbf{r}_1) h \psi_2(\mathbf{r}_1) \\ &= (2|h|2) \end{aligned} $$

$$ \begin{aligned} \langle 4 \,|\, h \,|\, 4 \rangle &= \int \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\omega_2 \;\; \psi_2^*(\mathbf{r}_2)\beta^*(\omega_2) h \psi_2(\mathbf{r}_2)\beta(\omega_2) \\ &= \int \mathrm{d}\mathbf{r}_2 \;\; \psi_2^*(\mathbf{r}_2) h \psi_2(\mathbf{r}_2) \\ &= (2|h|2) \end{aligned} $$

$$
\begin{aligned}
\langle 34 \,|\, 34 \rangle &= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\omega_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\omega_2 \;\psi_2^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_2^*(\mathbf{r}_2)\beta^*(\omega_2) \\
&\qquad\qquad\qquad\qquad \times r_{12}^{-1}\psi_2(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2) \\
&= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \;\psi_2^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2) r_{12}^{-1}\psi_2(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\
&= (22|22) \\
\langle 34 \,|\, 43 \rangle &= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\omega_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\omega_2 \;\psi_2^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_2^*(\mathbf{r}_2)\beta^*(\omega_2) \\
&\qquad\qquad\qquad\qquad \times r_{12}^{-1}\psi_2(\mathbf{r}_1)\beta(\omega_1)\psi_2(\mathbf{r}_2)\alpha(\omega_2) \\
&= 0
\end{aligned}
$$

Therefore

$$
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle = 2(2|h|2) + (22|22)
$$

$$
\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \langle 12 \,|\, 34 \rangle \\
&= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\omega_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\omega_2 \;\psi_1^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_1^*(\mathbf{r}_2)\beta^*(\omega_2) \\
&\qquad\qquad\qquad\qquad \times r_{12}^{-1}\psi_2(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2) \\
&= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \;\psi_1^*(\mathbf{r}_1)\psi_1^*(\mathbf{r}_2) r_{12}^{-1}\psi_2(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\
&= (12|12)
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \Psi_0 \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle &= \langle 34 \,|\, 12 \rangle \\
&= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\omega_1 \,\mathrm{d}\mathbf{r}_2 \,\mathrm{d}\omega_2 \;\psi_2^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_2^*(\mathbf{r}_2)\beta^*(\omega_2) \\
&\qquad\qquad\qquad\qquad \times r_{12}^{-1}\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2) \\
&= \int \mathrm{d}\mathbf{r}_1 \,\mathrm{d}\mathbf{r}_2 \;\psi_2^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2) r_{12}^{-1}\psi_1(\mathbf{r}_1)\psi_1(\mathbf{r}_2) \\
&= (21|21)
\end{aligned}
$$

Exercise 2.18

Solution:

$$
\begin{aligned}
\sum_{abrs} \big| \langle ab \,\|\, rs \rangle \big|^2 &= \sum_{abrs} \big| \langle ab \,|\, rs \rangle - \langle ab \,|\, sr \rangle \big|^2 \\
&= \sum_{abrs} \big(\langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle + \langle ab \,|\, sr \rangle \langle sr \,|\, ab \rangle - \langle ab \,|\, rs \rangle \langle sr \,|\, ab \rangle - \langle ab \,|\, sr \rangle \langle rs \,|\, ab \rangle \big)
\end{aligned}
$$

We let I_1, I_2, I_3, I_4 be equal to each part.

$$
\begin{aligned}
I_1 &= \sum_{abrs} \langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle \\
&= \sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{2K}\sum_{s=N+1}^{2K} \big(\langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle + \langle \bar{a}b \,|\, rs \rangle \langle rs \,|\, \bar{a}b \rangle + \langle a\bar{b} \,|\, rs \rangle \langle rs \,|\, a\bar{b} \rangle \\
&\qquad + \langle ab \,|\, \bar{r}s \rangle \langle \bar{r}s \,|\, ab \rangle + \langle ab \,|\, r\bar{s} \rangle \langle r\bar{s} \,|\, ab \rangle + \langle \bar{a}\bar{b} \,|\, rs \rangle \langle rs \,|\, \bar{a}\bar{b} \rangle \\
&\qquad + \langle \bar{a}b \,|\, \bar{r}s \rangle \langle \bar{r}s \,|\, \bar{a}b \rangle + \langle \bar{a}b \,|\, r\bar{s} \rangle \langle r\bar{s} \,|\, \bar{a}b \rangle + \langle a\bar{b} \,|\, \bar{r}s \rangle \langle \bar{r}s \,|\, a\bar{b} \rangle \\
&\qquad + \langle a\bar{b} \,|\, r\bar{s} \rangle \langle r\bar{s} \,|\, a\bar{b} \rangle + \langle ab \,|\, \bar{r}\bar{s} \rangle \langle \bar{r}\bar{s} \,|\, ab \rangle + \langle \bar{a}\bar{b} \,|\, \bar{r}s \rangle \langle \bar{r}s \,|\, \bar{a}\bar{b} \rangle \\
&\qquad + \langle \bar{a}\bar{b} \,|\, r\bar{s} \rangle \langle r\bar{s} \,|\, \bar{a}\bar{b} \rangle + \langle \bar{a}b \,|\, \bar{r}\bar{s} \rangle \langle \bar{r}\bar{s} \,|\, \bar{a}b \rangle + \langle a\bar{b} \,|\, \bar{r}\bar{s} \rangle \langle \bar{r}\bar{s} \,|\, a\bar{b} \rangle \\
&\qquad + \langle \bar{a}\bar{b} \,|\, \bar{r}\bar{s} \rangle \langle \bar{r}\bar{s} \,|\, \bar{a}\bar{b} \rangle \big) \\
&= \sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{2K}\sum_{s=N+1}^{2K} \big(\langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle + \langle \bar{a}b \,|\, \bar{r}s \rangle \langle \bar{r}s \,|\, \bar{a}b \rangle + \langle a\bar{b} \,|\, r\bar{s} \rangle \langle r\bar{s} \,|\, a\bar{b} \rangle + \langle \bar{a}\bar{b} \,|\, \bar{r}\bar{s} \rangle \langle \bar{r}\bar{s} \,|\, \bar{a}\bar{b} \rangle \big) \\
&= 4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle
\end{aligned}
$$

Similarly, we can get the second term after cancelling the 0 term from the summation:

$$
I_2 = 4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \langle ab \,|\, sr \rangle \langle sr \,|\, ab \rangle
$$

By interchange the spartial orbitals s, r, I_1 and I_2 are found to be equal.

$$
I_1 = I_2
$$

The I_3 part has some differences with either I_1 or I_2:

$$
\begin{aligned}
I_3 &= \sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{2K}\sum_{s=N+1}^{2K} \big(\langle ab \,|\, rs \rangle \langle sr \,|\, ab \rangle + \langle \bar{a}\bar{b} \,|\, \bar{r}\bar{s} \rangle \langle \bar{s}\bar{r} \,|\, \bar{a}\bar{b} \rangle \big) \\
&= 2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \langle ab \,|\, rs \rangle \langle sr \,|\, ab \rangle
\end{aligned}
$$

And I_4 is the same:

$$
\begin{aligned}
I_4 &= \sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{2K}\sum_{s=N+1}^{2K} \big(\langle ab \,|\, sr \rangle \langle rs \,|\, ab \rangle + \langle \bar{a}\bar{b} \,|\, \bar{s}\bar{r} \rangle \langle \bar{r}\bar{s} \,|\, \bar{a}\bar{b} \rangle \big) \\
&= 2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \langle ab \,|\, sr \rangle \langle rs \,|\, ab \rangle
\end{aligned}
$$

$$
I_3 = I_4
$$

Because $\varepsilon_i = \varepsilon_{\bar{i}}$, the denominators in each term are all equal to $\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s$. Thus

$$
\begin{aligned}
E_0^{(2)} &= \frac{1}{4}\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \frac{8\langle ab \,|\, rs \rangle \langle rs \,|\, ab \rangle + 4\langle ab \,|\, rs \rangle \langle sr \,|\, ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=N/2+1}^{K}\sum_{s=N/2+1}^{K} \frac{\langle ab \,|\, rs \rangle \big(2\langle rs \,|\, ab \rangle + \langle sr \,|\, ab \rangle\big)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned}
$$

Exercise 2.19

Solution:

$$J_{ii} = (ii|ii) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) r_{12}^{-1} \psi_i^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)$$

$$K_{ii} = (ii|ii) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) r_{12}^{-1} \psi_i^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)$$

It is obviously that

$$J_{ii} = K_{ii}$$

$$J_{ij} = (ii|jj) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) r_{12}^{-1} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)$$

$$J_{ij}^* = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i(\mathbf{r}_1)\psi_i^*(\mathbf{r}_1) r_{12}^{-1} \psi_j(\mathbf{r}_2)\psi_j^*(\mathbf{r}_2)$$

$$J_{ij} = J_{ij}^*$$

$$K_{ij} = (ij|ji) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)$$

$$K_{ij}^* = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_i(\mathbf{r}_1)\psi_j^*(\mathbf{r}_1) r_{12}^{-1} \psi_j(\mathbf{r}_2)\psi_i^*(\mathbf{r}_2)$$

If we exchange the label of electron 1 and electron 2, we find that

$$K_{ij} = K_{ij}^*$$

$$J_{ji} = (jj|ii) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_j^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_i^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)$$

$$K_{ji} = (ji|ij) = \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \; \psi_j^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) r_{12}^{-1} \psi_i^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)$$

Thus

$$J_{ij} = J_{ji}$$
$$K_{ij} = K_{ji}$$

Exercise 2.19

Solution:

Exercise 2.21

Solution:

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}$$

Because the spatial molecular orbitals are real, thus

$$(21|21) = (12|12) = K_{12}$$

Therefore

$$\mathbf{H} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix}$$

Exercise 2.22

Solution:

$$\begin{aligned}\left\langle \Psi^{\mathrm{HP}}_{\uparrow\downarrow} \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{\mathrm{HP}}_{\uparrow\downarrow} \right\rangle &= \int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\;\; \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)(h_1 + h_2 + r_{12}^{-1})\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\ &\qquad\qquad \times \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\;\; \alpha^*(\omega_1)\beta^*(\omega_2)\alpha(\omega_1)\beta(\omega_2) \\ &= h_{11} + h_{22} + J_{12}\end{aligned}$$

With exactly the same procedure, the result of parallel spin is

$$\begin{aligned}\left\langle \Psi^{\mathrm{HP}}_{\downarrow\downarrow} \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{\mathrm{HP}}_{\uparrow\downarrow} \right\rangle &= \int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\;\; \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)(h_1 + h_2 + r_{12}^{-1})\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\ &\qquad\qquad \times \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\;\; \beta^*(\omega_1)\beta^*(\omega_2)\beta(\omega_1)\beta(\omega_2) \\ &= h_{11} + h_{22} + J_{12}\end{aligned}$$

Exercise 2.24

Solution:

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_1\chi_2\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_1\chi_2\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_1\chi_2\right\rangle \\ &= 0 + 0 = 0\end{aligned}$$

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_1\chi_3\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_1\chi_3\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_1\chi_3\right\rangle \\ &= 0 + 0 = 0\end{aligned}$$

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_1\chi_4\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_1\chi_4\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_1\chi_4\right\rangle \\ &= 0 + 0 = 0\end{aligned}$$

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_2\chi_3\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_2\chi_3\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_2\chi_3\right\rangle \\ &= 0 + 0 = 0\end{aligned}$$

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_1\chi_2\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_2\chi_4\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_2\chi_4\right\rangle \\ &= 0 + 0 = 0\end{aligned}$$

$$\begin{aligned}(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\left|\chi_1\chi_2\right\rangle &= a_1^\dagger a_2^\dagger \left|\chi_3\chi_4\right\rangle + a_2^\dagger a_1^\dagger \left|\chi_3\chi_4\right\rangle \\ &= \left|\chi_1\chi_2\chi_3\chi_4\right\rangle + \left|\chi_2\chi_1\chi_3\chi_4\right\rangle \\ &= \left|\chi_1\chi_2\chi_3\chi_4\right\rangle - \left|\chi_1\chi_2\chi_3\chi_4\right\rangle = 0\end{aligned}$$

Exercise 2.25

Solution:

$$\begin{aligned}(a_1 a_2^\dagger + a_2^\dagger a_1)\left|\chi_1\chi_2\right\rangle &= a_1 a_2^\dagger \left|\chi_1\chi_2\right\rangle + a_2^\dagger a_1 \left|\chi_1\chi_2\right\rangle \\ &= a_2^\dagger \left|\chi_2\right\rangle \\ &= 0\end{aligned}$$

$$\begin{aligned}(a_1 a_1^\dagger + a_1^\dagger a_1)\left|\chi_1\chi_2\right\rangle &= a_1 a_1^\dagger \left|\chi_1\chi_2\right\rangle + a_1^\dagger a_1 \left|\chi_1\chi_2\right\rangle \\ &= a_1^\dagger \left|\chi_2\right\rangle \\ &= \left|\chi_1\chi_2\right\rangle\end{aligned}$$

Exercise 2.26

Solution:

$$\begin{aligned}\left\langle \middle| a_i a_j^\dagger \middle| \right\rangle &= \left\langle \middle| \delta_{ij} - a_j^\dagger a_i \middle| \right\rangle \\ &= \delta_{ij} \left\langle \middle| \right\rangle \\ &= \delta_{ij}\end{aligned}$$

Exercise 2.27

Solution:

$$\left\langle \chi_1\chi_2\dots\chi_N \middle| a_i^\dagger a_j \middle| \chi_1\chi_2\dots\chi_N \right\rangle$$

i and j must be in $\{1, 2, \dots, N\}$, otherwise the integral is zero.

$$\begin{aligned}\left\langle \chi_1\chi_2\dots\chi_N \middle| a_i^\dagger a_j \middle| \chi_1\chi_2\dots\chi_N \right\rangle &= \left\langle \chi_1\chi_2\dots\chi_N \middle| \delta_{ij} - a_j a_i^\dagger \middle| \chi_1\chi_2\dots\chi_N \right\rangle \\ &= \delta_{ij} \left\langle \chi_1\chi_2\dots\chi_N \middle| \chi_1\chi_2\dots\chi_N \right\rangle - \left\langle \chi_1\chi_2\dots\chi_N \middle| a_j a_i^\dagger \middle| \chi_1\chi_2\dots\chi_N \right\rangle \\ &= \delta_{ij}\end{aligned}$$

Exercise 2.28

Solution:

(a)

χ_r is a virtual orbital, which is not involved in HF wave function.

$$a_r \left|\Psi_0\right\rangle = 0 = \left\langle\Psi_0\right| a_r^\dagger$$

(b)

χ_a is already in HF wave function.

$$a_a^\dagger \left|\Psi_0\right\rangle = 0 = \left\langle\Psi_0\right| a_a$$

(c)

$$\begin{aligned}a_r^\dagger a_a \left|\chi_1 \dots \chi_a \dots \chi_N\right\rangle &= -a_r^\dagger a_a \left|\chi_a \dots \chi_1 \dots \chi_N\right\rangle \\ &= -a_r^\dagger \left|\dots \chi_1 \dots \chi_N\right\rangle \\ &= -\left|\chi_r \dots \chi_1 \dots \chi_N\right\rangle \\ &= \left|\chi_1 \dots \chi_r \dots \chi_N\right\rangle\end{aligned}$$

(d)

$$\left(\left|\Psi_0\right\rangle\right)^\dagger = \left(a_r^\dagger a_a \left|\Psi_0\right\rangle\right)^\dagger$$

$$\left\langle\Psi_0\right| = \left\langle\Psi_0\right| a_a^\dagger a_r$$

Exercise 2.29

Solution:

$$\begin{aligned}\langle \Psi_0 \,|\, \mathscr{O}_1 \,|\, \Psi_0 \rangle &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \,\middle|\, a_2 a_1 a_i^\dagger a_j a_1^\dagger a_2^\dagger \,\middle|\, \right\rangle \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \,\middle|\, a_2 a_1 (\delta_{ij} - a_j a_i^\dagger) a_1^\dagger a_2^\dagger \,\middle|\, \right\rangle \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ij} \left\langle \,\middle|\, a_2 a_1 a_1^\dagger a_2^\dagger \,\middle|\, \right\rangle - \left\langle \,\middle|\, a_2 a_1 a_j a_i^\dagger a_1^\dagger a_2^\dagger \,\middle|\, \right\rangle \right) \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ij} \langle \Psi_0 \,|\, \Psi_0 \rangle - \left\langle \Psi_0 \,\middle|\, a_j a_i^\dagger \,\middle|\, \Psi_0 \right\rangle \right)\end{aligned}$$

Because i and j fall within 1 and 2. The second term has creation operators acting on the existing spin orbitals and is zero as a result.

$$\langle \Psi_0 \,|\, \mathscr{O}_1 \,|\, \Psi_0 \rangle = \sum_{ij} \langle i \,|\, h \,|\, j \rangle \, \delta_{ij} = \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle$$

Exercise 2.30

Solution:

$$\begin{aligned}\langle \Psi_a^r \,|\, \mathscr{O}_1 \,|\, \Psi_0 \rangle &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_r a_i^\dagger a_j \,\middle|\, \Psi_0 \right\rangle \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ir} \langle \Psi_0 \,|\, a_a^\dagger a_j \,|\, \Psi_0 \rangle - \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j \,\middle|\, \Psi_0 \right\rangle \right) \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ir} \langle \Psi_0 \,|\, \delta_{aj} - a_j a_a^\dagger \,|\, \Psi_0 \rangle - \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j \,\middle|\, \Psi_0 \right\rangle \right)\end{aligned}$$

χ_r is not in $|\Psi_0\rangle$. Creation operator $a_r^\dagger$ acting on it makes a result of zero.

$$\begin{aligned}\langle \Psi_a^r \,|\, \mathscr{O}_1 \,|\, \Psi_0 \rangle &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ir} \langle \Psi_0 \,|\, \delta_{aj} - a_j a_a^\dagger \,|\, \Psi_0 \rangle \right) \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left(\delta_{ir} \delta_{aj} \langle \Psi_0 \,|\, \Psi_0 \rangle - \delta_{ir} \langle \Psi_0 \,|\, a_j a_a^\dagger \,|\, \Psi_0 \rangle \right) \\ &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \, \delta_{ir} \delta_{aj} \\ &= \langle r \,|\, h \,|\, a \rangle\end{aligned}$$

Exercise 2.31

Solution:

$$\begin{aligned}\langle \Psi_a^r \,|\, \mathscr{O}_2 \,|\, \Psi_0 \rangle &= \frac{1}{2} \sum_{ijkl} \langle ij \,|\, kl \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \\ &= \frac{1}{2} \sum_{ijkl} \langle ij \,|\, kl \rangle \left(\delta_{ir} \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle - \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \right)\end{aligned}$$

$$\begin{aligned}\delta_{ir} \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle &= -\delta_{ir} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_a^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \\ &= -\delta_{ir} \delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle + \delta_{ir} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l a_a^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \\ &= -\delta_{ir} \delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle + \delta_{ir} \delta_{ak} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle - \delta_{ir} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l a_k a_a^\dagger \,\middle|\, \Psi_0 \right\rangle \\ &= -\delta_{ir} \delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle + \delta_{ir} \delta_{ak} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle\end{aligned}$$

$$
\begin{aligned}
-\left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle &= -\delta_{rj} \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle + \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_j^\dagger a_r a_l a_k \,\middle|\, \Psi_0 \right\rangle \\
&= \delta_{rj} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_a^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \\
&= \delta_{rj}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle - \delta_{rj} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l a_a^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \\
&= \delta_{rj}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle - \delta_{rj}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l \,\middle|\, \Psi_0 \right\rangle + \delta_{rj} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l a_k a_a^\dagger \,\middle|\, \Psi_0 \right\rangle \\
&= \delta_{rj}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle - \delta_{rj}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l \,\middle|\, \Psi_0 \right\rangle
\end{aligned}
$$

$$
\begin{aligned}
\langle \Psi_a^r \,|\, \mathscr{O}_2 \,|\, \Psi_0 \rangle = \frac{1}{2} \sum_{ijkl} \langle ij \,|\, kl \rangle \Big(&\delta_{rj}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle - \delta_{rj}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l \,\middle|\, \Psi_0 \right\rangle \\
&- \delta_{ir}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle + \delta_{ir}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle \Big) \\
&= \frac{1}{2} \Bigg(\sum_i \langle ir \,|\, ia \rangle - \sum_i \langle ir \,|\, ai \rangle - \sum_j \langle rj \,|\, ja \rangle + \sum_j \langle rj \,|\, aj \rangle \Bigg) \\
&= \frac{1}{2} \Bigg(\sum_i \langle ri \,|\, ai \rangle - \sum_i \langle ri \,|\, ia \rangle - \sum_i \langle ri \,|\, ia \rangle + \sum_i \langle ri \,|\, ai \rangle \Bigg) \\
&= \sum_b \big(\langle rb \,|\, ab \rangle - \langle rb \,|\, ba \rangle \big) \\
&= \sum_b \langle rb \,\|\, ab \rangle
\end{aligned}
$$

Exercise 2.32

Solution:
a)

$$
\begin{aligned}
s_+ \left|\alpha\right\rangle &= (s_x + i s_y) \left|\alpha\right\rangle \\
&= \frac{1}{2} \left|\beta\right\rangle + i \cdot \frac{i}{2} \left|\beta\right\rangle \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
s_+ \left|\beta\right\rangle &= (s_x + i s_y) \left|\beta\right\rangle \\
&= \frac{1}{2} \left|\alpha\right\rangle + i \cdot -\frac{i}{2} \left|\alpha\right\rangle \\
&= \left|\alpha\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
s_- \left|\alpha\right\rangle &= (s_x - i s_y) \left|\alpha\right\rangle \\
&= \frac{1}{2} \left|\beta\right\rangle - i \cdot \frac{i}{2} \left|\beta\right\rangle \\
&= \left|\beta\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
s_- \left|\beta\right\rangle &= (s_x - i s_y) \left|\beta\right\rangle \\
&= \frac{1}{2} \left|\alpha\right\rangle - i \cdot -\frac{i}{2} \left|\alpha\right\rangle \\
&= 0
\end{aligned}
$$

b)

$$
s^2 = s_x^2 + s_y^2 + s_z^2
$$

$$
\begin{aligned}
s_+s_- = (s_x + is_y)(s_x - is_y) &= s_x^2 + s_y^2 - i(s_xs_y - s_ys_x) \\
&= s_x^2 + s_y^2 - i[s_x, s_y] \\
&= s_x^2 + s_y^2 + s_z \\
s_-s_+ = (s_x - is_y)(s_x + is_y) &= s_x^2 + s_y^2 + i(s_xs_y - s_ys_x) \\
&= s_x^2 + s_y^2 + i[s_x, s_y] \\
&= s_x^2 + s_y^2 - s_z
\end{aligned}
$$

Therefore

$$
\begin{aligned}
s^2 &= s_+s_- - s_z + s_z^2 \\
s^2 &= s_-s_+ + s_z + s_z^2
\end{aligned}
$$

Exercise 2.33

Solution:

$$
\mathbf{s}^2 = \begin{pmatrix} \langle \alpha \,|\, s^2 \,|\, \alpha \rangle & \langle \alpha \,|\, s^2 \,|\, \beta \rangle \\ \langle \beta \,|\, s^2 \,|\, \alpha \rangle & \langle \beta \,|\, s^2 \,|\, \beta \rangle \end{pmatrix} = \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix}
$$

$$
\mathbf{s}_z = \begin{pmatrix} \langle \alpha \,|\, s_z \,|\, \alpha \rangle & \langle \alpha \,|\, s_z \,|\, \beta \rangle \\ \langle \beta \,|\, s_z \,|\, \alpha \rangle & \langle \beta \,|\, s_z \,|\, \beta \rangle \end{pmatrix} = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}
$$

$$
\mathbf{s}_+ = \begin{pmatrix} \langle \alpha \,|\, s_+ \,|\, \alpha \rangle & \langle \alpha \,|\, s_+ \,|\, \beta \rangle \\ \langle \beta \,|\, s_+ \,|\, \alpha \rangle & \langle \beta \,|\, s_+ \,|\, \beta \rangle \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}
$$

$$
\mathbf{s}_- = \begin{pmatrix} \langle \alpha \,|\, s_- \,|\, \alpha \rangle & \langle \alpha \,|\, s_- \,|\, \beta \rangle \\ \langle \beta \,|\, s_- \,|\, \alpha \rangle & \langle \beta \,|\, s_- \,|\, \beta \rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
$$

And

$$
\mathbf{s}_+\mathbf{s}_- = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}
$$

$$
\mathbf{s}_-\mathbf{s}_+ = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}
$$

It is obvious that

$$
\begin{aligned}
\mathbf{s}^2 &= \mathbf{s}_+\mathbf{s}_- - \mathbf{s}_z + \mathbf{s}_z^2 \\
\mathbf{s}^2 &= \mathbf{s}_-\mathbf{s}_+ + \mathbf{s}_z + \mathbf{s}_z^2
\end{aligned}
$$

Exercise 2.34

Solution:

$$
\begin{aligned}
\left[s^2, s_z\right] &= s^2 s_z - s_z s^2 \\
&= \left(s_x^2 + s_y^2 + s_z^2\right) s_z - s_z \left(s_x^2 + s_y^2 + s_z^2\right) \\
&= s_x^2 s_z + s_y^2 s_z - s_z s_x^2 - s_z s_y^2
\end{aligned}
$$

Because

$$
s_xs_y - s_ys_x = is_z
$$

$$
s_ys_z - s_zs_y = is_x
$$

$$s_z s_x - s_x s_z = i s_y$$

Therefore

$$\begin{aligned}
\left[s^2, s_z\right] &= s_x(s_z s_x - i s_y) + s_y(s_z s_y + i s_x) - (s_x s_z + i s_y)s_x - (s_y s_z - i s_x)s_y \\
&= s_x s_z s_x - i s_x s_y + s_y s_z s_y + i s_y s_x - s_x s_z s_x - i s_y s_x - s_y s_z s_y + i s_x s_y \\
&= 0
\end{aligned}$$

Exercise 2.35

Solution:
Because operator $\mathscr{A}$ commutes with $\mathscr{H}$,

$$\mathscr{H}(\mathscr{A}\,|\Phi\rangle) = \mathscr{H}\mathscr{A}\,|\Phi\rangle = \mathscr{A}\mathscr{H}\,|\Phi\rangle = \mathscr{A}E\,|\Phi\rangle = E(\mathscr{A}\,|\Phi\rangle)$$

Thus $\mathscr{A}\,|\Phi\rangle$ is the eigenfunction of Hamiltonian operator with eigenvalue E.
Both $|\Phi\rangle$ and $\mathscr{A}\,|\Phi\rangle$ have the same eigenvalue E. If $|\Phi\rangle$ is nondegenerate, $|\Phi\rangle$ and $\mathscr{A}\,|\Phi\rangle$ must describe the same state(based on superposition principle). Therefore

$$\mathscr{A}\,|\Phi\rangle = a\,|\Phi\rangle$$

where a is a constant.
Eigenfunctions $|\Phi_i\rangle$ of Hermitian operator $\mathscr{H}$ form a complete basis set. Suppose eigenfunction $|\psi\rangle$ with eigenvalue k can be expanded as

$$|\psi\rangle = \sum_i c_i\,|\Phi_i\rangle$$

The coefficient c_i can be determined as following:

$$\langle\Phi_i\,|\,\psi\rangle = \sum_j c_j\,\langle\Phi_i\,|\,\Phi_j\rangle = c_i$$

Because $|\psi\rangle$ and $|\Phi_i\rangle$ are eigenfunctions of Hermitian operator $\mathscr{H}$, $|\phi\rangle$ and $|\Psi_i\rangle$ will be orthognal if they have different eigenvalues and the corresponding coeffcient will vanish.

$$|\psi\rangle = \sum_{i=1}^{n} c_i\,|\Phi_i\rangle$$

where $|\Phi_i\rangle$ are n degeneracy and all have the eigenvalue k.
With the same process, we know that $\mathscr{A}\,|\psi\rangle$ is also the eigenfunction of $\mathscr{H}$ with eigenvalue k. We can conclude that

$$\mathscr{A}\,|\psi\rangle = a\,|\psi\rangle$$

And therefore

$$\mathscr{A}\,|\psi\rangle = a\sum_{i=1}^{n} c_i\,|\Phi_i\rangle$$

Exercise 2.36

Solution:
$\mathscr{A}$ is a Hermitian operator, so eigenfunctions $|\Psi_1\rangle$ and $|\Psi_2\rangle$ with different eigenvalues are orthognal. In addition, we have already know $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are eigenfunctions of $\mathscr{H}$ as well:

$$\mathscr{H}\,|\Psi_1\rangle = k_1\,|\Psi_1\rangle$$

$$\mathscr{H}\,|\Psi_2\rangle = k_2\,|\Psi_2\rangle$$

And

$$\langle\Psi_1\,|\,\mathscr{H}\,|\,\Psi_2\rangle = k_2\,\langle\Psi_1\,|\,\Psi_2\rangle = 0$$

If $\mathscr{A}$ is $\mathscr{S}^2$, while $|\Psi_1\rangle$ and $|\Psi_2\rangle$ being singlet and triplet spin-adapted configurations wavefinctions:

$$\mathscr{S}^2 |\Psi_1\rangle = 0 |\Psi_1\rangle$$

$$\mathscr{S}^2 |\Psi_2\rangle = 2 |\Psi_2\rangle$$

Thus we can affirm that the element of the Hamiltonian between singlet and triplet spin-adapted configurations is zero.

Exercise 2.37

Solution:

$$\begin{aligned}\mathscr{S}_z |\chi_i\chi_j \dots \chi_k\rangle &= \mathscr{S}_z \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{P}_i \{\chi_i\chi_j \dots \chi_k\} \\ &= \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{S}_z \mathscr{P}_i \{\chi_i\chi_j \dots \chi_k\}\end{aligned}$$

Because $\mathscr{S}_z$ is invariant to permutation and therefore commutes with $\mathscr{P}_i$:

$$\mathscr{S}_z |\chi_i\chi_j \dots \chi_k\rangle = \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{P}_i \mathscr{S}_z \{\chi_i\chi_j \dots \chi_k\}$$

$$\mathscr{S}_z \{\chi_i\chi_j \dots \chi_k\} = M_s \{\chi_i\chi_j \dots \chi_k\} = \frac{1}{2}(N_\alpha - N_\beta)\{\chi_i\chi_j \dots \chi_k\}$$

No matter how we permute the labels of spin orbtals, the total spin's z component will never change.

$$\begin{aligned}\mathscr{S}_z |\chi_i\chi_j \dots \chi_k\rangle &= \frac{1}{2}(N_\alpha - N_\beta) \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{P}_i \{\chi_i\chi_j \dots \chi_k\} \\ &= \frac{1}{2}(N_\alpha - N_\beta) |\chi_i\chi_j \dots \chi_k\rangle\end{aligned}$$

Exercise 2.38

Solution:

$$\mathscr{S}_z |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\rangle = 0$$

And therefore

$$\mathscr{S}_z^2 |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\rangle = 0$$

As for operator $\mathscr{S}_+$:

$$\begin{aligned}\mathscr{S}_+ |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\rangle &= \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{S}_+ \mathscr{P}_i \{\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\} \\ &= \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{p_i} \mathscr{P}_i \mathscr{S}_+ \{\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\}\end{aligned}$$

Because $\mathscr{S}_+$ commutes with $\mathscr{P}_i$.

$$\begin{aligned}\mathscr{S}_+ \{\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\} &= \sum_j^{2K} s_+(j) \{\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j \dots\} \\ &= \{\psi_i\psi_i\psi_j\bar{\psi}_j \dots\} + \{\psi_i\bar{\psi}_i\psi_j\psi_j \dots\} + \dots \\ &= \sum_j^{K} \{\psi_i\psi_i\psi_j\bar{\psi}_j \dots\}\end{aligned}$$

$$
\begin{aligned}
\mathscr{S}_+ |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\ldots\rangle &= \frac{1}{\sqrt{N!}}\sum_i^{N!}(-1)^{p_i}\mathscr{P}_i\sum_j^K\{\psi_i\psi_i\psi_j\bar{\psi}_j\ldots\} \\
&= \sum_j^K\frac{1}{\sqrt{N!}}\sum_i^{N!}(-1)^{p_i}\mathscr{P}_i\{\psi_i\psi_i\psi_j\bar{\psi}_j\ldots\} \\
&= 0
\end{aligned}
$$

Because there are same columns in the determinant.

$$
\mathscr{S}_-\mathscr{S}_+ |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\ldots\rangle
$$

In the end:

$$
\mathscr{S}^2 |\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\ldots\rangle = 0
$$

Exercise 2.39

Solution:
a)

$$
\begin{aligned}
\mathscr{S}^2\left(\alpha(1)\beta(2)-\beta(1)\alpha(2)\right) &= \left(\mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2\right)\left(\alpha(1)\beta(2)-\beta(1)\alpha(2)\right) \\
&= \mathscr{S}_-\mathscr{S}_+(\alpha(1)\beta(2)) - \mathscr{S}_-\mathscr{S}_+(\beta(1)\alpha(2)) + \mathscr{S}_z(\alpha(1)\beta(2)) \\
&\quad - \mathscr{S}_z(\beta(1)\alpha(2)) + \mathscr{S}_z^2(\alpha(1)\beta(2)) - \mathscr{S}_z^2(\beta(1)\alpha(2))
\end{aligned}
$$

$$
\begin{aligned}
\mathscr{S}_+(\alpha(1)\beta(2)) &= \sum_{i=1}^{2} s_+(i)(\alpha(1)\beta(2)) \\
&= \alpha(1)\alpha(2) \\
\mathscr{S}_+(\beta(1)\alpha(2)) &= \sum_{i=1}^{2} s_+(i)(\beta(1)\alpha(2)) \\
&= \alpha(1)\alpha(2)
\end{aligned}
$$

Therefore the sum of first two terms diminishes.

$$
\mathscr{S}_z(\alpha(1)\beta(2)) = \mathscr{S}_z(\beta(1)\alpha(2)) = 0
$$

And

$$
\mathscr{S}_z^2(\alpha(1)\beta(2)) = \mathscr{S}_z^2(\beta(1)\alpha(2)) = 0
$$

Thus

$$
\mathscr{S}^2\left(\alpha(1)\beta(2)-\beta(1)\alpha(2)\right) = 0
$$

So $|{}^1\Psi_1^2\rangle$ is a singlet.

b)

$$
\begin{aligned}
\mathscr{S}^2\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right) &= \left(\mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2\right)\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right) \\
&= \mathscr{S}_-\mathscr{S}_+(\alpha(1)\beta(2)) + \mathscr{S}_-\mathscr{S}_+(\beta(1)\alpha(2)) + \mathscr{S}_z(\alpha(1)\beta(2)) \\
&\quad + \mathscr{S}_z(\beta(1)\alpha(2)) + \mathscr{S}_z^2(\alpha(1)\beta(2)) + \mathscr{S}_z^2(\beta(1)\alpha(2))
\end{aligned}
$$

$$
\begin{aligned}
\mathscr{S}_-\mathscr{S}_+(\alpha(1)\beta(2)) &= \beta(1)\alpha(2) + \alpha(1)\beta(2) \\
\mathscr{S}_-\mathscr{S}_+(\beta(1)\alpha(2)) &= \beta(1)\alpha(2) + \alpha(1)\beta(2)
\end{aligned}
$$

We have the result that

$$
\mathscr{S}^2\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right) = 2\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right)
$$

Therefore $|{}^3\Psi_1^2\rangle$ is a triplet.

Exercise 2.40

Solution:

$$\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_1^2 \right\rangle = \left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{O}_1 \,\middle|\, {}^1\Psi_1^2 \right\rangle + \left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{O}_2 \,\middle|\, {}^1\Psi_1^2 \right\rangle$$
$$\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{O}_1 \,\middle|\, {}^1\Psi_1^2 \right\rangle = \left\langle {}^1\Psi_1^2 \,\middle|\, h_1 \,\middle|\, {}^1\Psi_1^2 \right\rangle + \left\langle {}^1\Psi_1^2 \,\middle|\, h_2 \,\middle|\, {}^1\Psi_1^2 \right\rangle$$

$$\begin{aligned}
\left\langle {}^1\Psi_1^2 \,\middle|\, h_1 \,\middle|\, {}^1\Psi_1^2 \right\rangle &= \int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \;\left[\frac{1}{2}\left(\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\right]^* h_1 \\
&\qquad \left[\frac{1}{2}\left(\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\right] \\
&= \frac{1}{4}\int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \;\left(\alpha^*(1)\beta^*(2) - \beta^*(1)\alpha^*(2)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\Big\{\psi_1^*(1)\psi_2^*(2)h_1\psi_1(1)\psi_2(2) \\
&\qquad + \psi_1^*(1)\psi_2^*(2)h_1\psi_1(2)\psi_2(1) + \psi_1^*(2)\psi_2^*(1)h_1\psi_1(1)\psi_2(2) + \psi_1^*(2)\psi_2^*(1)h_1\psi_1(2)\psi_2(1)\Big\} \\
&= \frac{1}{2}(h_{11} + h_{22})
\end{aligned}$$

With the same procedure

$$\left\langle {}^1\Psi_1^2 \,\middle|\, h_2 \,\middle|\, {}^1\Psi_1^2 \right\rangle = \frac{1}{2}(h_{11} + h_{22})$$

So

$$\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{O}_1 \,\middle|\, {}^1\Psi_1^2 \right\rangle = h_{11} + h_{22}$$

$$\begin{aligned}
\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{O}_2 \,\middle|\, {}^1\Psi_1^2 \right\rangle &= \left\langle {}^1\Psi_1^2 \,\middle|\, r_{12}^{-1} \,\middle|\, {}^1\Psi_1^2 \right\rangle \\
&= \frac{1}{2}\int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \;\Big[\psi_1^*(1)\psi_2^*(2)r_{12}^{-1}\psi_1(1)\psi_2(2) + \psi_1^*(1)\psi_2^*(2)r_{12}^{-1}\psi_1(2)\psi_2(1) \\
&\qquad + \psi_1^*(2)\psi_2^*(1)r_{12}^{-1}\psi_1(1)\psi_2(2) + \psi_1^*(2)\psi_2^*(1)r_{12}^{-1}\psi_1(2)\psi_2(1)\Big] \\
&= \frac{1}{2}(J_{12} + K_{12} + K_{12} + J_{12}) \\
&= J_{12} + K_{12}
\end{aligned}$$

Finally the result is

$$\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_1^2 \right\rangle = h_{11} + h_{22} + J_{12} + K_{12}$$

Exercise 2.41

Solution:
a)

$$\mathscr{S}^2 = \mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2$$
$$\mathscr{S}_z\, |\psi_1^\alpha \bar{\psi}_1^\beta\rangle = 0$$
$$\mathscr{S}_z^2\, |\psi_1^\alpha \bar{\psi}_1^\beta\rangle = 0$$

$$\begin{aligned}
\mathscr{S}^2\, |\psi_1^\alpha \bar{\psi}_1^\beta\rangle &= \mathscr{S}_-\mathscr{S}_+\, |\psi_1^\alpha \bar{\psi}_1^\beta\rangle \\
&= \mathscr{S}_-\mathscr{S}_+ \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\bar{\psi}_1^\beta(2) - \psi_1^\alpha(2)\bar{\psi}_1^\beta(1)\right) \\
&= \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2)\mathscr{S}_-\mathscr{S}_+\alpha(1)\beta(2) - \psi_1^\alpha(2)\psi_1^\beta(1)\mathscr{S}_-\mathscr{S}_+\alpha(2)\beta(1)\right) \\
&= \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2)\mathscr{S}_-\alpha(1)\alpha(2) - \psi_1^\alpha(2)\psi_1^\beta(1)\mathscr{S}_-\alpha(2)\alpha(1)\right) \\
&= \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2)(\beta(1)\alpha(2) + \alpha(1)\beta(2)) - \psi_1^\alpha(2)\psi_1^\beta(1)(\alpha(2)\beta(1) + \beta(2)\alpha(1))\right) \\
&= \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\alpha(2)\psi_1^\beta(1)\right)(\alpha(2)\beta(1) + \beta(2)\alpha(1))
\end{aligned}$$

If $\psi_1^\alpha = \psi_1^\beta = \psi_1$, two terms is equal and the last formula diminishes. Therefore $|\psi_1^\alpha \bar{\psi_1^\beta}\rangle$ is the eigenfunction of $\mathscr{S}^2$ and is pure singlet. Otherwise, $|\psi_1^\alpha \bar{\psi_1^\beta}\rangle$ can't be the eigenfunction of $\mathscr{S}^2$.
b)

$$\begin{aligned}
\mathscr{S}^2 \, |\psi_1^\alpha \bar{\psi_1^\beta}\rangle &= \frac{1}{\sqrt{2}} \left(\psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\alpha(2)\psi_1^\beta(1) \right) (\alpha(2)\beta(1) + \beta(2)\alpha(1)) \\
&= \frac{1}{\sqrt{2}} \left(\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2) - \psi_1^\alpha(2)\alpha(2)\psi_1^\beta(1)\beta(1) \right) \\
&\quad - \frac{1}{\sqrt{2}} \left(\psi_1^\beta(1)\alpha(1)\psi_1^\alpha(2)\beta(2) - \psi_1^\alpha(1)\beta(1)\psi_1^\beta(2)\alpha(2) \right) \\
&= K - J
\end{aligned}$$

Therefore

$$\left\langle K \,\middle|\, \mathscr{S}^2 \,\middle|\, K \right\rangle = \langle K \,|\, K - J \rangle = \langle K \,|\, K \rangle - \langle K \,|\, J \rangle$$

$|K\rangle$ is normalized, so $\langle K \,|\, K\rangle = 1$. And

$$\begin{aligned}
\langle K \,|\, J \rangle &= \frac{1}{2} \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \; \left(\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2) - \psi_1^\alpha(2)\alpha(2)\psi_1^\beta(1)\beta(1) \right)^* \\
&\qquad \left(\psi_1^\beta(1)\alpha(1)\psi_1^\alpha(2)\beta(2) - \psi_1^\alpha(1)\beta(1)\psi_1^\beta(2)\alpha(2) \right) \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \; \psi_1^{\alpha *}(1)\psi_1^{\beta^*}(2)\psi_1^\beta(1)\psi_1^\alpha(2)\alpha^*(1)\beta^*(2)\alpha(1)\beta(2) \\
&\qquad + \psi_1^{\alpha *}(2)\psi_1^{\beta^*}(1)\psi_1^\alpha(1)\psi_1^\beta(2)\alpha^*(2)\beta^*(1)\beta(1)\alpha(2) \\
&= \left| S_{11}^{\alpha\beta} \right|^2
\end{aligned}$$

In conclusion,

$$\left\langle K \,\middle|\, \mathscr{S}^2 \,\middle|\, K \right\rangle = 1 - \left| S_{11}^{\alpha\beta} \right|^2$$

3 Chapter 3

Exercise 3.1

Solution:

$$\langle \chi_i \,|\, f \,|\, \chi_j \rangle = \langle \chi_i \,|\, h \,|\, \chi_j \rangle + \left\langle \chi_i \,\middle|\, v^{\mathrm{HF}} \,\middle|\, \chi_j \right\rangle$$

$$\begin{aligned}
\left\langle \chi_i \,\middle|\, v^{\mathrm{HF}} \,\middle|\, \chi_j \right\rangle &= \sum_b \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_i^*(1)\chi_b^*(2) r_{12}^{-1} (1 - \mathscr{P}_{12}) \{\chi_b(2)\chi_j(1)\} \\
&= \sum_b \Big(\int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_i^*(1)\chi_b^*(2) r_{12}^{-1} \chi_b(2)\chi_j(1) \\
&\qquad - \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_i^*(1)\chi_b^*(2) r_{12}^{-1} \chi_j(2)\chi_b(1) \Big) \\
&= \sum_b ([ij|bb] - [ib|bj]) \\
&= \sum_b \langle ib \,\|\, jb \rangle
\end{aligned}$$

Therefore

$$\langle \chi_i \,|\, f \,|\, \chi_j \rangle = \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle$$

Exercise 3.2

Solution:

$$\mathscr{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_a \sum_b \varepsilon_{ba}([a|b] - \delta_{ab})$$

$$\mathscr{L}^*[\{\chi_a\}] = E_0^*[\{\chi_a\}] - \sum_a \sum_b \varepsilon_{ba}^*([a|b]^* - \delta_{ab}^*)$$

Because $\mathscr{L}$ and E_0 are real, and $[a|b]^* = [b|a], \delta_{ab}^* = \delta_{ba}$.

$$\mathscr{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_a \sum_b \varepsilon_{ba}^*([b|a] - \delta_{ba})$$

Because a, b are dummy variables, we can just exchange them.

$$\mathscr{L}[\{\chi_b\}] = E_0[\{\chi_b\}] - \sum_a \sum_b \varepsilon_{ab}([b|a] - \delta_{ba})$$

By comparing the last two equations, we conclude that ε_{ba}^* must be equal to ε_{ab}.

Exercise 3.3

Solution:
h is Hermitian operator, so

$$[\chi_a|h|\delta\chi_a] = [\delta\chi_a|h|\chi_a]^*$$

$$[\delta\chi_a\chi_a|\chi_b\chi_b] = [\chi_a\delta\chi_a|\chi_b\chi_b]$$

The complex conjugate of first two terms is the last two terms(we can just exchange the subscripts).

$$[\delta\chi_a\chi_a|\chi_b\chi_b]^* = [\chi_b\chi_b|\delta\chi_a\chi_a] = [\chi_a\chi_a|\delta\chi_b\chi_b]$$

The second summation is therefore

$$\begin{aligned}\frac{1}{2}\sum_a \sum_b \Big([\delta\chi_a\chi_a|\chi_b\chi_b] + [\delta\chi_a\chi_a|\chi_b\chi_b] + [\delta\chi_a\chi_a|\chi_b\chi_b]^* + [\delta\chi_a\chi_a|\chi_b\chi_b]^*\Big) \\ = \sum_a \sum_b [\delta\chi_a\chi_a|\chi_b\chi_b] + \text{complex conjugate}\end{aligned}$$

Exercise 3.4

Solution:
From the previous result,

$$\langle \chi_i \,|\, f \,|\, \chi_j \rangle = \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle$$

And it is obviously that

$$\langle \chi_j \,|\, f \,|\, \chi_i \rangle = \langle j \,|\, h \,|\, i \rangle + \sum_b \langle jb \,\|\, ib \rangle$$

h is a Hermitian operator, so $\langle i \,|\, h \,|\, j \rangle = \langle j \,|\, h \,|\, i \rangle^*$. And

$$\begin{aligned}\sum_b \langle ib \,\|\, jb \rangle = \sum_b \Big(\int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_i^*(1)\chi_b^*(2) r_{12}^{-1} \chi_b(2)\chi_j(1) \\ - \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_i^*(1)\chi_b^*(2) r_{12}^{-1} \chi_j(2)\chi_b(1) \Big)\end{aligned}$$

$$\begin{aligned}\sum_b \langle jb \,\|\, ib \rangle = \sum_b \Big(\int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_j^*(1)\chi_b^*(2) r_{12}^{-1} \chi_b(2)\chi_i(1) \\ - \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \; \chi_j^*(1)\chi_b^*(2) r_{12}^{-1} \chi_i(2)\chi_b(1) \Big)\end{aligned}$$

It is easy to find that $\sum\limits_b \langle ib \,\|\, jb\rangle = \sum\limits_b \langle jb \,\|\, ib\rangle^*$. So $\langle \chi_i \,|\, f \,|\, \chi_j\rangle = \langle \chi_j \,|\, f \,|\, \chi_i\rangle^*$, and Fock operator is a Hermitian operator.

Exercise 3.5

Solution:

$$
\begin{aligned}
{}^{N-2}E_{cd} &= \left\langle {}^{N-2}\Psi_{cd} \,\middle|\, \mathscr{H} \,\middle|\, {}^{N-2}\Psi_{cd}\right\rangle - \left\langle {}^{N}\Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^{N}\Psi_0\right\rangle \\
\left\langle {}^{N}\Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^{N}\Psi_0\right\rangle &= \sum_a^N \langle a \,|\, h \,|\, a\rangle + \frac{1}{2}\sum_{a,b}^N \langle ab \,\|\, ab\rangle \\
\left\langle {}^{N-2}\Psi_{cd} \,\middle|\, \mathscr{H} \,\middle|\, {}^{N-2}\Psi_{cd}\right\rangle &= \sum_{a\neq c,d}^N \langle a \,|\, h \,|\, a\rangle + \frac{1}{2}\sum_{a,b\neq c,d}^N \langle ab \,\|\, ab\rangle
\end{aligned}
$$

Therefore

$$
\begin{aligned}
{}^{N-2}E_{cd} =& -\langle c \,|\, h \,|\, c\rangle - \langle d \,|\, h \,|\, d\rangle - \frac{1}{2}\Bigg[\Big(\sum_a^N \langle ac \,\|\, ac\rangle + \sum_a^N \langle ad \,\|\, ad\rangle + \sum_a^N \langle ca \,\|\, ca\rangle + \sum_a^N \langle da \,\|\, da\rangle\Big) \\
&\qquad - \langle cd \,\|\, cd\rangle - \langle dc \,\|\, dc\rangle\Bigg] \\
=& -\Big(\langle c \,|\, h \,|\, c\rangle + \sum_a^N \langle ca \,\|\, ca\rangle\Big) - \Big(\langle d \,|\, h \,|\, d\rangle + \sum_a^N \langle da \,\|\, da\rangle\Big) + \langle cd \,\|\, cd\rangle \\
=& -\varepsilon_c - \varepsilon_d + \langle cd \,|\, cd\rangle - \langle cd \,|\, dc\rangle
\end{aligned}
$$

Exercise 3.6

Solution:

$$
\begin{aligned}
{}^{N}E_0 - {}^{N+1}E^r &= \Big(\sum_a^N \langle a \,|\, h \,|\, a\rangle + \frac{1}{2}\sum_{a,b}^N \langle ab \,\|\, ab\rangle\Big) - \Big(\sum_a^{N+1} \langle a \,|\, h \,|\, a\rangle + \frac{1}{2}\sum_{a,b}^{N+1} \langle ab \,\|\, ab\rangle\Big) \\
&= -\langle r \,|\, h \,|\, r\rangle - \frac{1}{2}\Big(\sum_{a(b\equiv r)}^N \langle ar \,\|\, ar\rangle + \sum_{b(a\equiv r)}^N \langle rb \,\|\, rb\rangle\Big) \\
&= -\langle r \,|\, h \,|\, r\rangle - \sum_b^N \langle rb \,\|\, rb\rangle \\
&= -\varepsilon_r
\end{aligned}
$$

Exercise 3.7

Solution:

$$
\begin{aligned}
\mathscr{H}\,|\Psi_0\rangle &= \mathscr{H}\frac{1}{\sqrt{N!}}\sum_i^{N!}(-1)^{p_i}\mathscr{P}_i\,\{\chi_1\chi_2\ldots\chi_N\} \\
&= \frac{1}{\sqrt{N!}}\sum_i^{N!}(-1)^{p_i}\mathscr{H}\mathscr{P}_i\,\{\chi_1\chi_2\ldots\chi_N\} \\
&= \frac{1}{\sqrt{N!}}\sum_i^{N!}(-1)^{p_i}\mathscr{P}_i\mathscr{H}\,\{\chi_1\chi_2\ldots\chi_N\}
\end{aligned}
$$

Because

$$\begin{aligned}\mathscr{H}_0\left\{\chi_1\chi_2\ldots\chi_N\right\} &= \sum_{a=1}^{N} f(a)\left\{\chi_1\chi_2\ldots\chi_N\right\}\\ &= \sum_{a=1}^{N}\varepsilon_a\left\{\chi_1\chi_2\ldots\chi_N\right\}\end{aligned}$$

$$\mathscr{H}_0\left|\Psi_0\right\rangle = \sum_{a=1}^{N}\varepsilon_a\frac{1}{\sqrt{N!}}\sum_{i}^{N!}(-1)^{p_i}\mathscr{P}_i\left\{\chi_1\chi_2\ldots\chi_N\right\}$$

Slater determinant is the eigenfunction of Hartree-Fock Hamiltonian $\mathscr{H}_0$ with eigenvalue $\sum_a \varepsilon_a$.
Suppose

$$\mathscr{H}_0 = f(1)+f(2)+\ldots+f(i)+f(j)+\ldots+f(N)$$

And after permutation operator $\mathscr{P}_ij$ being applied on it, it becomes

$$\mathscr{P}_{ij}\mathscr{H}_0 = f(1)+f(2)+\ldots+f(j)+f(i)+\ldots+f(N)$$

It is obvious that thay are just identical.

$$\mathscr{P}_{ij}\mathscr{H}_0 = \mathscr{H}_0\mathscr{P}_{ij}$$

So $\mathscr{H}_0$ commutes with $\mathscr{P}_{ij}$.

Exercise 3.9

Solution:
Suppose χ_i has α spin function.

$$\begin{aligned}\left\langle\chi_i\,|\,h\,|\,\chi_i\right\rangle &= \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\omega_1\;\psi_j^*(\mathbf{r}_1)\alpha^*(\omega_1)h(1)\psi_j(\mathbf{r}_1)\alpha(\omega_1)\\ &= \int \mathrm{d}\mathbf{r}_1\;\psi_j^*(\mathbf{r}_1)h(1)\psi_j(\mathbf{r}_1)\\ &= (\psi_j|h|\psi_j)\end{aligned}$$

$$\sum_b^N\left\langle\chi_i\chi_b\,\|\,\chi_i\chi_b\right\rangle = \sum_b^{N/2}\left\langle\psi_j\psi_b\,\|\,\psi_j\chi_b\right\rangle + \sum_b^{N/2}\left\langle\psi_j\bar{\psi}_b\,\|\,\psi_j\bar{\psi}_b\right\rangle$$

The first term:

$$\begin{aligned}\sum_b^{N/2}\left\langle\psi_j\psi_b\,\|\,\psi_j\psi_b\right\rangle &= \sum_b^{N/2}\Big[\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2\;\psi_j^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_b^*(\mathbf{r}_2)\alpha^*(\omega_2)r_{12}^{-1}\psi_j(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\alpha(\omega_2)\\ &\qquad - \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2\;\psi_j^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_b^*(\mathbf{r}_2)\alpha^*(\omega_2)r_{12}^{-1}\psi_b(\mathbf{r}_1)\alpha(\omega_1)\psi_j(\mathbf{r}_2)\alpha(\omega_2)\Big]\\ &= \sum_b^{N/2}\Big[\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\;\psi_j^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)r_{12}^{-1}\psi_j(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\\ &\qquad - \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\;\psi_j^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)r_{12}^{-1}\psi_b(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\Big]\\ &= \sum_b^{N/2}\big[(jj|bb)-(jb|bj)\big]\end{aligned}$$

The last term:

$$
\begin{aligned}
\sum_{b}^{N/2} \langle \psi_j \bar{\psi}_b \, \| \, \psi_j \bar{\psi}_b \rangle &= \sum_{b}^{N/2} \Bigg[\int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \ \psi_j^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_b^*(\mathbf{r}_2)\beta^*(\omega_2) r_{12}^{-1} \psi_j(\mathbf{r}_1)\alpha(\omega_1)\psi_b(\mathbf{r}_2)\beta(\omega_2) \\
&\qquad - \int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \ \psi_j^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_b^*(\mathbf{r}_2)\beta^*(\omega_2) r_{12}^{-1} \psi_b(\mathbf{r}_1)\beta(\omega_1)\psi_j(\mathbf{r}_2)\alpha(\omega_2) \Bigg] \\
&= \sum_{b}^{N/2} \Bigg[\int \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \ \psi_j^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2) r_{12}^{-1} \psi_j(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \Bigg] \\
&= \sum_{b}^{N/2} (jj|bb)
\end{aligned}
$$

We have

$$
\sum_{b}^{N} \langle \chi_i \chi_b \, \| \, \chi_i \chi_b \rangle = \sum_{b}^{N/2} \left[2(jj|bb) - (jb|bj) \right]
$$

The orbital energies in closed-shell expression is

$$
\begin{aligned}
\varepsilon_j &= (\psi_j|h|\psi_j) + \sum_{b}^{N/2} \left[2(jj|bb) - (jb|bj) \right] \\
&= h_{jj} + \sum_{b}^{N/2} (2J_{jb} - K_{jb})
\end{aligned}
$$

Exercise 3.10

Solution:

$$
|\psi_i\rangle = \sum_{\mu=1}^{K} |\phi_\mu\rangle \, C_{\mu i}
$$

$$
\langle\psi_i| = \sum_{\mu=1}^{K} C_{i\mu}^* \, \langle\phi_\mu|
$$

Because molecular orbitals are orthonormal,

$$
\begin{aligned}
\delta_{ij} &= \langle \psi_i \mid \psi_j \rangle \\
&= \sum_{\mu=1}^{K} C_{i\mu}^* \, \langle\phi_\mu| \cdot \sum_{\nu=1}^{K} |\phi_\nu\rangle \, C_{\nu j} \\
&= \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} C_{i\mu}^* \, \langle \phi_\mu \mid \phi_\nu \rangle \, C_{\nu j} \\
&= \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} C_{i\mu}^* S_{\mu\nu} C_{\nu j}
\end{aligned}
$$

It is equivalent with the following expression:

$$
\mathbf{I} = \mathbf{C}^\dagger \mathbf{S} \mathbf{C}
$$

Exercise 3.11

Solution:

$$\begin{aligned}\rho(\mathbf{r}) &= \langle \Psi_0 \,|\, \hat{\rho}(\mathbf{r}) \,|\, \Psi_0 \rangle \\ &= \sum_s^N \frac{1}{N!} \sum_i^{N!} \sum_j^{N!} (-1)^{p_i} (-1)^{p_j} \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_N \; \mathscr{P}_i \left\{ \chi_1(1)\chi_2(2) \ldots \chi_N(N) \right\}^* \\ &\qquad \delta(\mathbf{r}_s - \mathbf{r}) \mathscr{P}_j \left\{ \chi_1(1)\chi_2(2) \ldots \chi_N(N) \right\}\end{aligned}$$

Because spin orbitals are orthogonal, the intergral will be zero if permutaions i and j are different.

$$\begin{aligned}\rho(\mathbf{r}) = \sum_s^N \frac{1}{N!} \sum_i^{N!} \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_N \; \mathscr{P}_i \left\{ \chi_1(1)\chi_2(2) \ldots \chi_N(N) \right\}^* \\ \delta(\mathbf{r}_s - \mathbf{r}) \mathscr{P}_i \left\{ \chi_1(1)\chi_2(2) \ldots \chi_N(N) \right\}\end{aligned}$$

The electron labeled s occupies spin orbitals $\{\chi_i | i = 1, 2, \ldots N\}$ in turn, and other $N-1$ electrons have $(N-1)!$ kinds of arrangement.

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_s^N \frac{(N-1)!}{N!} \sum_i^N \int \mathrm{d}\mathbf{x}_s \; \chi_i(\mathbf{x}_s)^* \delta(\mathbf{r}_s - \mathbf{r}) \chi_i(\mathbf{x}_s) \\ &= \sum_s^N \frac{1}{N} \sum_i^N \int \mathrm{d}\mathbf{x}_s \; \chi_i(\mathbf{x}_s)^* \delta(\mathbf{r}_s - \mathbf{r}) \chi_i(\mathbf{x}_s) \\ &= \sum_s^N \frac{2}{N} \sum_i^{N/2} \int \mathrm{d}\mathbf{r}_s \; \psi_i(\mathbf{r}_s)^* \delta(\mathbf{r}_s - \mathbf{r}) \psi_i(\mathbf{r}_s) \\ &= \sum_s^N \frac{2}{N} \sum_i^{N/2} \psi_i(\mathbf{r})^* \psi_i(\mathbf{r}) \\ &= 2 \sum_i^{N/2} \psi_i(\mathbf{r})^* \psi_i(\mathbf{r})\end{aligned}$$

Exercise 3.12

Solution:

$$\begin{aligned}(\mathbf{PSP})_{\mu\delta} &= \sum_{\nu\omega} P_{\mu\nu} S_{\nu\omega} P_{\omega\delta} \\ &= \sum_{\nu\omega} \left(2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \cdot S_{\nu\omega} \cdot 2 \sum_b^{N/2} C_{\omega b} C_{\delta b}^* \right) \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} \left[C_{\mu a} \left(\sum_{\nu\omega} C_{\nu a}^* S_{\nu\omega} C_{\omega b} \right) C_{\delta b}^* \right] \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \delta_{ab} C_{\delta b}^* \\ &= 4 \sum_a^{N/2} C_{\mu a} C_{\delta a}^* \\ &= 2 P_{\mu\delta}\end{aligned}$$

i.e.

$$\mathbf{PSP} = 2\mathbf{P}$$

Exercise 3.13

Solution:

$$
\begin{aligned}
f(\mathbf{r}_1) &= h(\mathbf{r}_1) + \sum_b^{N/2} \left[\int \mathrm{d}\mathbf{r}_2 \ \psi_b^*(\mathbf{r}_2)(2 - \mathscr{P}_{12}) r_{12}^{-1} \psi_b(\mathbf{r}_2) \right] \\
&= h(\mathbf{r}_1) + \sum_b^{N/2} \left[\int \mathrm{d}\mathbf{r}_2 \ \sum_\sigma \phi_\sigma^*(\mathbf{r}_2) C_{\sigma b}^* (2 - \mathscr{P}_{12}) r_{12}^{-1} \sum_\lambda \phi_\lambda^*(\mathbf{r}_2) C_{\lambda b}^* \right] \\
&= h(\mathbf{r}_1) + \sum_{\sigma\lambda} \sum_b^{N/2} C_{\sigma b}^* C_{\lambda b} \left[\int \mathrm{d}\mathbf{r}_2 \ \phi_\sigma^*(\mathbf{r}_2)(2 - \mathscr{P}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \right] \\
&= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\sigma\lambda} P_{\sigma\lambda} \left[\int \mathrm{d}\mathbf{r}_2 \ \phi_\sigma^*(\mathbf{r}_2)(2 - \mathscr{P}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \right]
\end{aligned}
$$

Exercise 3.15

Solution:

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s}$$

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s}$$

$$\sum_\nu S_{\mu\nu} c_\nu^i = s_i c_\mu^i$$

Multiply by c_μ^{i*} on both side and sum

$$\sum_{\mu\nu} c_\mu^{i*} S_{\mu\nu} c_\nu^i = \sum_{\mu\nu} c_\mu^{i*} s_i c_\mu^i$$

$$\sum_{\mu\nu} c_\mu^{i*} \int \mathrm{d}\mathbf{r} \ \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \ c_\nu^i = \sum_\mu s_i \left| c_\mu^i \right|^2$$

$$\int \mathrm{d}\mathbf{r} \ \phi_i^{\prime *}(\mathbf{r}) \phi_i^\prime(\mathbf{r}) = \sum_\mu s_i \left| c_\mu^i \right|^2$$

$$\int \mathrm{d}\mathbf{r} \ \phi_i^{\prime *}(\mathbf{r}) \phi_i^\prime(\mathbf{r}) = s_i \sum_\mu \left| c_\mu^i \right|^2$$

$$\int \mathrm{d}\mathbf{r} \ \left| \phi_i^\prime(\mathbf{r}) \right|^2 = s_i \sum_\mu \left| c_\mu^i \right|^2$$

Because intergral and summation are positive, the eigenvalues s_i must be positive.

Exercise 3.16

Solution:

$$\psi_i = \sum_{\mu=1}^K C_{\mu i}^\prime \phi_\mu^\prime$$

The expansion by original basis set is

$$\psi_i = \sum_{\nu=1}^K C_{\nu i} \phi_\nu$$

The transformation within two basis set is

$$\phi_\mu^\prime = \sum_\nu^K X_{\nu\mu} \phi_\nu$$

$$\psi_i = \sum_{\mu=1}^{K} C'_{\mu i}\phi'_\mu = \sum_{\mu=1}^{K} C'_{\mu i} \sum_{\nu}^{K} X_{\nu\mu}\phi_\nu$$

It is obviously that

$$C_{\nu i} = \sum_{\mu=1}^{K} C'_{\mu i} X_{\nu\mu}$$

i.e.

$$\mathbf{C} = \mathbf{X}\mathbf{C}'$$

$$\begin{aligned}
\left(\mathbf{X}^\dagger\mathbf{F}\mathbf{X}\right)_{\mu\nu} &= \sum_{ij} \left(\mathbf{X}^\dagger\right)_{\mu i} F_{ij} X_{j\nu} \\
&= \sum_{ij} X^*_{i\mu} \int \mathrm{d}\mathbf{r}\ \phi^*_i(1) f(1)\phi_j(1)\ X_{j\nu} \\
&= \int \mathrm{d}\mathbf{r}\ \phi'^*_\mu(1) f(1)\phi'_\nu(1) \\
&= F'_{\mu\nu}
\end{aligned}$$

Exercise 3.17

Solution:

$$\begin{aligned}
E_0 &= \sum_{a}^{N/2}(h_{aa} + f_{aa}) \\
&= \sum_{a}^{N/2}\left(2\left\langle\psi_a \,|\, h \,|\, \psi_a\right\rangle + \sum_{b}^{N/2}(2J_{ab} - K_{ab})\right) \\
&= \sum_{a}^{N/2}\Bigg(2\sum_{\mu\nu}^{K} C^*_{\mu a}C_{\nu a}\int \mathrm{d}\mathbf{r}\ \phi^*_\mu(1)h(1)\phi_\nu(1) + \\
&\qquad \sum_{b}^{N/2}\left(2\sum_{\mu\nu}^{K} C^*_{\mu a}C_{\nu a}\int \mathrm{d}\mathbf{r}\ \phi^*_\mu(1)\phi_\nu(1)r_{12}^{-1}\psi^*_b(2)\psi_b(2) - \sum_{\mu\nu}^{K} C^*_{\mu a}C_{\nu a}\int \mathrm{d}\mathbf{r}\ \phi^*_\mu(1)\psi_b(1)r_{12}^{-1}\psi^*_b(2)\phi_\nu(2)\right)\Bigg) \\
&= \sum_{a}^{N/2}\sum_{\mu\nu}^{K} C^*_{\mu a}C_{\nu a}\left(2H^{\text{core}}_{\mu\nu} + \sum_{b}^{N/2}\left(2(\mu\nu|bb) - (\mu b|b\nu)\right)\right) \\
&= \frac{1}{2}\sum_{\mu\nu}^{K} P_{\nu\mu}(H^{\text{core}}_{\mu\nu} + F_{\mu\nu})
\end{aligned}$$

Exercise 3.19

Solution:

$$\phi^{\text{GF}}_{1s}(\alpha, \mathbf{r} - \mathbf{R}_A)\phi^{\text{GF}}_{1s}(\beta, \mathbf{r} - \mathbf{R}_B) = \left(\frac{4\alpha\beta}{\pi^2}\right)^{3/4} \exp\Big(-\alpha|\mathbf{r} - \mathbf{R}_A|^2 - \beta|\mathbf{r} - \mathbf{R}_B|^2\Big)$$

The exponent in the result can be changed as following:

$$-\alpha|\mathbf{r} - \mathbf{R}_A|^2 - \beta|\mathbf{r} - \mathbf{R}_B|^2 = -(\alpha+\beta)|\mathbf{r}|^2 + (2\alpha\mathbf{R}_A + 2\beta\mathbf{R}_B)\cdot\mathbf{r} - \Big(\alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\Big)$$

We set $p = \alpha + \beta$,

$$
\begin{aligned}
-\alpha|\mathbf{r}-\mathbf{R}_A|^2 - \beta|\mathbf{r}-\mathbf{R}_B|^2 = -p|\mathbf{r}|^2 + 2p\mathbf{r}\cdot\frac{\alpha\mathbf{R}_A+\beta\mathbf{R}_B}{\alpha+\beta} - p\left|\frac{\alpha\mathbf{R}_A+\beta\mathbf{R}_B}{\alpha+\beta}\right|^2 \\
+ p\left|\frac{\alpha\mathbf{R}_A+\beta\mathbf{R}_B}{\alpha+\beta}\right|^2 - \Big(\alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\Big)
\end{aligned}
$$

Set $\mathbf{R}_P = (\alpha\mathbf{R}_A + \beta\mathbf{R}_B)/(\alpha+\beta)$:

$$
\begin{aligned}
-\alpha|\mathbf{r}-\mathbf{R}_A|^2 - \beta|\mathbf{r}-\mathbf{R}_B|^2 &= \Big(-p|\mathbf{r}|^2 + 2p\mathbf{r}\cdot\mathbf{R}_P - p|\mathbf{R}_P|^2\Big) - \frac{\alpha\beta}{\alpha+\beta}\Big(|\mathbf{R}_A|^2 + |\mathbf{R}_B|^2 - 2\mathbf{R}_A\cdot\mathbf{R}_B\Big) \\
&= -p|\mathbf{r}-\mathbf{R}_P|^2 - \frac{\alpha\beta}{\alpha+\beta}|\mathbf{R}_A-\mathbf{R}_B|^2
\end{aligned}
$$

On the other hand,

$$
\begin{aligned}
\left(\frac{4\alpha\beta}{\pi^2}\right)^{3/4} &= \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi}\frac{2(\alpha+\beta)}{\pi}\right)^{3/4} \\
&= \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi}\right)^{3/4}\left(\frac{2p}{\pi}\right)^{3/4}
\end{aligned}
$$

Therefore, the result is

$$
\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\beta, \mathbf{r}-\mathbf{R}_B) = K_{AB}\phi_{1s}^{\mathrm{GF}}(p, \mathbf{r}-\mathbf{R}_P)
$$

Where

$$
\begin{aligned}
K_{AB} &= \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi}\right)^{3/4} \exp\Big(\alpha\beta/(\alpha+\beta)|\mathbf{R}_A-\mathbf{R}_B|^2\Big) \\
\phi_{1s}^{\mathrm{GF}}(p, \mathbf{r}-\mathbf{R}_P) &= \left(\frac{2p}{\pi}\right)^{3/4} \exp\Big(-p|\mathbf{r}-\mathbf{R}_P|^2\Big)
\end{aligned}
$$

Exercise 3.21

Solution:

$$
\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(0.270950)
$$

Because $\alpha' = \alpha(\zeta = 1.0) \times \zeta^2$

$$
\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.24, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(0.41661272)
$$

ϕ_{1s}^{GF} is already normalized.

$$
\begin{aligned}
S_{12} &= \int \left(\frac{2\alpha}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \cdot \left(\frac{2\alpha}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_B|^2}\, \mathrm{d}\mathbf{r} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \cdot \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_B|^2}\, \mathrm{d}\mathbf{r} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \widetilde{K} \int \mathrm{e}^{-p|\mathbf{r}-\mathbf{R}_P|^2}\, \mathrm{d}\mathbf{r} \\
&= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \widetilde{K} \int_0^\infty r^2 \mathrm{e}^{-pr^2}\, \mathrm{d}r \\
&= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \widetilde{K} \cdot \frac{1}{4}\left(\frac{\pi}{p^3}\right)^{1/2}
\end{aligned}
$$

Because

$$\widetilde{K} = \exp\left[-\frac{\alpha\beta}{\alpha+\beta}\cdot|\mathbf{R}_A-\mathbf{R}_B|^2\right] = \exp\left[-\frac{\alpha}{2}\cdot|\mathbf{R}_A-\mathbf{R}_B|^2\right]$$

$$p = \alpha+\beta = 2\alpha$$

Therefore

$$\begin{aligned} S_{12} &= 4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\cdot \mathrm{e}^{-\alpha/2\cdot|\mathbf{R}_A-\mathbf{R}_B|^2}\cdot\frac{1}{4}\left(\frac{\pi}{8\alpha^3}\right)^{1/2} \\ &= \mathrm{e}^{-\alpha/2\cdot|\mathbf{R}_A-\mathbf{R}_B|^2} \\ &= 0.6648 \end{aligned}$$

Exercise 3.22

Solution:
ψ_1 is σ_g symmetry and ψ_2 is σ_u symmetry. So they have the corresponding formation:

$$\psi_1 = C_1(\phi_1+\phi_2), \quad \psi_2 = C_1(\phi_1-\phi_2)$$

Both ψ_1 and ψ_2 are normalized.

$$\langle\psi_1\,|\,\psi_1\rangle = 1$$

$$C_1^2\big(\langle\psi_1\,|\,\psi_1\rangle+\langle\psi_2\,|\,\psi_2\rangle+\langle\psi_1\,|\,\psi_2\rangle+\langle\psi_2\,|\,\psi_1\rangle\big) = 1$$

$$C_1^2 = \frac{1}{2+2S_{12}}$$

$$C_1 = \pm[2(1+S_{12})]^{-1/2}$$

There is no matter whether C_1 is positive or negative. We just set it positive.

$$C_1 = [2(1+S_{12})]^{-1/2}$$

With the same procedure

$$C_2 = [2(1-S_{12})]^{-1/2}$$

Exercise 3.23

Solution:

$$\mathbf{H}^{\mathrm{core}}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon$$

Use matrix presentation

$$\begin{pmatrix} H_{11}^{\mathrm{core}} & H_{12}^{\mathrm{core}} \\ H_{21}^{\mathrm{core}} & H_{22}^{\mathrm{core}} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix}\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$

$$\begin{cases} H_{11}^{\mathrm{core}}C_1 + H_{12}^{\mathrm{core}}C_1 = \varepsilon_1(S_{11}C_1+S_{12}C_1) \\ H_{11}^{\mathrm{core}}C_2 - H_{12}^{\mathrm{core}}C_2 = \varepsilon_2(S_{11}C_2-S_{12}C_2) \end{cases}$$

Eliminate C_1 and C_2 on both side, and $S_{11} = 1$

$$\begin{aligned} \varepsilon_1 &= (H_{11}^{\mathrm{core}}+H_{12}^{\mathrm{core}})/(1+S_{12}) \\ &= (-1.1204-0.9584)/(1+0.6593) \\ &= -1.2528 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} \varepsilon_2 &= (H_{11}^{\mathrm{core}}-H_{12}^{\mathrm{core}})/(1-S_{12}) \\ &= (-1.1204+0.9584)/(1-0.6593) \\ &= -0.4755 \text{ a.u.} \end{aligned}$$

Exercise 3.24

Solution:

$$\begin{cases} C_{11} = C_1 = [2(1+S_{12})]^{-1/2} \\ C_{21} = C_1 = [2(1+S_{12})]^{-1/2} \end{cases}$$

$$\begin{cases} C_{12} = C_2 = [2(1-S_{12})]^{-1/2} \\ C_{22} = -C_2 = -[2(1-S_{12})]^{-1/2} \end{cases}$$

Because $P_{\mu\nu} = 2\sum_{a=1}^{1} C_{\mu a} C_{\nu a}^*$

$$\begin{cases} P_{11} = 2C_{11}C_{11}^* = (1+S_{12})^{-1} \\ P_{12} = 2C_{11}C_{21}^* = (1+S_{12})^{-1} \\ P_{21} = 2C_{21}C_{11}^* = (1+S_{12})^{-1} \\ P_{22} = 2C_{21}C_{21}^* = (1+S_{12})^{-1} \end{cases}$$

$$\mathbf{P} = (1+S_{12})^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

The corresponding density matrix for H_2^+ is

$$\mathbf{P}' = \frac{1}{2}\mathbf{P} = [2(1+S_{12})]^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

Exercise 3.25

Solution:

$$\begin{aligned} F_{11} &= H_{11}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma}\Big[(\phi_1\phi_1|\phi_\sigma\phi_\lambda) - \frac{1}{2}(\phi_1\phi_\lambda|\phi_\sigma\phi_1)\Big] \\ &= H_{11}^{\text{core}} + P_{11}\Big[(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)\Big] \\ &\quad + P_{12}\Big[(\phi_1\phi_1|\phi_2\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_2\phi_1)\Big] \\ &\quad + P_{21}\Big[(\phi_1\phi_1|\phi_1\phi_2) - \frac{1}{2}(\phi_1\phi_2|\phi_1\phi_1)\Big] \\ &\quad + P_{22}\Big[(\phi_1\phi_1|\phi_2\phi_2) - \frac{1}{2}(\phi_1\phi_2|\phi_2\phi_1)\Big] \end{aligned}$$

Because

$$(\phi_1\phi_1|\phi_2\phi_1) = (\phi_1\phi_1|\phi_2\phi_1) = (\phi_1\phi_1|\phi_1\phi_2) = (\phi_1\phi_2|\phi_1\phi_1)$$

$$F_{11} = H_{11}^{\text{core}} + (1+S_{12})^{-1}\Big[\frac{1}{2}(\phi_1\phi_1|\phi_2\phi_1) + (\phi_1\phi_1|\phi_1\phi_2) + (\phi_1\phi_1|\phi_2\phi_2) - \frac{1}{2}(\phi_1\phi_2|\phi_2\phi_1)\Big]$$

Exercise 3.33

Solution:

$$f^\alpha(\mathbf{r}_1) = \int \mathrm{d}\omega_1\ \alpha^*(\omega_1) f(\mathbf{r}_1,\omega_1)\alpha(\omega_1)$$

$$f(\mathbf{r}_1,\omega_1) = h(1) + \sum_a \int \mathrm{d}\mathbf{x}_2\ \chi_a^*(2) r_{12}^{-1}(1-\mathscr{P}_{12})\chi_a(2)$$

Therefore

$$f^{\alpha}(\mathbf{r}_1) = \int \mathrm{d}\omega_1 \ \alpha^*(\omega_1)h(1)\alpha(\omega_1) + \int \mathrm{d}\omega_1 \ \alpha^*(\omega_1)\left[\sum_a \int \mathrm{d}\mathbf{x}_2 \ \chi_a^*(2)r_{12}^{-1}(1-\mathscr{P}_{12})\chi_a(2)\right]\alpha(\omega_1)$$

The first term, where core-Hamiltonian has nothing to do with spin:

$$\int \mathrm{d}\omega_1 \ \alpha^*(\omega_1)h(1)\alpha(\omega_1) = h(1)$$

The next term can be divided into two parts based on spin:

$$\begin{aligned}
\sum_a^{N^\alpha} \int \mathrm{d}\omega_1\mathbf{x}_2 \ \alpha^*(\omega_1)\chi_a^*(\mathbf{x}_2)r_{12}^{-1}(1-\mathscr{P}_{12})\chi_a(\mathbf{x}_2)\alpha(\omega_1) &= \sum_a^{N^\alpha} \int \mathrm{d}\omega_1\mathbf{x}_2 \ \alpha^*(\omega_1)\chi_a^*(\mathbf{x}_2)r_{12}^{-1}\chi_a(\mathbf{x}_2)\alpha(\omega_1) \\
&\quad - \sum_a^{N^\alpha} \int \mathrm{d}\omega_1\mathbf{x}_2 \ \alpha^*(\omega_1)\chi_a^*(\mathbf{x}_2)r_{12}^{-1}\chi_a(\mathbf{x}_1)\alpha(\omega_2) \\
&= \sum_a^{N^\alpha} \int \mathrm{d}\omega_1\mathbf{r}_2\omega_2 \ \alpha^*(\omega_1)\alpha^*(\omega_2)\psi_a^{*\alpha}(\mathbf{r}_2)r_{12}^{-1}\alpha(\omega_2)\psi_a^{\alpha}(\mathbf{r}_2)\alpha(\omega_1) \\
&\quad - \sum_a^{N^\alpha} \int \mathrm{d}\omega_1\mathbf{r}_2\omega_2 \ \alpha^*(\omega_1)\alpha^*(\omega_2)\psi_a^{*\alpha}(\mathbf{r}_2)r_{12}^{-1}\alpha(\omega_1)\psi_a^{\alpha}(\mathbf{r}_1)\alpha(\omega_2) \\
&= \sum_a^{N^\alpha} \int \mathrm{d}\mathbf{r}_2 \ \psi_a^{*\alpha}(\mathbf{r}_2)r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_2) \\
&\quad - \sum_a^{N^\alpha} \int \mathrm{d}\mathbf{r}_2 \ \psi_a^{*\alpha}(\mathbf{r}_2)r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_1) \\
&= \sum_a^{N^\alpha} \left[J_a^{\alpha}(1) - K_a^{\alpha}(1)\right]
\end{aligned}$$

Similarly

$$\begin{aligned}
\sum_a^{N^\beta} \int \mathrm{d}\omega_1\mathbf{x}_2 \ \alpha^*(\omega_1)\chi_a^*(\mathbf{x}_2)r_{12}^{-1}(1-\mathscr{P}_{12})\chi_a(\mathbf{x}_2)\alpha(\omega_1) &= \sum_a^{N^\beta} \int \mathrm{d}\omega_1\mathbf{r}_2\omega_2 \ \alpha^*(\omega_1)\beta^*(\omega_2)\psi_a^{*\beta}(\mathbf{r}_2)r_{12}^{-1}\beta(\omega_2)\psi_a^{\beta}(\mathbf{r}_2)\alpha(\omega_1) \\
&\quad - \sum_a^{N^\beta} \int \mathrm{d}\omega_1\mathbf{r}_2\omega_2 \ \alpha^*(\omega_1)\beta^*(\omega_2)\psi_a^{*\beta}(\mathbf{r}_2)r_{12}^{-1}\beta(\omega_1)\psi_a^{\beta}(\mathbf{r}_1)\alpha(\omega_2) \\
&= \sum_a^{N^\beta} \int \mathrm{d}\mathbf{r}_2 \ \psi_a^{*\beta}(\mathbf{r}_2)r_{12}^{-1}\psi_a^{\beta}(\mathbf{r}_2) \\
&= \sum_a^{N^\beta} J_a^{\beta}(1)
\end{aligned}$$

So the result is

$$f^{\alpha}(\mathbf{r}_1) = h(1) + \sum_a^{N^\alpha} \left[J_a^{\alpha}(1) - K_a^{\alpha}(1)\right] + \sum_a^{N^\beta} J_a^{\beta}(1)$$

Exercise 3.35

Solution:

$$\int \mathrm{d}\mathbf{r}_1 \ \psi_i^{*\alpha} h \psi_i^{\alpha} = h_{ii}^{\alpha}$$

$$\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ \psi_i^{*\alpha}(1)\psi_a^{*\alpha}(2)r_{12}^{-1}\psi_a^{\alpha}(2)\psi_i^{\alpha}(1) = J_{ia}^{\alpha\alpha}$$

$$\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ \psi_i^{*\alpha}(1)\psi_a^{*\alpha}(2)r_{12}^{-1}\psi_a^{\alpha}(1)\psi_i^{\alpha}(2) = K_{ia}^{\alpha\alpha}$$

$$\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ \psi_i^{*\alpha}(1)\psi_a^{*\beta}(2)r_{12}^{-1}\psi_a^{\beta}(2)\psi_i^{\alpha}(1) = J_{ia}^{\alpha\beta}$$

Therefore

$$\begin{aligned}
\varepsilon_i^{\alpha} &= (\psi_i^{\alpha}|f^{\alpha}|\psi_i^{\alpha}) \\
&= h_{ii}^{\alpha} + \sum_a^{N^\alpha}(J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) + \sum_a^{N^\beta} J_{ia}^{\alpha\beta} \\
\varepsilon_i^{\beta} &= (\psi_i^{\beta}|f^{\beta}|\psi_i^{\beta}) \\
&= h_{ii}^{\beta} + \sum_a^{N^\beta}(J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) + \sum_a^{N^\alpha} J_{ia}^{\beta\alpha}
\end{aligned}$$

$$\begin{aligned}
E_0 = \sum_i^{N^\alpha}\varepsilon_i^{\alpha} + \sum_i^{N^\beta}\varepsilon_i^{\beta} - \frac{1}{2}\sum_i^{N^\alpha}\sum_a^{N^\alpha}(J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) \\
- \frac{1}{2}\sum_i^{N^\beta}\sum_a^{N^\beta}(J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) - \sum_i^{N^\alpha}\sum_a^{N^\beta} J_{ia}^{\alpha\beta}
\end{aligned}$$

Exercise 3.36

Solution:

$$\begin{aligned}
\int \rho^S(\mathbf{r})\,\mathrm{d}\mathbf{r} &= \int \big(\rho^{\alpha}(\mathbf{r}) - \rho^{\beta}(\mathbf{r})\big)\,\mathrm{d}\mathbf{r} \\
&= N^\alpha - N^\beta
\end{aligned}$$

Because

$$\mathscr{S}_z\,|\Psi\rangle = \frac{1}{2}\big(N^\alpha - N^\beta\big)\,|\Psi\rangle$$

So the eigenvalue(expectation value) of $\mathscr{S}_z$ is $\frac{1}{2}\big(N^\alpha - N^\beta\big)$.

$$\int \rho^S(\mathbf{r})\,\mathrm{d}\mathbf{r} = 2\langle\mathscr{S}_z\rangle$$

Exercise 3.37

Solution:

$$\rho^{\alpha}(\mathbf{r}) = \sum_a^{N^\alpha}|\psi_a^{\alpha}(\mathbf{r})|^2 = \sum_a^{N^\alpha}\psi_a^{\alpha *}(\mathbf{r})\cdot\psi_a^{\alpha}(\mathbf{r})$$

$$\psi_a^{\alpha} = \sum_\mu C_{\mu a}^{\alpha}\phi_\mu$$

$$\begin{aligned}
\rho^{\alpha}(\mathbf{r}) &= \sum_a^{N^\alpha}\left(\sum_\nu C_{\nu a}^{\alpha *}\phi_\nu^*(\mathbf{r})\cdot\sum_\mu C_{\mu a}^{\alpha}\phi_\mu(\mathbf{r})\right) \\
&= \sum_{\mu\nu}\sum_a^{N^\alpha} C_{\mu a}^{\alpha}C_{\nu a}^{\alpha *}\cdot\phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r})
\end{aligned}$$

Define density matrix for α electrons

$$P^{\alpha}_{\mu\nu} = \sum_{a}^{N^{\alpha}} C^{\alpha}_{\mu a} C^{\alpha *}_{\nu a}$$

$$\rho^{\alpha}(\mathbf{r}) = \sum_{\mu\nu} P^{\alpha}_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi^{*}_{\nu}(\mathbf{r})$$

Exercise 3.38

Solution:

$$\langle \mathscr{O}_1 \rangle = \sum_{i}^{N} \langle \Psi \,|\, h(i) \,|\, \Psi \rangle = \sum_{i}^{N} \langle \chi_i \,|\, h(i) \,|\, \chi_i \rangle$$

$$\sum_{i}^{N} \langle \chi_i \,|\, h(i) \,|\, \chi_i \rangle = \sum_{i}^{N^{\alpha}} \langle \psi^{\alpha}_i \,|\, h(i) \,|\, \psi^{\alpha}_i \rangle + \sum_{i}^{N^{\beta}} \left\langle \psi^{\beta}_i \,\middle|\, h(i) \,\middle|\, \psi^{\beta}_i \right\rangle$$

$$\begin{aligned} \sum_{i}^{N^{\alpha}} \langle \psi^{\alpha}_i \,|\, h(i) \,|\, \psi^{\alpha}_i \rangle &= \sum_{i}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} C_{\mu i} C^{*}_{\nu i} (\nu|h|\mu) \\ &= \sum_{\mu} \sum_{\nu} P^{\alpha}_{\mu\nu} (\nu|h|\mu) \end{aligned}$$

With the same procedure

$$\sum_{i}^{N^{\beta}} \left\langle \psi^{\beta}_i \,\middle|\, h(i) \,\middle|\, \psi^{\beta}_i \right\rangle = \sum_{\mu} \sum_{\nu} P^{\beta}_{\mu\nu} (\nu|h|\mu)$$

$$\begin{aligned} \langle \mathscr{O}_1 \rangle &= \sum_{\mu} \sum_{\nu} P^{\alpha}_{\mu\nu} (\nu|h|\mu) + \sum_{\mu} \sum_{\nu} P^{\beta}_{\mu\nu} (\nu|h|\mu) \\ &= \sum_{\mu} \sum_{\nu} P^{\mathrm{T}}_{\mu\nu} (\nu|h|\mu) \end{aligned}$$

Exercise 3.39

Solution:

$$\begin{aligned} \langle \hat{\rho}^{S} \rangle &= \left\langle \Psi_0 \,\middle|\, \hat{\rho}^{S} \,\middle|\, \Psi_0 \right\rangle \\ &= \frac{2}{N!} \sum_{ij}^{N!} \sum_{m}^{N} (-1)^{p_i} (-1)^{p_j} \int \mathrm{d}\mathbf{x}_1 \ldots \mathbf{x}_N \; \mathscr{P}_i \{\chi_1(1) \ldots \chi_k(N)\} \\ &\qquad \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \mathscr{P}_j \{\chi_1(1) \ldots \chi_k(N)\} \end{aligned}$$

The permutation $\mathscr{P}_i$ and $\mathscr{P}_j$ are required to be the same. Otherwise there must be electrons occupying different spin orbitals(not the electron m), and the corresponding term is equal to zero.

$$
\begin{aligned}
\langle\hat{\rho}^S\rangle &= \frac{2}{N!}\sum_i^{N!}\sum_m^N \int \mathrm{d}\mathbf{x}_1\ldots\mathbf{x}_N \;\mathscr{P}_i\{\chi_1(1)\ldots\chi_k(N)\} \\
&\qquad\qquad \delta(\mathbf{r}_m-\mathbf{R})s_z(m)\mathscr{P}_i\{\chi_1(1)\ldots\chi_k(N)\} \\
&= \frac{2}{N}\sum_i^N\sum_m^N \int \mathrm{d}\mathbf{x}_m\; \chi_i(m)\delta(\mathbf{r}_m-\mathbf{R})s_z(m)\chi_i(m) \\
&= \frac{2}{N}\sum_m^N \Bigg[\sum_i^{N^\alpha}\int \mathrm{d}\mathbf{r}_m\,\mathrm{d}\omega_m\; \psi_i^\alpha(m)\alpha(\omega_m)\delta(\mathbf{r}_m-\mathbf{R})s_z(m)\psi_i^\alpha(m)\alpha(\omega_m) \\
&\qquad + \sum_i^{N^\beta}\int \mathrm{d}\mathbf{r}_m\,\mathrm{d}\omega_m\; \psi_i^\beta(m)\beta(\omega_m)\delta(\mathbf{r}_m-\mathbf{R})s_z(m)\psi_i^\beta(m)\beta(\omega_m)\Bigg] \\
&= \frac{2}{N}\sum_m^N \Bigg[\frac{1}{2}\sum_i^{N^\alpha}\int \mathrm{d}\mathbf{r}_m\; \psi_i^\alpha(m)\delta(\mathbf{r}_m-\mathbf{R})\psi_i^\alpha(m) \\
&\qquad - \frac{1}{2}\sum_i^{N^\beta}\int \mathrm{d}\mathbf{r}_m\; \psi_i^\beta(m)\delta(\mathbf{r}_m-\mathbf{R})\psi_i^\beta(m)\Bigg] \\
&= \sum_i^{N^\alpha}\int \mathrm{d}\mathbf{R}\; \psi_i^\alpha(\mathbf{R})\psi_i^\alpha(\mathbf{R}) - \sum_i^{N^\beta}\int \mathrm{d}\mathbf{R}\; \psi_i^\beta(\mathbf{R})\psi_i^\beta(\mathbf{R}) \\
&= \rho^\alpha(\mathbf{R}) - \rho^\beta(\mathbf{R}) \\
&= \rho^S(\mathbf{R})
\end{aligned}
$$

Exercise 3.40

Solution:

$$
\begin{aligned}
E_0 = \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \frac{1}{2}\sum_a^{N^\alpha}\sum_b^{N^\alpha}\left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}\right) \\
+ \frac{1}{2}\sum_a^{N^\beta}\sum_b^{N^\beta}\left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}\right) + \sum_a^{N^\alpha}\sum_b^{N^\beta} J_{ab}^{\alpha\beta}
\end{aligned}
$$

$$h_{aa}^\alpha = (\psi_a^\alpha|h|\psi_a^\alpha) = \sum_{\mu\nu} C_{\mu a}^{\alpha *}(\phi_\mu|h|\phi_\nu)C_{\nu a}^\alpha$$

$$\sum_a^{N^\alpha} h_{aa}^\alpha = \sum_a^{N^\alpha}\sum_{\mu\nu} C_{\mu a}^{\alpha *}(\phi_\mu|h|\phi_\nu)C_{\nu a}^\alpha = \sum_{\mu\nu} P_{\nu\mu}^\alpha H_{\mu\nu}^{core}$$

In the same way,

$$\sum_a^{N^\beta} h_{aa}^\beta = \sum_a^{N^\beta}\sum_{\mu\nu} C_{\mu a}^{\beta *}(\phi_\mu|h|\phi_\nu)C_{\nu a}^\beta = \sum_{\mu\nu} P_{\nu\mu}^\beta H_{\mu\nu}^{core}$$

$$J_{ab}^{\alpha\alpha} = \left(\psi_a^\alpha\psi_a^\alpha|\psi_b^\alpha\psi_b^\alpha\right) = \sum_{\mu\nu\lambda\sigma} C_{\mu a}^{\alpha *}C_{\nu a}^\alpha C_{\lambda b}^{\alpha *}C_{\sigma b}^\alpha(\mu\nu|\lambda\sigma)$$

$$K_{ab}^{\alpha\alpha} = \left(\psi_a^\alpha\psi_b^\alpha|\psi_b^\alpha\psi_a^\alpha\right) = \sum_{\mu\nu\lambda\sigma} C_{\mu a}^{\alpha *}C_{\nu a}^\alpha C_{\lambda b}^{\alpha *}C_{\sigma b}^\alpha(\mu\lambda|\sigma\nu)$$

$$J_{ab}^{\beta\beta} = \left(\psi_a^\beta\psi_a^\beta|\psi_b^\beta\psi_b^\beta\right) = \sum_{\mu\nu\lambda\sigma} C_{\mu a}^{\beta *}C_{\nu a}^\beta C_{\lambda b}^{\beta *}C_{\sigma b}^\beta(\mu\nu|\lambda\sigma)$$

$$K_{ab}^{\beta\beta} = \left(\psi_a^\beta \psi_b^\beta | \psi_b^\beta \psi_a^\beta\right) = \sum_{\mu\nu\lambda\sigma} C_{\mu a}^{\beta *} C_{\nu a}^{\beta} C_{\lambda b}^{\beta *} C_{\sigma b}^{\beta} (\mu\lambda|\sigma\nu)$$

$$J_{ab}^{\alpha\beta} = \left(\psi_a^\alpha \psi_a^\alpha | \psi_b^\beta \psi_b^\beta\right) = \sum_{\mu\nu\lambda\sigma} C_{\mu a}^{\alpha *} C_{\nu a}^{\alpha} C_{\lambda b}^{\beta *} C_{\sigma b}^{\beta} (\mu\nu|\lambda\sigma)$$

$$\begin{aligned}
\frac{1}{2}\sum_a^{N^\alpha}\sum_b^{N^\alpha}\left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}\right) &= \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\sum_a^{N^\alpha} C_{\mu a}^{\alpha *} C_{\nu a}^{\alpha} \sum_b^{N^\alpha} C_{\lambda b}^{\alpha *} C_{\sigma b}^{\alpha}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big] \\
&= \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\alpha}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big]
\end{aligned}$$

$$\begin{aligned}
\frac{1}{2}\sum_a^{N^\beta}\sum_b^{N^\beta}\left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}\right) &= \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\sum_a^{N^\beta} C_{\mu a}^{\beta *} C_{\nu a}^{\beta} \sum_b^{N^\beta} C_{\lambda b}^{\beta *} C_{\sigma b}^{\beta}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big] \\
&= \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\beta} P_{\sigma\lambda}^{\beta}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big]
\end{aligned}$$

$$\begin{aligned}
\sum_a^{N^\alpha}\sum_b^{N^\beta} J_{ab}^{\alpha\beta} &= \sum_{\mu\nu\lambda\sigma}\sum_a^{N^\alpha} C_{\mu a}^{\alpha *} C_{\nu a}^{\alpha} \sum_b^{N^\beta} C_{\lambda b}^{\beta *} C_{\sigma b}^{\beta}(\mu\nu|\lambda\sigma) \\
&= \sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\beta}(\mu\nu|\lambda\sigma)
\end{aligned}$$

Therefore, the total energy is

$$\begin{aligned}
E_0 = &\sum_{\mu\nu} P_{\nu\mu}^{\alpha} H_{\mu\nu}^{core} + \sum_{\mu\nu} P_{\nu\mu}^{\beta} H_{\mu\nu}^{core} + \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\alpha}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big] \\
&+ \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\beta} P_{\sigma\lambda}^{\beta}\big[(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\big] + \sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\beta}(\mu\nu|\lambda\sigma) \\
= &\frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}^{\mathrm{T}} H_{\mu\nu}^{core} + \frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}^{\alpha} H_{\mu\nu}^{core} + \frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}^{\beta} H_{\mu\nu}^{core} \\
&+ \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\alpha}\Big[\big(P_{\sigma\lambda}^{\alpha} + P_{\sigma\lambda}^{\beta}\big)(\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha}(\mu\lambda|\sigma\nu)\Big] \\
&+ \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\sigma\lambda}^{\beta}\Big[\big(P_{\nu\mu}^{\alpha} + P_{\nu\mu}^{\beta}\big)(\mu\nu|\lambda\sigma) - P_{\nu\mu}^{\beta}(\mu\lambda|\sigma\nu)\Big]
\end{aligned}$$

Because $\mu, \nu, \lambda, \sigma$ are dumb variables, and $(\mu\nu|\lambda\sigma) = (\lambda\sigma|\mu\nu)$. The last term can be expressed as

$$\frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\nu\mu}^{\beta}\Big[\big(P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta}\big)(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\beta}(\mu\lambda|\sigma\nu)\Big]$$

$$
\begin{aligned}
E_0 &= \frac{1}{2}\sum_{\mu\nu} P^{\mathrm{T}}_{\nu\mu} H^{core}_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu} P^{\alpha}_{\nu\mu} H^{core}_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu} P^{\beta}_{\nu\mu} H^{core}_{\mu\nu} \\
&\quad + \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P^{\alpha}_{\nu\mu}\Big[\big(P^{\alpha}_{\sigma\lambda} + P^{\beta}_{\sigma\lambda}\big)(\mu\nu|\lambda\sigma) - P^{\alpha}_{\sigma\lambda}(\mu\lambda|\sigma\nu)\Big] \\
&\quad + \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P^{\beta}_{\nu\mu}\Big[\big(P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\lambda\sigma}\big)(\mu\nu|\lambda\sigma) - P^{\beta}_{\lambda\sigma}(\mu\lambda|\sigma\nu)\Big] \\
&= \frac{1}{2}\sum_{\mu\nu} P^{\mathrm{T}}_{\nu\mu} H^{core}_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu} P^{\alpha}_{\nu\mu}\Big\{H^{core}_{\mu\nu} + \sum_{\mu\nu}\Big[P^{\mathrm{T}}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\alpha}_{\sigma\lambda}(\mu\lambda|\sigma\nu)\Big]\Big\} \\
&\quad + \frac{1}{2}\sum_{\mu\nu} P^{\beta}_{\nu\mu}\Big\{H^{core}_{\mu\nu} + \sum_{\mu\nu}\Big[P^{\mathrm{T}}_{\sigma\lambda}(\mu\nu|\lambda\sigma) - P^{\beta}_{\sigma\lambda}(\mu\lambda|\sigma\nu)\Big]\Big\} \\
&= \frac{1}{2}\sum_{\mu\nu}\Big[P^{\mathrm{T}}_{\nu\mu} H^{core}_{\mu\nu} + P^{\alpha}_{\nu\mu} F^{\alpha}_{\mu\nu} + P^{\beta}_{\nu\mu} F^{\beta}_{\mu\nu}\Big]
\end{aligned}
$$

4 Chapter 4

Singly-excited singlet spin-adapted configurations:

$$
|{}^1\Psi^{r}_{a}\rangle = 2^{-1/2}\Big(\,|\Psi^{\bar{r}}_{\bar{a}}\rangle + |\Psi^{r}_{a}\rangle\,\Big)
$$

Doubly-excited singlet spin-adapted configurations:

$$
\begin{aligned}
|{}^1\Psi^{rr}_{aa}\rangle &= |\Psi^{r\bar{r}}_{a\bar{a}}\rangle \\
|{}^1\Psi^{rs}_{aa}\rangle &= 2^{-1/2}\Big(\,|\Psi^{r\bar{s}}_{a\bar{a}}\rangle + |\Psi^{s\bar{r}}_{a\bar{a}}\rangle\,\Big) \\
|{}^1\Psi^{rr}_{ab}\rangle &= 2^{-1/2}\Big(\,|\Psi^{\bar{r}r}_{\bar{a}b}\rangle + |\Psi^{r\bar{r}}_{a\bar{b}}\rangle\,\Big) \\
|{}^A\Psi^{rs}_{ab}\rangle &= (12)^{-1/2}\Big(2\,|\Psi^{rs}_{ab}\rangle + 2\,|\Psi^{\bar{r}\bar{s}}_{\bar{a}\bar{b}}\rangle - |\Psi^{\bar{s}r}_{\bar{a}b}\rangle + |\Psi^{\bar{r}s}_{\bar{a}b}\rangle + |\Psi^{r\bar{s}}_{a\bar{b}}\rangle - |\Psi^{s\bar{r}}_{a\bar{b}}\rangle\,\Big) \\
|{}^B\Psi^{rs}_{ab}\rangle &= \frac{1}{2}\Big(\,|\Psi^{\bar{s}r}_{\bar{a}b}\rangle + |\Psi^{\bar{r}s}_{\bar{a}b}\rangle + |\Psi^{r\bar{s}}_{a\bar{b}}\rangle + |\Psi^{s\bar{r}}_{a\bar{b}}\rangle\,\Big)
\end{aligned}
$$

$$
\begin{aligned}
\big\langle {}^1\Psi^{r}_{a}\,\big|\,\mathscr{H} - E_0\,\big|\,{}^1\Psi^{s}_{b}\big\rangle = \frac{1}{2}\Big(&\big\langle \Psi^{r}_{a}\,|\,\mathscr{H} - E_0\,|\,\Psi^{s}_{b}\big\rangle + \big\langle \Psi^{r}_{a}\,\big|\,\mathscr{H} - E_0\,\big|\,\Psi^{\bar{s}}_{\bar{b}}\big\rangle \\
&+ \big\langle \Psi^{\bar{r}}_{\bar{a}}\,\big|\,\mathscr{H} - E_0\,\big|\,\Psi^{s}_{b}\big\rangle + \big\langle \Psi^{\bar{r}}_{\bar{a}}\,\big|\,\mathscr{H} - E_0\,\big|\,\Psi^{\bar{s}}_{\bar{b}}\big\rangle\Big)
\end{aligned}
$$

	$\langle \Psi^{r}_{a}\,|\,\mathscr{O}_1\,|\,\Psi^{s}_{b}\rangle$	$\langle \Psi^{r}_{a}\,|\,\mathscr{O}_2\,|\,\Psi^{s}_{b}\rangle$
$a \neq b, r \neq s$	0	$\langle rb\,\Vert\,as\rangle$
$a = b, r \neq s$	$\langle r\,|\,h\,|\,s\rangle$	$\sum_{n}^{N}\langle rn\,\Vert\,sn\rangle - \langle ra\,\Vert\,sa\rangle$
$a \neq b, r = s$	$-\langle b\,|\,h\,|\,a\rangle$	$-\sum_{n}^{N}\langle bn\,\Vert\,an\rangle - \langle br\,\Vert\,ar\rangle$
$a = b, r = s$	$\sum_{m}^{N}\langle m\,|\,h\,|\,m\rangle - \langle a\,|\,h\,|\,a\rangle + \langle r\,|\,h\,|\,r\rangle$	$\frac{1}{2}\sum_{m,n}^{N}\langle mn\,\Vert\,mn\rangle - \sum_{n}^{N}\langle an\,\Vert\,an\rangle + \sum_{n}^{N}\langle rn\,\Vert\,rn\rangle - \langle ra\,\Vert\,ra\rangle$

	$\left\langle \Psi_a^r \middle| \mathscr{O}_1 \middle| \Psi_{\bar{b}}^{\bar{s}} \right\rangle$	$\left\langle \Psi_a^r \middle| \mathscr{O}_2 \middle| \Psi_{\bar{b}}^{\bar{s}} \right\rangle$
$a \neq b, r \neq s$	0	$\left\langle r\bar{b} \middle\| a\bar{s} \right\rangle$
$a = b, r \neq s$	0	$\langle r\bar{a} \| a\bar{s} \rangle$
$a \neq b, r = s$	0	$\left\langle r\bar{b} \middle\| a\bar{r} \right\rangle$
$a = b, r = s$	0	$\langle r\bar{a} \| a\bar{r} \rangle$

	$\langle \Psi_{\bar{a}}^{\bar{r}} \mid \mathscr{O}_1 \mid \Psi_b^s \rangle$	$\langle \Psi_{\bar{a}}^{\bar{r}} \mid \mathscr{O}_2 \mid \Psi_b^s \rangle$
$a \neq b, r \neq s$	0	$\langle \bar{r}b \| \bar{a}s \rangle$
$a = b, r \neq s$	0	$\langle a\bar{r} \| s\bar{a} \rangle$
$a \neq b, r = s$	0	$\langle \bar{r}b \| \bar{a}r \rangle$
$a = b, r = s$	0	$\langle a\bar{r} \| r\bar{a} \rangle$

	$\left\langle \Psi_{\bar{a}}^{\bar{r}} \middle| \mathscr{O}_1 \middle| \Psi_{\bar{b}}^{\bar{s}} \right\rangle$	$\left\langle \Psi_{\bar{a}}^{\bar{r}} \middle| \mathscr{O}_2 \middle| \Psi_{\bar{b}}^{\bar{s}} \right\rangle$
$a \neq b, r \neq s$	0	$\left\langle \bar{r}\bar{b} \middle\| \bar{a}\bar{s} \right\rangle$
$a = b, r \neq s$	$\langle \bar{r} \mid h \mid \bar{s} \rangle$	$\sum_n^N \langle \bar{r}n \| \bar{s}n \rangle - \langle \bar{r}\bar{a} \| \bar{s}\bar{a} \rangle$
$a \neq b, r = s$	$-\left\langle \bar{b} \middle| h \middle| \bar{a} \right\rangle$	$-\sum_n^N \left\langle \bar{b}n \middle\| \bar{a}n \right\rangle - \left\langle \bar{b}\bar{r} \middle\| \bar{a}\bar{r} \right\rangle$
$a = b, r = s$	$\sum_m^N \langle m \mid h \mid m \rangle - \langle \bar{a} \mid h \mid \bar{a} \rangle + \langle \bar{r} \mid h \mid \bar{r} \rangle$	$\frac{1}{2}\sum_{m,n}^N \langle mn \| mn \rangle - \sum_n^N \langle \bar{a}n \| \bar{a}n \rangle + \sum_n^N \langle \bar{r}n \| \bar{r}n \rangle - \langle \bar{r}\bar{a} \| \bar{r}\bar{a} \rangle$

In addition, only when $a = b$ and $r = s$, the following terms are not zero:

$$\langle \Psi_a^r \mid E_0 \mid \Psi_b^s \rangle = \left\langle \Psi_{\bar{a}}^{\bar{r}} \middle| E_0 \middle| \Psi_{\bar{b}}^{\bar{s}} \right\rangle = E_0$$

With the above results, we can evaluate the matrix elements.
$a \neq b, r \neq s$

$$\begin{aligned}\left\langle {}^1\Psi_a^r \middle| \mathscr{H} - E_0 \middle| {}^1\Psi_b^s \right\rangle &= \frac{1}{2}\Big(\langle rb \| as \rangle + \left\langle r\bar{b} \middle\| a\bar{s} \right\rangle + \langle \bar{r}b \| \bar{a}s \rangle + \left\langle \bar{r}\bar{b} \middle\| \bar{a}\bar{s} \right\rangle \Big) \\ &= 2(ra|bs) - (rs|ba)\end{aligned}$$

$a = b, r \neq s$

$$\begin{aligned}\left\langle {}^1\Psi_a^r \middle| \mathscr{H} - E_0 \middle| {}^1\Psi_b^s \right\rangle = \frac{1}{2}\Big(&\langle r \mid h \mid s \rangle + \sum_n^N \langle rn \| sn \rangle - \langle ra \| sa \rangle + \langle r\bar{a} \| a\bar{s} \rangle \\ &+ \langle a\bar{r} \| s\bar{a} \rangle + \langle \bar{r} \mid h \mid \bar{s} \rangle + \sum_n^N \langle \bar{r}n \| \bar{s}n \rangle - \langle \bar{r}\bar{a} \| \bar{s}\bar{a} \rangle \Big)\end{aligned}$$

$$\langle r \mid h \mid s \rangle + \sum_n^N \langle rn \| sn \rangle = \langle r \mid f \mid s \rangle$$

$$\langle \bar{r} \,|\, h \,|\, \bar{s} \rangle + \sum_{n}^{N} \langle \bar{r}n \,\|\, \bar{s}n \rangle = \langle \bar{r} \,|\, f \,|\, \bar{s} \rangle$$

These two terms are the non-diagonal of Fock matrix, which are zero. The remaining is

$$\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = \frac{1}{2}\Big(4(ra|as) - 2(rs|aa)\Big)$$

Because $a = b$, we can be free to substitute a with b.

$$\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = 2(ra|bs) - (rs|ba)$$

With the same procedure, when $a \neq b$ and $r = s$, the result is

$$\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = 2(ra|bs) - (rs|ba)$$

$a = b, r = s$

$$\begin{aligned}
\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = \frac{1}{2}\Big(&\sum_{m}^{N} \langle m \,|\, h \,|\, m \rangle - \langle a \,|\, h \,|\, a \rangle + \langle r \,|\, h \,|\, r \rangle + \frac{1}{2}\sum_{m,n}^{N} \langle mn \,\|\, mn \rangle \\
&- \sum_{n}^{N} \langle an \,\|\, an \rangle + \sum_{n}^{N} \langle rn \,\|\, rn \rangle - \langle ra \,\|\, ra \rangle + \langle r\bar{a} \,\|\, a\bar{r} \rangle \\
&+ \langle a\bar{r} \,\|\, r\bar{a} \rangle + \sum_{m}^{N} \langle m \,|\, h \,|\, m \rangle - \langle \bar{a} \,|\, h \,|\, \bar{a} \rangle + \langle \bar{r} \,|\, h \,|\, \bar{r} \rangle \\
&+ \frac{1}{2}\sum_{m,n}^{N} \langle mn \,\|\, mn \rangle - \sum_{n}^{N} \langle \bar{a}n \,\|\, \bar{a}n \rangle + \sum_{n}^{N} \langle \bar{r}n \,\|\, \bar{r}n \rangle \\
&- \langle \bar{r}\bar{a} \,\|\, \bar{r}\bar{a} \rangle - 2E_0\Big) \\
= \frac{1}{2}\Big(& - 2\varepsilon_a + 2\varepsilon_r + 4(ra|ar) - 2(rr|aa)\Big)
\end{aligned}$$

After selective substitutions, the result is

$$\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = -\varepsilon_a + \varepsilon_r + 2(ra|bs) - (rs|ba)$$

And we can conclude that

$$\left\langle {}^1\Psi_a^r \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_b^s \right\rangle = (-\varepsilon_a + \varepsilon_r)\delta_{ab}\delta_{rs} + 2(ra|bs) - (rs|ba)$$

$$\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_{aa}^{rr} \right\rangle &= \left\langle \Psi_0 \,\middle|\, \mathscr{O}_1 \,\middle|\, \Psi_{a\bar{a}}^{r\bar{r}} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{O}_2 \,\middle|\, \Psi_{a\bar{a}}^{r\bar{r}} \right\rangle \\
&= \langle a\bar{a} \,\|\, r\bar{r} \rangle \\
&= [ar|\bar{a}\bar{r}] - [a\bar{r}|\bar{a}r] \\
&= K_{ar}
\end{aligned}$$

$$\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_{aa}^{rs} \right\rangle &= \frac{1}{\sqrt{2}}\Big(\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big(\left\langle \Psi_0 \,\middle|\, \mathscr{O}_2 \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{O}_2 \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big([ar|\bar{a}\bar{s}] - [a\bar{s}|\bar{a}r] + [as|\bar{a}\bar{r}] - [a\bar{r}|\bar{a}s]\Big) \\
&= \frac{1}{\sqrt{2}}\Big((ar|as) + (as|ar)\Big) \\
&= \sqrt{2}(sa|ra)
\end{aligned}$$

Similarly,

$$
\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_{ab}^{rr} \right\rangle &= \frac{1}{\sqrt{2}}\Big(\left\langle \Psi_0 \,\middle|\, \mathscr{O}_2 \,\middle|\, \Psi_{\bar{a}a}^{\bar{r}r} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{O}_2 \,\middle|\, \Psi_{a\bar{b}}^{r\bar{r}} \right\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big([\bar{a}\bar{r}|br] - [\bar{a}r|b\bar{r}] + [ar|\bar{b}\bar{r}] - [a\bar{r}|\bar{b}r] \Big) \\
&= \frac{1}{\sqrt{2}}\Big((ar|ar) + (ar|br) \Big) \\
&= \sqrt{2}(rb|ra)
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^A\Psi_{ab}^{rs} \right\rangle &= \frac{1}{\sqrt{12}}\Big(2\left\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs} \right\rangle + 2\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{a}\bar{b}}^{\bar{r}\bar{s}} \right\rangle - \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{a}b}^{\bar{s}r} \right\rangle \\
&\qquad + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{a}b}^{\bar{r}s} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{r\bar{s}} \right\rangle - \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{s\bar{r}} \right\rangle \Big) \\
&= \frac{1}{\sqrt{12}}\Big[2\Big([ar|bs] - [as|br] \Big) + 2\Big([\bar{a}\bar{r}|\bar{b}\bar{s}] - [\bar{a}\bar{s}|\bar{b}\bar{r}] \Big) - [\bar{a}\bar{s}|br] + [\bar{a}r|b\bar{s}] \\
&\qquad + [\bar{a}\bar{r}|bs] - [\bar{a}s|b\bar{r}] + [ar|\bar{b}\bar{s}] - [a\bar{s}|\bar{b}r] - [as|\bar{b}\bar{r}] + [a\bar{r}|\bar{b}s] \Big] \\
&= \frac{1}{\sqrt{12}}\Big[2(ar|bs) - 2(as|br) + 2(ar|bs) - 2(as|br) \\
&\qquad - (as|br) + (ar|bs) + (ar|bs) - (as|br) \Big] \\
&= \sqrt{3}\Big[(ra|sb) - (rb|sa) \Big]
\end{aligned}
$$

$$
\begin{aligned}
\left\langle {}^1\Psi_{aa}^{rr} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_{aa}^{rr} \right\rangle &= \left\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{r}} \right\rangle - E_0 \\
&= \sum_m^N \langle m \,|\, h \,|\, m \rangle - \langle a \,|\, h \,|\, a \rangle - \langle \bar{a} \,|\, h \,|\, \bar{a} \rangle + \langle rh \,|\, r \rangle + \langle \bar{r} \,|\, h \,|\, \bar{r} \rangle \\
&\qquad + \frac{1}{2}\sum_{m,n}^N \langle mn \,\|\, mn \rangle - \sum_n^N \langle an \,\|\, an \rangle - \sum_n^N \langle \bar{a}n \,\|\, \bar{a}n \rangle \\
&\qquad + \langle \bar{a}a \,\|\, \bar{a}a \rangle + \sum_n^N \langle rn \,\|\, rn \rangle + \sum_n^N \langle \bar{r}n \,\|\, \bar{r}n \rangle + \langle \bar{r}r \,\|\, \bar{r}r \rangle \\
&\qquad - \langle ar \,\|\, ar \rangle - \langle a\bar{r} \,\|\, a\bar{r} \rangle - \langle \bar{a}r \,\|\, \bar{a}r \rangle \\
&\qquad - \langle \bar{a}\bar{r} \,\|\, \bar{a}\bar{r} \rangle - \left(\sum_m^N \langle m \,|\, h \,|\, m \rangle + \frac{1}{2}\sum_{m,n}^N \langle mn \,\|\, mn \rangle \right) \\
&= -2\varepsilon_a + 2\varepsilon_r + J_{aa} + J_{rr} - 4J_{ra} + 2K_{ra}
\end{aligned}
$$

$$
\begin{aligned}
\left\langle {}^1\Psi_{aa}^{rs} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^1\Psi_{aa}^{rs} \right\rangle = \frac{1}{2}\Big(&\left\langle \Psi_{a\bar{a}}^{r\bar{s}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle + \left\langle \Psi_{a\bar{a}}^{s\bar{r}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle \\
&+ \left\langle \Psi_{a\bar{a}}^{r\bar{s}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle + \left\langle \Psi_{a\bar{a}}^{s\bar{r}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle - 2E_0 \Big)
\end{aligned}
$$

For each part,

$$\begin{aligned}
\left\langle \Psi_{a\bar{a}}^{r\bar{s}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle = \sum_{m}^{N} &\langle m \,|\, h \,|\, m \rangle - \langle a \,|\, h \,|\, a \rangle - \langle \bar{a} \,|\, h \,|\, \bar{a} \rangle + \langle r \,|\, h \,|\, r \rangle + \langle \bar{s} \,|\, h \,|\, \bar{s} \rangle \\
&+ \frac{1}{2} \sum_{m,n} \langle mn \,\|\, mn \rangle - \sum_{n}^{N} \langle an \,\|\, an \rangle - \sum_{n}^{N} \langle \bar{a}n \,\|\, \bar{a}n \rangle + \langle \bar{a}a \,\|\, \bar{a}a \rangle \\
&+ \sum_{n}^{N} \langle rn \,\|\, rn \rangle + \sum_{n}^{N} \langle \bar{s}n \,\|\, \bar{s}n \rangle + \langle r\bar{s} \,\|\, r\bar{s} \rangle \\
&- \langle ar \,\|\, ar \rangle - \langle a\bar{s} \,\|\, a\bar{s} \rangle - \langle \bar{a}r \,\|\, \bar{a}r \rangle - \langle \bar{a}\bar{s} \,\|\, \bar{a}\bar{s} \rangle
\end{aligned}$$

$$\begin{aligned}
\left\langle \Psi_{a\bar{a}}^{s\bar{r}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle = \sum_{m}^{N} &\langle m \,|\, h \,|\, m \rangle - \langle a \,|\, h \,|\, a \rangle - \langle \bar{a} \,|\, h \,|\, \bar{a} \rangle + \langle s \,|\, h \,|\, s \rangle + \langle \bar{r} \,|\, h \,|\, \bar{r} \rangle \\
&+ \frac{1}{2} \sum_{m,n} \langle mn \,\|\, mn \rangle - \sum_{n}^{N} \langle an \,\|\, an \rangle - \sum_{n}^{N} \langle \bar{a}n \,\|\, \bar{a}n \rangle + \langle \bar{a}a \,\|\, \bar{a}a \rangle \\
&+ \sum_{n}^{N} \langle sn \,\|\, sn \rangle + \sum_{n}^{N} \langle \bar{r}n \,\|\, \bar{r}n \rangle + \langle \bar{r}s \,\|\, \bar{r}s \rangle \\
&- \langle as \,\|\, as \rangle - \langle a\bar{r} \,\|\, a\bar{r} \rangle - \langle \bar{a}s \,\|\, \bar{a}s \rangle - \langle \bar{a}\bar{r} \,\|\, \bar{a}\bar{r} \rangle
\end{aligned}$$

$$\left\langle \Psi_{a\bar{a}}^{r\bar{s}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{s\bar{r}} \right\rangle = \langle r\bar{s} \,\|\, s\bar{r} \rangle = K_{rs}$$

$$\left\langle \Psi_{a\bar{a}}^{s\bar{r}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{a}}^{r\bar{s}} \right\rangle = \langle s\bar{r} \,\|\, r\bar{s} \rangle = K_{rs}$$

Therefore

$$\begin{aligned}
\left\langle {}^{1}\Psi_{aa}^{rs} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^{1}\Psi_{aa}^{rs} \right\rangle &= \frac{1}{2}\Big(- 4\varepsilon_a + 2\varepsilon_r + 2\varepsilon_s + 2J_{aa} + 2J_{rs} \\
&\qquad - 4J_{ra} - 4J_{sa} + 2K_{ra} + 2K_{sa} + 2K_{rs}\Big) \\
&= \varepsilon_r + \varepsilon_s - 2\varepsilon_a + J_{aa} + J_{rs} + K_{rs} \\
&\qquad - 2J_{sa} - 2J_{ra} + K_{sa} + K_{ra}
\end{aligned}$$

Exercise 4.1

Solution:

$$\sum_{\substack{c<d<e \\ t<u<v}} c_{cde}^{tuv} \left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{cde}^{tuv} \right\rangle$$

If there is no one in c, d, e equal to a, and no one in t, u, v equal to r, the integral will be zero. This requires at least one term in c, d, e to be equal to a. And the similar requirment is applied to t, u, v. For example, we let c be a, and t be r, after which we change the dumb variables. The result is:

$$\sum_{\substack{c<d \\ t<u}} c_{acd}^{rtu} \left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{acd}^{rtu} \right\rangle$$

Exercise 4.2

Solution:

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{pmatrix} -E & K_{12} \\ K_{12} & 2\Delta - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\begin{vmatrix} -E & K_{12} \\ K_{12} & 2\Delta - E \end{vmatrix} = 0$$

$$E^2 - 2\Delta E - K_{12}^2 = 0$$

$$\begin{aligned} E &= \frac{2\Delta \pm \sqrt{4\Delta^2 + 4K_{12}^2}}{2} \\ &= \Delta \pm \left(\Delta^2 + K_{12}^2\right)^{1/2} \end{aligned}$$

E_{corr} is the lowest eigenvalue.

$$E_{\text{corr}} = \Delta - \left(\Delta^2 + K_{12}^2\right)^{1/2}$$

Exercise 4.3

Solution:

$$E_{\text{corr}} = -0.020562$$

$$K_{12} = 0.1813$$

$$c = E_{\text{corr}}/K_{12} = -0.1134$$

As $R \to \infty$, two-electron integral tends to $\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$, and $\varepsilon_1, \varepsilon_2 \to E(\text{H})$. That is

$$\lim_{R\to\infty} K_{12} = \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$$

$$\lim_{R\to\infty} \Delta = 0$$

Therefore

$$\begin{aligned} \lim_{R\to\infty} c &= \frac{\lim_{R\to\infty} K_{12}}{\lim_{R\to\infty}\left(\Delta - \left(\Delta^2 + K_{12}^2\right)^{1/2} - 2\Delta\right)} \\ &= \frac{\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)}{-\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)} \\ &= -1 \end{aligned}$$

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \bar{\psi}_1(1) & \bar{\psi}_1(2) \end{vmatrix}$$

$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_2(1) & \psi_2(2) \\ \bar{\psi}_2(1) & \bar{\psi}_2(2) \end{vmatrix}$$

Because ψ_1 and ψ_2 are the linear combination of ϕ_1 and ϕ_2.

$$\psi_1 = c_1(\phi_1 + \phi_2)$$

$$\psi_2 = c_2(\phi_1 - \phi_2)$$

Substitute the expands into determinants

$$\begin{aligned} |\Psi_0\rangle = \frac{c_1^2}{\sqrt{2}} \Big[&\big(\phi_1(1)\bar{\phi}_1(2) + \phi_1(1)\bar{\phi}_2(2) + \phi_2(1)\bar{\phi}_1(2) + \phi_2(1)\bar{\phi}_2(2)\big) \\ &- \big(\phi_1(1)\bar{\phi}_1(2) + \phi_1(1)\bar{\phi}_2(2) + \phi_2(1)\bar{\phi}_1(2) + \phi_2(1)\bar{\phi}_2(2)\big)\Big] \\ = \frac{1}{2 + 2S_{12}} &\big(\,|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\,\big) \end{aligned}$$

$$
\begin{aligned}
|\Psi_{1\bar{1}}^{2\bar{2}}\rangle &= \frac{c_2^2}{\sqrt{2}}\Big[\big(\phi_1(1)\bar{\phi}_1(2) - \phi_1(1)\bar{\phi}_2(2) - \phi_2(1)\bar{\phi}_1(2) + \phi_2(1)\bar{\phi}_2(2)\big) \\
&\qquad - \big(\phi_1(1)\bar{\phi}_1(2) - \phi_1(1)\bar{\phi}_2(2) - \phi_2(1)\bar{\phi}_1(2) + \phi_2(1)\bar{\phi}_2(2)\big)\Big] \\
&= \frac{1}{2-2S_{12}}\big(\,|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\,\big)
\end{aligned}
$$

As $R \to \infty$, $c \to -1$, and $S_{12} \to 0$:

$$
\begin{aligned}
|\Phi_0\rangle &= |\Psi_0\rangle - |\Psi_{1\bar{1}}^{2\bar{2}}\rangle \\
&= \frac{1}{2}\big(2\,|\phi_1\bar{\phi}_2\rangle + 2\,|\phi_2\bar{\phi}_1\rangle\,\big) \\
&= |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle
\end{aligned}
$$

After normalization:

$$
|\Phi_0\rangle = \frac{1}{\sqrt{2}}\big(\,|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle\,\big)
$$

Exercise 4.4

Solution:

$$
\begin{aligned}
\gamma_{ij} &= \int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_i^*(\mathbf{x}_1)\gamma(\mathbf{x}_1,\mathbf{x}_1')\chi_j(\mathbf{x}_1') \\
\gamma_{ji}^* &= \Big[\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_j^*(\mathbf{x}_1)\gamma(\mathbf{x}_1,\mathbf{x}_1')\chi_i(\mathbf{x}_1')\Big]^* \\
&= \int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_i^*(\mathbf{x}_1')\big[\gamma(\mathbf{x}_1,\mathbf{x}_1')\big]^*\chi_j(\mathbf{x}_1)
\end{aligned}
$$

Substitute $\gamma(\mathbf{x}_1,\mathbf{x}_1')$ with its definition:

$$
\gamma_{ij} = N\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1')\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N\;\Phi(\mathbf{x}_1,\ldots,\mathbf{x}_N)\Phi^*(\mathbf{x}_1',\ldots,\mathbf{x}_N)
$$

$$
\gamma_{ji}^* = N\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_i^*(\mathbf{x}_1')\chi_j(\mathbf{x}_1)\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N\;\Phi(\mathbf{x}_1',\ldots,\mathbf{x}_N)\Phi^*(\mathbf{x}_1,\ldots,\mathbf{x}_N)
$$

Because $\mathbf{x}_1$ and $\mathbf{x}_1'$ are dumb variables, $\gamma_{ij} = \gamma_{ji}^*$. And that matrix γ is a Hermitian matrix is proved.

Exercise 4.5

Solution:

$$
\begin{aligned}
\mathrm{tr}\;\gamma = \sum_i^N \gamma_{ii} &= \sum_i^N \int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\chi_i^*(\mathbf{x}_1)\gamma(\mathbf{x}_1,\mathbf{x}_1')\chi_i^*(\mathbf{x}_1') \\
&= \sum_i^N \int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_1'\;\chi_i^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_1')\cdot N\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N\;\Phi(\mathbf{x}_1,\ldots,\mathbf{x}_N)\Phi^*(\mathbf{x}_1',\ldots,\mathbf{x}_N)
\end{aligned}
$$

Make $\mathbf{x}_1 = \mathbf{x}_1'$. Then the result of integral is obvious:

$$
\mathrm{tr}\;\gamma = N
$$

Exercise 4.6

Solution:
(a)

$$
\begin{aligned}
\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle &= \sum_i^N \langle \Phi \mid h(\mathbf{x}_1) \mid \Phi \rangle \\
&= N \int \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N \; \Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) h(\mathbf{x}_1) \Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \\
&= N \int \mathrm{d}\mathbf{x}_1 \; h(\mathbf{x}_1) \cdot \int \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N \; \Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) \Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \\
&= N \cdot \frac{1}{N} \int \mathrm{d}\mathbf{x}_1 \; \Big[h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1') \Big]_{\mathbf{x}_1' = \mathbf{x}_1} \\
&= \int \mathrm{d}\mathbf{x}_1 \; \Big[h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1') \Big]_{\mathbf{x}_1' = \mathbf{x}_1}
\end{aligned}
$$

(b)

$$
\begin{aligned}
\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle &= \int \mathrm{d}\mathbf{x}_1 \; h(\mathbf{x}_1) \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}_1) \\
&= \sum_{ij} \int \mathrm{d}\mathbf{x}_1 \; \chi_j^*(\mathbf{x}_1) h(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \cdot \gamma_{ij} \\
&= \sum_{ij} h_{ji} \gamma_{ij} \\
&= \sum_j (\mathbf{h}\gamma)_{jj} \\
&= \mathrm{tr} \; \mathbf{h}\gamma
\end{aligned}
$$

Exercise 4.8

Solution:
(a)

$$
\begin{aligned}
|{}^1\Phi_0\rangle &= c_0 \, |\psi_1 \bar{\psi}_1\rangle + \sum_{r=2}^K c_1^r \Big[2^{-1/2} (|\psi_1 \bar{\psi}_r\rangle + |\psi_r \bar{\psi}_1\rangle) \Big] + \frac{1}{2} \sum_{r=2}^K \sum_{s=2}^K c_{11}^{rs} \Big[2^{-1/2} (|\psi_r \bar{\psi}_s\rangle + |\psi_s \bar{\psi}_r\rangle) \Big] \\
&= c_0 \, |\psi_i \bar{\psi}_j\rangle \big|_{\substack{i=1 \\ j=1}} + \frac{1}{\sqrt{2}} \sum_{j=2}^K c_1^j \big(\, |\psi_i \bar{\psi}_j\rangle \big|_{i=1} + |\psi_i \bar{\psi}_j\rangle \big|_{i=1} \big) + \frac{1}{2\sqrt{2}} \sum_{i=2}^K \sum_{j=2}^K c_{11}^{ij} \big(\, |\psi_i \bar{\psi}_j\rangle + |\psi_j \bar{\psi}_i\rangle \big) \\
&= c_0^{11} \, |\psi_i \bar{\psi}_j\rangle \big|_{\substack{i=1 \\ j=1}} + \frac{1}{\sqrt{2}} \sum_{i=2}^K c_1^{i1} \, |\psi_i \bar{\psi}_j\rangle \big|_{j=1} + \frac{1}{\sqrt{2}} \sum_{j=2}^K c_1^{1j} \, |\psi_i \bar{\psi}_j\rangle \big|_{i=1} + \frac{1}{2\sqrt{2}} \sum_{i=2}^K \sum_{j=2}^K c_{11}^{ij} \, |\psi_i \bar{\psi}_j\rangle + \frac{1}{2\sqrt{2}} \sum_{i=2}^K \sum_{j=2}^K c_{11}^{ji} \, |\psi_i \bar{\psi}_j\rangle
\end{aligned}
$$

Clearly CI expansion can be expressed as

$$
|{}^1\Phi_0\rangle = \sum_{i=1}^K \sum_{j=1}^K C_{ij} \, |\psi_i \bar{\psi}_j\rangle
$$

For configurations $|\psi_r \bar{\psi}_s\rangle$ and $|\psi_s \bar{\psi}_r\rangle$, they are the same in some sense. Thus c_{11}^{rs} and c_{11}^{sr} are equal. And it can be concluded in general that

$$
C_{ij} = C_{ji}
$$

$\mathbf{C}$ is a symmetric matrix.
(b)

$$
|{}^1\Phi_0\rangle = \frac{1}{\sqrt{2}} \sum_{ij} C_{ij} \big(i(\mathbf{1}) \bar{j}(\mathbf{2}) - i(\mathbf{2}) \bar{j}(\mathbf{1}) \big)
$$

$$
\begin{aligned}
\gamma(\mathbf{1},\mathbf{1}') &= 2\int \mathrm{d}\mathbf{x}_2 \left[\frac{1}{\sqrt{2}}\sum_{ij} C_{ij}\big(i(\mathbf{1})\bar{j}(\mathbf{2}) - i(\mathbf{2})\bar{j}(\mathbf{1})\big)\right]\cdot\left[\frac{1}{\sqrt{2}}\sum_{kl} C^*_{kl}\big(k^*(\mathbf{1}')\bar{l}^*(\mathbf{2}) - k^*(\mathbf{2})\bar{l}^*(\mathbf{1}')\big)\right] \\
&= \sum_{ij}\sum_{kl}\int \mathrm{d}\mathbf{x}_2\ C_{ij}C^*_{kl}\ \big[i(\mathbf{1})\bar{j}(\mathbf{2})k^*(\mathbf{1}')\bar{l}^*(\mathbf{2}) - i(\mathbf{1})\bar{j}(\mathbf{2})k^*(\mathbf{2})\bar{l}^*(\mathbf{1}') \\
&\qquad - i(\mathbf{2})\bar{j}(\mathbf{1})k^*(\mathbf{1}')\bar{l}^*(\mathbf{2}) + i(\mathbf{2})\bar{j}(\mathbf{1})k^*(\mathbf{2})\bar{l}^*(\mathbf{1}')\big] \\
&= \sum_{ij}\sum_{kl} C_{ij}C^*_{kl}\ \big[i(\mathbf{1})k^*(\mathbf{1}')\delta_{jl} + \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}')\delta_{ik}\big]
\end{aligned}
$$

For the first part

$$
\begin{aligned}
I_1 &= \sum_{ij}\sum_{kl} C_{ij}C^*_{kl}\ i(\mathbf{1})k^*(\mathbf{1}')\delta_{jl} \\
&= \sum_{ij}\sum_{k} C_{ij}C^*_{kj}\ i(\mathbf{1})k^*(\mathbf{1}') \\
&= \sum_{ik}\sum_{j} C_{ij}(C^\dagger)_{jk}\ i(\mathbf{1})k^*(\mathbf{1}') \\
&= \sum_{ik}(CC^\dagger)_{ik}\ i(\mathbf{1})k^*(\mathbf{1}') \\
&= \sum_{ij}(CC^\dagger)_{ij}\ i(\mathbf{1})j^*(\mathbf{1}')
\end{aligned}
$$

The second part

$$
\begin{aligned}
I_2 &= \sum_{ij}\sum_{kl} C_{ij}C^*_{kl}\ \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}')\delta_{ik} \\
&= \sum_{ij}\sum_{l} C_{ij}C^*_{il}\ \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}') \\
&= \sum_{ij}\sum_{l} C_{ij}(C^\dagger)_{li}\ \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}') \\
&= \sum_{jl}\sum_{i} C_{ji}(C^\dagger)_{il}\ \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}') \\
&= \sum_{jl}(CC^\dagger)_{jl}\ \bar{j}(\mathbf{1})\bar{l}^*(\mathbf{1}') \\
&= \sum_{ij}(CC^\dagger)_{ij}\ \bar{i}(\mathbf{1})\bar{j}^*(\mathbf{1}')
\end{aligned}
$$

$$
\gamma(\mathbf{1},\mathbf{1}') = \sum_{ij}(CC^\dagger)_{ij}\ \big[i(\mathbf{1})j^*(\mathbf{1}') + \bar{i}(\mathbf{1})\bar{j}^*(\mathbf{1}')\big]
$$

(c)

$$
\begin{aligned}
\mathbf{U}^\dagger\mathbf{C}\mathbf{U} &= \mathbf{d} \\
\mathbf{U}\mathbf{C}^\dagger\mathbf{U} &= \mathbf{d}^\dagger = \mathbf{d}
\end{aligned}
$$

Because $\mathbf{d}$ is diagonal.

$$
\begin{aligned}
\mathbf{U}^\dagger\mathbf{C} &= \mathbf{d}\mathbf{U}^\dagger \\
\mathbf{C}^\dagger\mathbf{U} &= \mathbf{U}^\dagger\mathbf{d}
\end{aligned}
$$

$$
\mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U} = \mathbf{d}\mathbf{U}^\dagger\mathbf{U}^\dagger\mathbf{d} = \mathbf{d}\mathbf{U}^\dagger\mathbf{U}^{-1}\mathbf{d} = \mathbf{d}^2
$$

(d)

$$
\zeta_i = \sum_k \psi_k U_{ki}
$$

$$\psi_i = \sum_k (U^\dagger)_{ik}\zeta_k$$

$$\begin{aligned}
\gamma(\mathbf{1},\mathbf{1}') &= \sum_{ij}(CC^\dagger)_{ij}\ \left[\sum_k (U^\dagger)_{ik}\zeta_k(\mathbf{1})\cdot\sum_l (U^\dagger)^*_{lj}\zeta^*_l(\mathbf{1}') + \sum_k (U^\dagger)_{ik}\bar\zeta_k(\mathbf{1})\cdot\sum_l (U^\dagger)^*_{lj}\bar\zeta^*_l(\mathbf{1}')\right] \\
&= \sum_{ij}\sum_{kl}(U^\dagger)_{ik}(CC^\dagger)_{ij}(U^\dagger)^*_{lj}\Big[\zeta_k(\mathbf{1})\zeta^*_l(\mathbf{1}') + \bar\zeta_k(\mathbf{1})\bar\zeta^*_l(\mathbf{1}')\Big] \\
&= \sum_{ij}\sum_{kl}(U^\dagger)_{ki}(CC^\dagger)_{ij}U_{jl}\Big[\zeta_k(\mathbf{1})\zeta^*_l(\mathbf{1}') + \bar\zeta_k(\mathbf{1})\bar\zeta^*_l(\mathbf{1}')\Big] \\
&= \sum_{kl} d_k^2\delta_{kl}\Big[\zeta_k(\mathbf{1})\zeta^*_l(\mathbf{1}') + \bar\zeta_k(\mathbf{1})\bar\zeta^*_l(\mathbf{1}')\Big] \\
&= \sum_i d_i^2\Big[\zeta_i(\mathbf{1})\zeta^*_i(\mathbf{1}') + \bar\zeta_i(\mathbf{1})\bar\zeta^*_i(\mathbf{1}')\Big]
\end{aligned}$$

(e)

$$\begin{aligned}
|{}^1\Phi_0\rangle &= \sum_{ij} 2^{-1/2}C_{ij}\left[i(\mathbf{1})\bar{j}(\mathbf{2}) - i(\mathbf{2})\bar{j}(\mathbf{1})\right] \\
&= \sum_{ij} 2^{-1/2}C_{ij}\left[\sum_k (U^\dagger)_{ik}\zeta_k(\mathbf{1})\cdot\sum_l (U^\dagger)_{jl}\bar\zeta_l(\mathbf{2}) - \sum_k (U^\dagger)_{ik}\zeta_k(\mathbf{2})\cdot\sum_l (U^\dagger)_{jl}\bar\zeta_l(\mathbf{1})\right] \\
&= \sum_{ij}\sum_{kl}(U^\dagger)_{ik}C_{ij}(U^\dagger)_{jl}\ 2^{-1/2}\Big[\zeta_k(\mathbf{1})\bar\zeta_l(\mathbf{2}) - \zeta_k(\mathbf{2})\bar\zeta_l(\mathbf{1})\Big] \\
&= \sum_{ij}\sum_{kl}(U^\dagger)_{ki}C_{ij}U_{jl}\ 2^{-1/2}\Big[\zeta_k(\mathbf{1})\bar\zeta_l(\mathbf{2}) - \zeta_k(\mathbf{2})\bar\zeta_l(\mathbf{1})\Big] \\
&= \sum_{kl} d_k\delta_{kl}\,|\zeta_k\bar\zeta_l\rangle \\
&= \sum_i d_i\,|\zeta_i\bar\zeta_i\rangle
\end{aligned}$$

Exercise 4.9

Solution:
(a)

$$\langle u\,|\,u\rangle = K^2(a^2+b^2) = 1$$

$$\langle u\,|\,v\rangle = K^2(a^2-b^2) = \frac{a^2-b^2}{a^2+b^2}$$

(b) It's just obvious and skip it.

Exercise 4.10

Solution:

$$\begin{aligned}
\langle 1_1\bar1_1 1_2\bar1_2\,|\,\mathscr{H}\,|\,1_1\bar1_1 2_1\bar2_1\rangle &= \langle 1_1\bar1_1 1_2\bar1_2\,|\,\mathscr{O}_1\,|\,1_1\bar1_1 2_1\bar2_1\rangle + \langle 1_1\bar1_1 1_2\bar1_2\,|\,\mathscr{O}_2\,|\,1_1\bar1_1 2_1\bar2_1\rangle \\
&= \langle 1_1\bar1_1 1_2\bar1_2\,|\,\mathscr{O}_2\,|\,1_1\bar1_1 2_1\bar2_1\rangle \\
&= [1_2 2_1|\bar1_2\bar2_1] - [1_2\bar2_1|\bar1_2 2_1] \\
&= (1_2 2_1|1_2 2_1) \\
&= 0
\end{aligned}$$

Exercise 4.9

Solution:
(a)

$$\left\langle \Psi_0 \middle| \mathscr{H} - E \middle| \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \right\rangle = K_{12}$$

$$\left\langle \Psi_0 \middle| \mathscr{H} - E \middle| \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} \right\rangle = K_{12}$$

$$\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \middle| \mathscr{H} - E \middle| \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} \right\rangle = 0$$

$$\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \middle| \mathscr{H} - E \middle| \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \right\rangle = K_{12}$$

$$\left\langle \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} \middle| \mathscr{H} - E \middle| \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \right\rangle = K_{12}$$

$$\left\langle \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \middle| \mathscr{H} \middle| \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \right\rangle = 4h_{22} + 2J_{22}$$

The integrals, such as $(2_1(\mathbf{1})2_1(\mathbf{1})|2_2(\mathbf{2})2_2(\mathbf{2})) = J_{22}$ and $(2_1(\mathbf{1})2_2(\mathbf{1})|2_2(\mathbf{2})2_1(\mathbf{2})) = K_{22}$, are zero.

$$\begin{aligned}
\left\langle \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \middle| \mathscr{H} - E \middle| \Psi_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} \right\rangle &= 4h_{22} + 2J_{22} - E_0 \\
&= 4\varepsilon_2 - 8J_{12} + 4K_{12} + 2J_{22} - 4\varepsilon_1 + 2J_{11} \\
&= 4(\varepsilon_2 - \varepsilon_1) + 2J_{11} + 2J_{22} - 8J_{12} + 4K_{12} \\
&= 4\Delta
\end{aligned}$$

Thus we could construct the full CI equation:

$$\begin{pmatrix} 0 & K_{12} & K_{12} & 0 \\ K_{12} & 2\Delta & 0 & K_{12} \\ K_{12} & 0 & 2\Delta & K_{12} \\ 0 & K_{12} & K_{12} & 4\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} =^2 E_{\mathrm{corr}} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

5 Chapter 5

Exercise 5.1

Solution:
(a)

$$E_{\mathrm{corr}}(\mathrm{FO}) = \sum_{a<b}\sum_{r<s} \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \frac{|\langle 1\bar{1} \,\|\, 2\bar{2}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} = \frac{|(12|21)|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

(b)

$$\begin{aligned}
{}^1E_{\mathrm{corr}} &= \Delta - (\Delta^2 + K_{12}^2)^{1/2} = \Delta\left(\frac{\Delta - (\Delta^2 + K_{12}^2)^{1/2}}{\Delta}\right) \\
&= \Delta\left(1 - \left(1 + \frac{K_{12}^2}{\Delta^2}\right)^{1/2}\right) \\
&\approx \Delta\left(1 - \left(1 + \frac{K_{12}^2}{2\Delta^2}\right)\right) \\
&= -\frac{K_{12}^2}{2\Delta} = -\frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)} \\
&= E_{\mathrm{corr}}(\mathrm{FO})
\end{aligned}$$

Exercise 5.2

Solution:

$$
\begin{aligned}
e_{1_i\bar{1}_i} &= \sum_{t<u} c^{tu}_{1_i\bar{1}_i} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{tu}_{1_i\bar{1}_i} \right\rangle \\
&= c^{2_i\bar{2}_i}_{1_i\bar{1}_i} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \right\rangle \\
&= c^{2_i\bar{2}_i}_{1_i\bar{1}_i} K_{12}
\end{aligned}
$$

$$
\begin{aligned}
e_{1_i\bar{1}_i} c^{2_i\bar{2}_i}_{1_i\bar{1}_i} &= \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{tu}_{1_i\bar{1}_i} \right\rangle c^{tu}_{1_i\bar{1}_i} \\
&= K_{12} + \sum_{kl} \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_k\bar{2}_l}_{1_i\bar{1}_i} \right\rangle c^{2_k\bar{2}_l}_{1_i\bar{1}_i}
\end{aligned}
$$

For $\left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_k\bar{2}_l}_{1_i\bar{1}_i} \right\rangle$,

case 1: $i = k = l$

$$
\left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_k\bar{2}_l}_{1_i\bar{1}_i} \right\rangle = \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \right\rangle = 2\Delta
$$

case 2: $i \neq k = l = j$

$$
\left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_k\bar{2}_l}_{1_i\bar{1}_i} \right\rangle = \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_j\bar{2}_j}_{1_i\bar{1}_i} \right\rangle = \langle 2_i\bar{2}_i \,\|\, 2_j\bar{2}_j \rangle = 0
$$

case 3: $i = k \neq l$

$$
\left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_k\bar{2}_l}_{1_i\bar{1}_i} \right\rangle = \left\langle \Psi^{2_i\bar{2}_i}_{1_i\bar{1}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{2_i\bar{2}_l}_{1_i\bar{1}_i} \right\rangle = \sum_a \langle \bar{2}_i a \,\|\, \bar{2}_l a \rangle = 0
$$

$$
e_{1_i\bar{1}_i} c^{2_i\bar{2}_i}_{1_i\bar{1}_i} = K_{12} + 2\Delta c^{2_i\bar{2}_i}_{1_i\bar{1}_i}
$$

Exercise 5.4

Solution:

$$
\begin{aligned}
|a\bar{a}b\bar{b}\rangle &= (2^{-1/2})^4 \, |(1_1 + 1_2)(\bar{1}_1 + \bar{1}_2)(1_1 - 1_2)(\bar{1}_1 - \bar{1}_2)\rangle \\
&= \frac{1}{4}\Big(|1_1(\bar{1}_1 + \bar{1}_2)(1_1 - 1_2)(\bar{1}_1 - \bar{1}_2)\rangle + |1_2(\bar{1}_1 + \bar{1}_2)(1_1 - 1_2)(\bar{1}_1 - \bar{1}_2)\rangle \Big) \\
&= \frac{1}{4}\Big(- |1_1(\bar{1}_1 + \bar{1}_2)1_2(\bar{1}_1 - \bar{1}_2)\rangle + |1_2(\bar{1}_1 + \bar{1}_2)1_1(\bar{1}_1 - \bar{1}_2)\rangle \Big) \\
&= \frac{1}{4}\Big(- \big(|1_1\bar{1}_1 1_2(\bar{1}_1 - \bar{1}_2)\rangle + |1_1\bar{1}_2 1_2(\bar{1}_1 - \bar{1}_2)\rangle \big) + \big(|1_2\bar{1}_1 1_1(\bar{1}_1 - \bar{1}_2)\rangle + |1_2\bar{1}_2 1_1(\bar{1}_1 - \bar{1}_2)\rangle \big) \Big) \\
&= \frac{1}{4}\Big(- \big(- |1_1\bar{1}_1 1_2\bar{1}_2\rangle + |1_1\bar{1}_2 1_2\bar{1}_1\rangle \big) + \big(- |1_2\bar{1}_1 1_1\bar{1}_2\rangle + |1_2\bar{1}_2 1_1\bar{1}_1\rangle \big) \Big) \\
&= \frac{1}{4}\Big(|1_1\bar{1}_1 1_2\bar{1}_2\rangle - |1_1\bar{1}_2 1_2\bar{1}_1\rangle - |1_2\bar{1}_1 1_1\bar{1}_2\rangle + |1_2\bar{1}_2 1_1\bar{1}_1\rangle \Big) \\
&= |1_1\bar{1}_1 1_2\bar{1}_2\rangle
\end{aligned}
$$

Exercise 5.5

Solution:

$$
\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi^{**}_{a\bar{a}} \rangle &= 2^{-1/2}\Big(\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{r\bar{r}}_{a\bar{a}} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi^{s\bar{s}}_{a\bar{a}} \right\rangle \Big) \\
&= 2^{-1/2}\Big(\langle a\bar{a} \,\|\, r\bar{r} \rangle + \langle a\bar{a} \,\|\, s\bar{s} \rangle \Big) \\
&= 2^{-1/2} K_{12}
\end{aligned}
$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = \frac{1}{2}\Big(\big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle + \big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{s\bar{s}} \big\rangle$$
$$+ \big\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle + \big\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{s\bar{s}} \big\rangle \Big)$$

$$\big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle = 2h_{bb} + 2h_{rr} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}$$
$$E_0 = 2h_{aa} + 2h_{bb} + 2J_{11}$$

$$\varepsilon_a = h_{aa} + J_{11}$$
$$\varepsilon_b = h_{bb} + J_{11}$$

$$\big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle = 2(\varepsilon_b + \varepsilon_r) - \frac{3}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12}$$
$$E_0 = \varepsilon_a + \varepsilon_b - 2J_{11}$$

$$\big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle = 2(\varepsilon_2 - \varepsilon_1) + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12}$$

$$\big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{s\bar{s}} \big\rangle = \langle r\bar{r} \,\|\, s\bar{s} \rangle = \frac{1}{2}J_{22}$$

$$\big\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle = \big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{s\bar{s}} \big\rangle = \frac{1}{2}J_{22}$$

$$\big\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{s\bar{s}} \big\rangle = \big\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\big|\, \mathscr{H} - E_0 \,\big|\, \Psi_{a\bar{a}}^{r\bar{r}} \big\rangle = 2(\varepsilon_2 - \varepsilon_1) + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12}$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2(\varepsilon_2 - \varepsilon_1) + \frac{1}{2}J_{11} + J_{22} - 2J_{12} + K_{12} = 2\Delta'$$

6 Chapter 6

Exercise 6.3

Solution:

$$\begin{aligned} E_0^{(2)} &= \sum_n{}' \frac{\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle \langle n \,|\, \mathscr{V} \,|\, \Psi_0 \rangle}{E_0^{(0)} - E_n^{(0)}} \\ &= \sum_n{}' \frac{\langle \Psi_0 \,|\, \sum_i v(i) \,|\, n \rangle \langle n \,|\, \sum_i v(i) \,|\, \Psi_0 \rangle}{E_0^{(0)} - E_n^{(0)}} \end{aligned}$$

Because perturbation operator is the sum of one-particle operator, $|n\rangle$ and $|\Psi_0\rangle$ must differ with no more than two spin orbitals. And since n can't be 0, $|n\rangle$ must be single-excited determinant, which can be noted as $|\Psi_a^r\rangle$.

$$E_0^{(2)} = \sum_{ar} \frac{\langle \Psi_0 \,|\, \sum_i v(i) \,|\, \Psi_a^r \rangle \langle \Psi_a^r \,|\, \sum_i v(i) \,|\, \Psi_0 \rangle}{\langle \Psi_0 \,|\, \mathscr{H}_0 \,|\, \Psi_0 \rangle - \langle \Psi_a^r \,|\, \mathscr{H}_0 \,|\, \Psi_a^r \rangle}$$

Based on the rule of the element of one-particle operator matrix

$$\left\langle \Psi_0 \,\middle|\, \sum_i v(i) \,\middle|\, \Psi_a^r \right\rangle = \langle a \,|\, v \,|\, r \rangle$$

And the eigenvalue of $\mathscr{H}_0$ is the sum of spin orbital energy

$$\langle \Psi_0 \,|\, \mathscr{H}_0 \,|\, \Psi_0 \rangle = \sum_b \varepsilon_b^{(0)}$$

$$\langle \Psi_a^r \,|\, \mathscr{H}_0 \,|\, \Psi_a^r \rangle = \sum_{b \neq a} \varepsilon_b^{(0)} + \varepsilon_r^{(0)}$$

$$E_0^{(2)} = \sum_{ar} \frac{\langle a \,|\, v \,|\, r \rangle \langle r \,|\, v \,|\, a \rangle}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} = \sum_{ar} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

Exercise 6.4

Solution:
a.

$$\begin{aligned}
B_0^{(3)} &= -E_0^{(1)} {\sum_n}' \frac{|\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle|^2}{\left(E_0^{(0)} - E_n^{(0)}\right)^2} \\
&= -\sum_a v_{aa} \sum_{ar} \frac{v_{ar} v_{ra}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)^2} \\
&= -\sum_{abr} \frac{v_{aa} v_{br} v_{rb}}{\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)^2}
\end{aligned}$$

b. With the same discussion stated in last exercise, $|n\rangle$ and $|m\rangle$ are single-excited determinant. We note them as $|\Psi_a^r\rangle$ and $|\Psi_b^s\rangle$ correspondingly.

$$A_0^{(3)} = \sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_b^s \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}\right)}$$

c. Just follow the rule of evaluating element of one-particle operator matrix.

d.

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}\right)} - \sum_{abr} \frac{v_{aa} v_{br} v_{rb}}{\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)^2}$$

First, seperate the first term based on whether s is equal to r.

$$\sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}\right)} = \sum_{abr} \frac{v_{ar} v_{rb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^r \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)} + \sum_{\substack{abrs \\ s \neq r}} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}\right)}$$

Then for two situations $b = a$ and $b \neq a$, each term can be divided into two parts.

$$\begin{aligned}
\sum_{abr} \frac{v_{ar} v_{rb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^r \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)} &= \sum_{ab} \frac{v_{ar} v_{ra} (\sum_c v_{cc} - v_{aa} + v_{rr})}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)^2} - \sum_{\substack{abr \\ b \neq a}} \frac{v_{ar} v_{rb} v_{ba}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)} \\
&= \sum_{abc} \frac{v_{ra} v_{ar} v_{cc}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)^2} - \sum_{ab} \frac{v_{ar} v_{ra} v_{aa}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)^2} \\
&\quad + \sum_{ab} \frac{v_{ar} v_{ra} v_{rr}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)^2} - \sum_{\substack{abr \\ b \neq a}} \frac{v_{ar} v_{rb} v_{ba}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)}
\end{aligned}$$

$$\sum_{\substack{abrs \\ s \neq r}} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_s^{(0)}\right)} = \sum_{\substack{ars \\ s \neq r}} \frac{v_{ar} v_{sb} v_{rs}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_a^{(0)} - \varepsilon_s^{(0)}\right)}$$

$$
\begin{aligned}
E_0^{(3)} = &\left[\sum_{\substack{ars\\ s\neq r}} \frac{v_{ar}v_{sb}v_{rs}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_a^{(0)}-\varepsilon_s^{(0)}\right)} + \sum_{ab} \frac{v_{ar}v_{ra}v_{rr}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)^2}\right] \\
&- \left[\sum_{\substack{abr\\ b\neq a}} \frac{v_{ar}v_{rb}v_{ba}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)}-\varepsilon_r^{(0)}\right)} + \sum_{ab} \frac{v_{ar}v_{ra}v_{aa}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)}-\varepsilon_r^{(0)}\right)}\right] \\
&+ \left[\sum_{abc} \frac{v_{ar}v_{ra}v_{cc}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)^2} - \sum_{abr} \frac{v_{aa}v_{br}v_{rb}}{\left(\varepsilon_b^{(0)}-\varepsilon_r^{(0)}\right)^2}\right] \\
= &\sum_{ars} \frac{v_{ar}v_{sb}v_{rs}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_a^{(0)}-\varepsilon_s^{(0)}\right)} - \sum_{abr} \frac{v_{ar}v_{rb}v_{ba}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)}-\varepsilon_r^{(0)}\right)} \\
= &\sum_{ars} \frac{v_{ar}v_{sb}v_{rs}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_a^{(0)}-\varepsilon_s^{(0)}\right)} - \sum_{abr} \frac{v_{br}v_{ar}v_{ab}}{\left(\varepsilon_a^{(0)}-\varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)}-\varepsilon_r^{(0)}\right)}
\end{aligned}
$$

e. No need to say more.

Exercise 6.8

Solution:

$$
\begin{aligned}
E_0^{(2)} &= \frac{1}{4}\sum_{abrs} \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} \\
&= \frac{1}{4}\sum_{abrs} \frac{(\langle ab\,|\,rs\rangle - \langle ab\,|\,sr\rangle)(\langle rs\,|\,ab\rangle - \langle sr\,|\,ab\rangle)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} \\
&= \frac{1}{4}\sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ab\rangle - \langle ab\,|\,rs\rangle\langle sr\,|\,ab\rangle - \langle ab\,|\,sr\rangle\langle rs\,|\,ab\rangle + \langle ab\,|\,sr\rangle\langle sr\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
\end{aligned}
$$

The second term:

$$
I_2 = \sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle sr\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} = \sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
$$

The third term

$$
I_3 = \sum_{abrs} \frac{\langle ab\,|\,sr\rangle\langle rs\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} = \sum_{abrs} \frac{\langle ba\,|\,sr\rangle\langle rs\,|\,ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
$$

Because a and b can exchange(the summation is symmetric in a and b)

$$
I_3 = \sum_{abrs} \frac{\langle ba\,|\,sr\rangle\langle rs\,|\,ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} = \sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
$$

The last term

$$
I_4 = \sum_{abrs} \frac{\langle ab\,|\,sr\rangle\langle sr\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} = \sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
$$

Therefore we got the result

$$
E_0^{(2)} = \frac{1}{2}\sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{1}{2}\sum_{abrs} \frac{\langle ab\,|\,rs\rangle\langle rs\,|\,ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
$$

Exercise 6.9

Solution:

Set $D = \varepsilon_2 - \varepsilon_1$ and $X = J_{11} + J_{22} - 4J_{12} + 2K_{12}$

$$E_{\mathrm{corr}} = \left(D + \frac{1}{2}X\right) - \left[\left(D + \frac{1}{2}X\right)^2 + K_{12}^2\right]^{1/2}$$

Introduce perturbation on each matrix element.

$$\begin{aligned}
E_{\mathrm{corr}} &= \left(D + \frac{1}{2}\lambda X\right) - \left[\left(D + \frac{1}{2}\lambda X\right)^2 + \lambda^2 K_{12}^2\right]^{1/2} \\
&= \left(D + \frac{1}{2}\lambda X\right) - \left(D + \frac{1}{2}\lambda X\right)\left[1 + \frac{\lambda^2 K_{12}^2}{\left(D + \frac{1}{2}\lambda X\right)^2}\right]^{1/2}
\end{aligned}$$

Use $(1+x)^{1/2} = 1 + \frac{1}{2}x + \dots$

$$\begin{aligned}
E_{\mathrm{corr}} &= \left(D + \frac{1}{2}\lambda X\right) - \left(D + \frac{1}{2}\lambda X\right)\left[1 + \frac{\lambda^2 K_{12}^2}{\left(D + \frac{1}{2}\lambda X\right)^2}\right]^{1/2} \\
&= \left(D + \frac{1}{2}\lambda X\right) - \left(D + \frac{1}{2}\lambda X\right)\left[1 + \frac{1}{2}\frac{\lambda^2 K_{12}^2}{\left(D + \frac{1}{2}\lambda X\right)^2}\right] \\
&= -\frac{1}{2}\frac{\lambda^2 K_{12}^2}{D + \frac{1}{2}\lambda X} \\
&= -\frac{\lambda^2 K_{12}^2}{2D}\frac{1}{1 + \frac{\lambda X}{2D}}
\end{aligned}$$

Use $(1-x)^{-1} = 1 + x + \dots$

$$\begin{aligned}
E_{\mathrm{corr}} &= -\frac{\lambda^2 K_{12}^2}{2D}\left(1 - \frac{\lambda X}{2D}\right) \\
&= -\frac{\lambda^2 K_{12}^2}{2D} + \frac{\lambda^3 K_{12}^2 X}{4D^2}
\end{aligned}$$

Second-order energy:

$$E_0^{(2)} = -\frac{K_{12}^2}{2D} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

Third-order energy:

$$E_0^{(3)} = \frac{K_{12}^2 X}{4D^2} = \frac{K_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_2 - \varepsilon_1)^2}$$

Exercise 6.10

Solution:

$$\begin{aligned}
E_0^{(1)} &= \langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_0 \rangle = -\frac{1}{2}\sum_{ab}^{2N} \langle ab \,\|\, ab \rangle \\
&= -\frac{1}{2}\left[\sum_i^N \langle 1_i \bar{1}_i \,\|\, 1_i \bar{1}_i \rangle + \sum_i^N \langle \bar{1}_i 1_i \,\|\, \bar{1}_i 1_i \rangle\right] \\
&= -NJ_{11}
\end{aligned}$$

$$\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H} - \mathscr{H}_0 \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle = \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H} \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle - \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H}_0 \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle$$

$$\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H} \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle = (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22}$$

$$\left\langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \middle| \mathscr{H}_0 \middle| \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \right\rangle = (2N-2)\varepsilon_1 + 2\varepsilon_2$$

Because $\varepsilon_1 = h_{11} + J_{11}$ and $\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$

$$\left\langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \middle| \mathscr{H} - \mathscr{H}_0 \middle| \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \right\rangle = (N-1)J_{11} + J_{22} - (2N-2)J_{11} - 4J_{12} + 2K_{12} = -NJ_{11} + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$