Modern Quantum Chemistry

solution 1

https://github.com/hebrewsnabla/S-O-MQC-HW

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Modern Quantum Chemistry, Szabo & Ostlund
HW

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Contents

1 Mathematical Review

1.1 Linear Algebra

1.1.1 3-D Vector Algebra

Ex 1.1

a)

$$\mathscr{O}\mathbf{e}_j = \sum_{i=1}^{3} \mathbf{e}_i O_{ij} \tag{1.1.1}$$

$$\mathbf{e}_i \cdot \mathscr{O}\mathbf{e}_j = \mathbf{e}_i \cdot \sum_{i=1}^{3} \mathbf{e}_i O_{ij} = O_{ij} \tag{1.1.2}$$

b)

$$\begin{aligned} \mathbf{b} = \mathscr{O}\mathbf{a} &= \sum_{i=1}^{3} a_i \sum_{j=1}^{3} \mathbf{e}_j O_{ji} \\ &= \sum_{j=1}^{3} a_j \sum_{i=1}^{3} \mathbf{e}_i O_{ij} = \sum_{i=1}^{3} \mathbf{e}_i \sum_{j=1}^{3} a_j O_{ij} \end{aligned} \tag{1.1.3}$$

thus

$$\mathbf{b}_i = \sum_{j=1}^{3} a_j O_{ij} \tag{1.1.4}$$

Ex 1.2

$$[\mathbf{A}, \mathbf{B}] = \begin{bmatrix} 0 & -2 & 4 \\ 2 & 0 & 3 \\ -4 & -3 & 0 \end{bmatrix} \tag{1.1.5}$$

$$\{\mathbf{A}, \mathbf{B}\} = \begin{bmatrix} 0 & 0 & -2 \\ 0 & -2 & 3 \\ -2 & 3 & -2 \end{bmatrix} \tag{1.1.6}$$

1.1.2 Matrices

Ex 1.3

$$(AB)_{nk} = \sum_{m}^{M} A_{nm} B_{mk} \tag{1.1.7}$$

$$(AB)^\dagger_{kn} = (AB)^*_{nk} = \sum_{m}^{M} A^*_{nm} B^*_{mk} = \sum_{m}^{M} B^\dagger_{km} A^\dagger_{mn} = (B^\dagger A^\dagger)_{kn} \tag{1.1.8}$$

thus

$$(\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger \tag{1.1.9}$$

Ex 1.4

a. suppose $\mathbf{A}$ is $N \times M$ and $\mathbf{B}$ is $M \times N$

$$\operatorname{tr} \mathbf{AB} = \sum_{n}^{N} (AB)_{nn} = \sum_{n}^{N} \sum_{m}^{M} A_{nm} B_{mn} = \sum_{m}^{M} \sum_{n}^{N} B_{mn} A_{nm} = \sum_{m}^{M} (BA)_{mm} = \operatorname{tr} \mathbf{BA} \tag{1.1.10}$$

b.

$$\mathbf{AB}(\mathbf{AB})^{-1} = \mathbf{1} \tag{1.1.11}$$
$$\mathbf{B}^{-1}\mathbf{A}^{-1}\mathbf{AB}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1}\mathbf{1} \tag{1.1.12}$$
$$\mathbf{B}^{-1}(\mathbf{A}^{-1}\mathbf{A})\mathbf{B}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \tag{1.1.13}$$
$$\mathbf{B}^{-1}\mathbf{1}\mathbf{B}(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \tag{1.1.14}$$

thus

$$(\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1} \tag{1.1.15}$$

c.

$$\mathbf{B} = \mathbf{U}^\dagger\mathbf{AU} \tag{1.1.16}$$
$$\mathbf{UBU}^\dagger = \mathbf{UU}^\dagger\mathbf{AUU}^\dagger = \mathbf{1A1} = \mathbf{A} \tag{1.1.17}$$

d. $\because$ **C** is Hermitian, $\therefore$

$$\mathbf{C} = \mathbf{C}^\dagger \tag{1.1.18}$$
$$\mathbf{AB} = (\mathbf{AB})^\dagger = \mathbf{B}^\dagger\mathbf{A}^\dagger \tag{1.1.19}$$

Since **A**, **B** are Hermitian,

$$\mathbf{AB} = \mathbf{B}^\dagger\mathbf{A}^\dagger = \mathbf{BA} \tag{1.1.20}$$

$\therefore$

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} = 0 \tag{1.1.21}$$

i.e. **A**, **B** commute

e. Since **A** is Hermitian,

$$\mathbf{A} = \mathbf{A}^\dagger \tag{1.1.22}$$

thus

$$(\mathbf{A}^{1-})^\dagger\mathbf{A} = (\mathbf{A}^{1-})^\dagger\mathbf{A}^\dagger = (\mathbf{AA}^{-1})^\dagger = \mathbf{1}^\dagger = \mathbf{1} \tag{1.1.23}$$

thus

$$(\mathbf{A}^{1-})^\dagger\mathbf{AA}^{-1} = \mathbf{A}^{-1} \tag{1.1.24}$$
$$(\mathbf{A}^{1-})^\dagger = \mathbf{A}^{-1} \tag{1.1.25}$$

i.e. $\mathbf{A}^{-1}$, if it exists, is Hermitian.

f. Suppose

$$\mathbf{A}^{-1} = \begin{pmatrix} x & y \\ z & w \end{pmatrix} \tag{1.1.26}$$

thus

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} x & y \\ z & w \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{1.1.27}$$

the solution is

$$\begin{aligned} x &= \frac{A_{22}}{A_{11}A_{22} - A_{12}A_{21}} \\ y &= \frac{-A_{12}}{A_{11}A_{22} - A_{12}A_{21}} \\ z &= \frac{-A_{21}}{A_{11}A_{22} - A_{12}A_{21}} \\ w &= \frac{A_{11}}{A_{11}A_{22} - A_{12}A_{21}} \end{aligned} \tag{1.1.28}$$

thus

$$\mathbf{A}^{-1} = \frac{1}{\det(\mathbf{A})}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix} \tag{1.1.29}$$

1.1.3 Determinants

Ex 1.5 Suppose

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \tag{1.1.30}$$

1.

$$\begin{vmatrix} 0 & 0 \\ A_{21} & A_{22} \end{vmatrix} = 0 \cdot A_{22} - 0 \cdot A_{21} = 0 \tag{1.1.31}$$

$$\begin{vmatrix} 0 & A_{12} \\ 0 & A_{22} \end{vmatrix} = 0 \cdot A_{22} - 0 \cdot A_{12} = 0 \tag{1.1.32}$$

2.

$$\det(\mathbf{A}) = A_{11}A_{22} - 0 \cdot 0 = A_{11}A_{22} \tag{1.1.33}$$

3.

$$\det(\mathbf{A}) = A_{11}A_{22} - A_{12}A_{21} \tag{1.1.34}$$

$$\begin{vmatrix} A_{21} & A_{22} \\ A_{11} & A_{12} \end{vmatrix} = A_{21}A_{12} - A_{22}A_{11} = -\det(\mathbf{A}) \tag{1.1.35}$$

4.

$$\det\left(\mathbf{A}^{\dagger}\right)^{*} = \begin{vmatrix} A_{11}^{*} & A_{21}^{*} \\ A_{12}^{*} & A_{22}^{*} \end{vmatrix}^{*} = (A_{11}^{*}A_{22}^{*} - A_{21}^{*}A_{12}^{*})^{*} = A_{11}A_{22} - A_{12}A_{21} = \det(\mathbf{A}) \tag{1.1.36}$$

5. Suppose $\mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$

$$\begin{aligned}
\det(\mathbf{AB}) &= \begin{vmatrix} A_{11}B_{11} + A_{12}B_{21} & A_{11}B_{12} + A_{12}B_{22} \\ A_{21}B_{11} + A_{22}B_{21} & A_{21}B_{12} + A_{22}B_{22} \end{vmatrix} \\
&= (A_{11}B_{11} + A_{12}B_{21})(A_{21}B_{12} + A_{22}B_{22}) - (A_{11}B_{12} + A_{12}B_{22})(A_{21}B_{11} + A_{22}B_{21}) \\
&= A_{11}B_{11}A_{21}B_{12} + A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} + A_{12}B_{21}A_{22}B_{22} \\
&\quad - (A_{11}B_{12}A_{21}B_{11} + A_{11}B_{12}A_{22}B_{21} + A_{12}B_{22}A_{21}B_{11} + A_{12}B_{22}A_{22}B_{21}) \\
&= A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} - A_{11}B_{12}A_{22}B_{21} - A_{12}B_{22}A_{21}B_{11}
\end{aligned} \tag{1.1.37}$$

$$\begin{aligned}
\det(\mathbf{A})\det(\mathbf{B}) &= (A_{11}A_{22} - A_{12}A_{21})(B_{11}B_{22} - B_{12}B_{21}) \\
&= A_{11}A_{22}B_{11}B_{22} - A_{11}A_{22}B_{12}B_{21} - A_{12}A_{21}B_{11}B_{22} + A_{12}A_{21}B_{12}B_{21} \\
&= A_{11}B_{11}A_{22}B_{22} + A_{12}B_{21}A_{21}B_{12} - A_{11}B_{12}A_{22}B_{21} - A_{12}B_{22}A_{21}B_{11}
\end{aligned} \tag{1.1.38}$$

$\therefore$

$$\det(\mathbf{A})\det(\mathbf{B}) = \det(\mathbf{AB}) \tag{1.1.39}$$

Ex 1.6

6. If two rows (e.g. ith and jth) are equal

$$\det(\mathbf{A}) = \begin{vmatrix} & ... & ... & \\ A_{i1} & A_{i2} & ... & A_{in} \\ & ... & ... & \\ A_{j1} & A_{j2} & ... & A_{jn} \\ & ... & ... & \end{vmatrix} \overset{1.5.3}{=\!=} - \begin{vmatrix} & ... & ... & \\ A_{j1} & A_{j2} & ... & A_{jn} \\ & ... & ... & \\ A_{i1} & A_{i2} & ... & A_{in} \\ & ... & ... & \end{vmatrix} = - \begin{vmatrix} & ... & ... & \\ A_{i1} & A_{i2} & ... & A_{in} \\ & ... & ... & \\ A_{j1} & A_{j2} & ... & A_{jn} \\ & ... & ... & \end{vmatrix} \tag{1.1.40}$$

i.e.

$$\det(\mathbf{A}) = -\det(\mathbf{A}) \tag{1.1.41}$$

thus

$$\det(\mathbf{A}) = 0 \tag{1.1.42}$$

7. From Ex 1.5.5, we have

$$\det(\mathbf{A})\det\left(\mathbf{A}^{-1}\right) = \det(\mathbf{1}) = 1 \tag{1.1.43}$$

thus

$$\det\left(\mathbf{A}^{-1}\right) = \det(\mathbf{A})^{-1} \tag{1.1.44}$$

8.

$$\mathbf{A}\mathbf{A}^{\dagger} = \mathbf{1} \Rightarrow \det(\mathbf{A})\det\left(\mathbf{A}^{\dagger}\right) = \det(\mathbf{1}) = 1 \tag{1.1.45}$$

From Ex 1.5.4, we have

$$\det(\mathbf{A})\det(\mathbf{A})^{*} = 1 \tag{1.1.46}$$

9. From Ex 1.5.5, we get

$$\det\left(\mathbf{U}^{\dagger}\right)\det(\mathbf{O})\det(\mathbf{U}) = \det(\mathbf{\Omega}) \tag{1.1.47}$$

and

$$\det\left(\mathbf{U}^{\dagger}\right)\det(\mathbf{U}) = \det(\mathbf{1}) = 1 \tag{1.1.48}$$

$\therefore$

$$\det(\mathbf{O}) = \det(\mathbf{\Omega}) \tag{1.1.49}$$

Ex 1.7 If $\det(\mathbf{A}) \neq 0$, thus $\mathbf{A}^{-1}$ exists, we have

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{c} = \mathbf{0} \Rightarrow \mathbf{c} = \mathbf{0} \tag{1.1.50}$$

□

1.1.4 N-D Complex Vector Spaces

1.1.5 Change of Basis

Ex 1.8

$$\Omega_{\alpha\beta} = \sum_{ij} U^{\dagger}_{\alpha i} O_{ij} U_{j\beta} \tag{1.1.51}$$

gives

$$\begin{aligned}\operatorname{tr}\mathbf{\Omega} &= \sum_{\alpha}\Omega_{\alpha\alpha} = \sum_{\alpha}\sum_{ij} U^{\dagger}_{\alpha i} O_{ij} U_{j\alpha} \\ &= \sum_{ij} O_{ij} \sum_{\alpha} U_{j\alpha} U^{\dagger}_{\alpha i} = \sum_{ij} O_{ij}\delta_{ji} = \operatorname{tr}\mathbf{O}\end{aligned} \tag{1.1.52}$$

1.1.6 The Eigenvalue Problem

Ex 1.9

$$\mathbf{O}\mathbf{U} = \mathbf{U}\boldsymbol{\omega} \Rightarrow \mathbf{O}\begin{pmatrix}\mathbf{c}^1 & \mathbf{c}^2 & \cdots & \mathbf{c}^N\end{pmatrix} = \begin{pmatrix}\omega_1\mathbf{c}_1 & \omega_2\mathbf{c}_2 & \cdots & \omega_N\mathbf{c}_N\end{pmatrix} \tag{1.1.53}$$

thus

$$\mathbf{O}\mathbf{c}^{\alpha} = \omega_{\alpha}\mathbf{c}^{\alpha} \tag{1.1.54}$$

Ex 1.10

$$\begin{cases} O_{11} - \omega + O_{12}c = 0 \\ O_{21} + (O_{22} - \omega)c = 0 \end{cases} \tag{1.1.55}$$

$$(O_{11} - \omega)(O_{22} - \omega) - O_{21}O_{12} = 0 \tag{1.1.56}$$

$$\omega^2 - (O_{11} + O_{22})\omega + O_{11}O_{22} - O_{21}O_{12} = 0 \tag{1.1.57}$$

$$\begin{cases} \omega_1 = \dfrac{1}{2}\left(O_{11} + O_{22} - \sqrt{(O_{11} - O_{22})^2 + 4O_{21}O_{12}}\right) \\ \omega_2 = \dfrac{1}{2}\left(O_{11} + O_{22} + \sqrt{(O_{11} - O_{22})^2 + 4O_{21}O_{12}}\right) \end{cases} \tag{1.1.58}$$

Ex 1.11

a)

$$\begin{vmatrix} 3-\omega & 1 \\ 1 & 3-\omega \end{vmatrix} = 0 \Rightarrow (3-\omega)^2 - 1 = 0 \tag{1.1.59}$$

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \tag{1.1.60}$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{1.1.61}$$

$$\begin{vmatrix} 3-\omega & 1 \\ 1 & 2-\omega \end{vmatrix} = 0 \Rightarrow (3-\omega)(2-\omega) - 1 = 0 \tag{1.1.62}$$

Eigenvalues

$$\omega_1 = \frac{5+\sqrt{5}}{2} \quad \omega_2 = \frac{5-\sqrt{5}}{2} \tag{1.1.63}$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \frac{1}{2}(1+\sqrt{5}) \\ 1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} \frac{1}{2}(1-\sqrt{5}) \\ 1 \end{pmatrix} \tag{1.1.64}$$

b)

$$\theta_0 = \frac{1}{2}\tan^{-1}\frac{2O_{12}}{O_{11}-O_{12}} \tag{1.1.65}$$

for **A**

$$\theta_0 = \frac{1}{2}\tan^{-1}\frac{2\times 1}{3-3} = \frac{\pi}{4} \tag{1.1.66}$$

Eigenvalues

$$\omega_1 = 2 \quad \omega_2 = 4 \tag{1.1.67}$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \sqrt{2}/2 \\ -\sqrt{2}/2 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} \sqrt{2}/2 \\ \sqrt{2}/2 \end{pmatrix} \tag{1.1.68}$$

for **B**

$$\theta_0 = \frac{1}{2}\tan^{-1}\frac{2\times 1}{3-2} = \frac{1}{2}\tan^{-1} 2 \tag{1.1.69}$$

Eigenvalues

$$\omega_1 = \frac{10}{5+\sqrt{5}} = \frac{5-\sqrt{5}}{2} \quad \omega_2 = \frac{10}{5-\sqrt{5}} = \frac{5+\sqrt{5}}{2} \tag{1.1.70}$$

Eigenvectors

$$\mathbf{c}^1 = \begin{pmatrix} \sqrt{\frac{\sqrt{5}+5}{10}} \\ \sqrt{\frac{2}{\sqrt{5}+5}} \end{pmatrix} = \sqrt{\frac{2}{\sqrt{5}+5}}\begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ 1 \end{pmatrix} \tag{1.1.71}$$

$$\mathbf{c}^2 = \begin{pmatrix} \sqrt{\frac{2}{\sqrt{5}+5}} \\ -\sqrt{\frac{\sqrt{5}+5}{10}} \end{pmatrix} = -\sqrt{\frac{\sqrt{5}+5}{10}}\begin{pmatrix} \frac{1-\sqrt{5}}{2} \\ 1 \end{pmatrix} \tag{1.1.72}$$

Details are in `1-1.nb`

1.1.7 Functions of Matrices

Ex 1.12

a.

$$\mathbf{A}^n = \mathbf{U}\mathbf{a}^n\mathbf{U}^\dagger \tag{1.1.73}$$

$$\det(\mathbf{A}^n) = \det(\mathbf{U})\det(\mathbf{a}^n)\det\big(\mathbf{U}^\dagger\big) = \det(\mathbf{U})\det\big(\mathbf{U}^\dagger\big)\begin{vmatrix} a_1^n & & & \\ & a_2^n & & \\ & & \ddots & \\ & & & a_N^n \end{vmatrix} = a_1^n a_2^n \cdots a_N^n \tag{1.1.74}$$

b. From 1.4.a, we have

$$\operatorname{tr}\mathbf{A}^n = \operatorname{tr}\big(\mathbf{U}\mathbf{a}^n\mathbf{U}^\dagger\big) = \operatorname{tr}\big(\mathbf{U}\mathbf{U}^\dagger\mathbf{a}^n\big) = \operatorname{tr}(\mathbf{a}^n) = \sum_{\alpha=1}^{N} a_\alpha^n \tag{1.1.75}$$

c.

$$\mathbf{U}^\dagger(\omega\mathbf{1} - \mathbf{A})\mathbf{U} = \omega\mathbf{1} - \mathbf{a} \tag{1.1.76}$$

$$(\omega\mathbf{1} - \mathbf{A})^{-1} = [(\mathbf{U}(\omega\mathbf{1} - \mathbf{a})\mathbf{U}^\dagger]^{-1} = \mathbf{U}(\omega\mathbf{1} - \mathbf{a})^{-1}\mathbf{U}^\dagger \tag{1.1.77}$$

while

$$(\omega\mathbf{1} - \mathbf{a})^{-1} = \begin{pmatrix} \omega - a_1 & & & \\ & \omega - a_2 & & \\ & & \ddots & \\ & & & \omega - a_N \end{pmatrix}^{-1} = \begin{pmatrix} \frac{1}{\omega - a_1} & & & \\ & \frac{1}{\omega - a_2} & & \\ & & \ddots & \\ & & & \frac{1}{\omega - a_N} \end{pmatrix} \tag{1.1.78}$$

thus

$$\mathbf{G}(\omega) = (\omega\mathbf{1} - \mathbf{A})^{-1} = \mathbf{U}\begin{pmatrix} \frac{1}{\omega - a_1} & & & \\ & \frac{1}{\omega - a_2} & & \\ & & \ddots & \\ & & & \frac{1}{\omega - a_N} \end{pmatrix}\mathbf{U}^\dagger \tag{1.1.79}$$

$$\mathbf{G}(\omega)_{ij} = \sum_\alpha U_{i\alpha}\frac{1}{\omega - a_\alpha}U_{\alpha j}^\dagger = \sum_\alpha \frac{U_{i\alpha}U_{j\alpha}^*}{\omega - a_\alpha} \tag{1.1.80}$$

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

$$\mathbf{G}(\omega)_{ij} = \sum_\alpha \frac{\langle i \,|\, \alpha \rangle \langle \alpha \,|\, j \rangle}{\omega - a_\alpha} \tag{1.1.81}$$

Ex 1.13 The eigenvalues and eigenvectors of **A** are

$$\omega_1 = a - b \quad \omega_2 = a + b \tag{1.1.82}$$

$$\mathbf{c}^1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \mathbf{c}^2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{1.1.83}$$

$$\mathbf{A} = \mathbf{U}\mathbf{a}\mathbf{U}^\dagger = \frac{\sqrt{2}}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} a+b & 0 \\ 0 & a-b \end{pmatrix}\frac{\sqrt{2}}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \tag{1.1.84}$$

$$\begin{aligned} f(\mathbf{A}) = \mathbf{U}f(\mathbf{a})\mathbf{U}^\dagger &= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} f(a+b) & 0 \\ 0 & f(a-b) \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} f(a+b) & f(a-b) \\ f(a+b) & -f(a-b) \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} f(a+b) + f(a-b) & f(a+b) - f(a-b) \\ f(a+b) - f(a-b) & f(a+b) + f(a-b) \end{pmatrix} \end{aligned} \tag{1.1.85}$$

1.2 Orthogonal Functions, Eigenfunctions, and Operators

Ex 1.14

$$\int_{-\infty}^{\infty} \mathrm{d}x a(x)\delta(x) = \lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon} \mathrm{d}x a(x)\frac{1}{2\varepsilon} = \lim_{\varepsilon\to 0}\frac{1}{2\varepsilon}\int_{-\varepsilon}^{\varepsilon} \mathrm{d}x a(x) \xlongequal{\text{L'Hôpital}} \lim_{\varepsilon\to 0}\frac{a(\varepsilon)-[-a(-\varepsilon)]}{2} = a(0) \tag{1.2.1}$$

Ex 1.15

$$\begin{aligned}\int \mathrm{d}x\psi_j^*(x)\mathcal{O}\psi_i(x) &= \int \mathrm{d}x\psi_j^*(x)\sum_k \psi_k(x)O_{ki} = \sum_k O_{ki}\int \mathrm{d}x\psi_j^*(x)\psi_k(x) \\ &= \sum_k O_{ki}\delta_{jk} = O_{ji}\end{aligned} \tag{1.2.2}$$

In bra-ket notation, (1) becomes

$$\mathcal{O}\,|i\rangle = \sum_j |j\rangle\,\langle j\,|\,\mathcal{O}\,|\,i\rangle \tag{1.2.3}$$

which is identical to Eq.(1.55) in the textbook.

Ex 1.16 With bra-ket notation,

$$\mathcal{O}\sum_{\mathrm{i}=1}^{\infty} c_i\,|i\rangle = \omega\sum_{\mathrm{i}=1}^{\infty} c_i\,|i\rangle \tag{1.2.4}$$

Multiply by $\langle j|$

$$\sum_{\mathrm{i}=1}^{\infty} c_i\,\langle j\,|\,\mathcal{O}\,|\,i\rangle = \omega\sum_{\mathrm{i}=1}^{\infty} c_i\,\langle j\,|\,i\rangle = \omega c_j \tag{1.2.5}$$

i.e.

$$\sum_{\mathrm{i}=1}^{\infty} O_{ji}c_i = \omega c_j \tag{1.2.6}$$

$$\mathbf{Oc} = \omega\mathbf{c} \tag{1.2.7}$$

It's similar to prove that without bra-ket notation.

Ex 1.17

a.

$$\int \mathrm{d}x\,\langle i|x|\,\langle x\,|\,j\rangle = \langle i\,|\,j\rangle = \delta_{ij} \tag{1.2.8}$$

i.e.

$$\int \mathrm{d}x\psi_i^*(x)\Psi_j(x) = \delta_{ij} \tag{1.2.9}$$

b.

$$\sum_{\mathrm{i}=1}^{\infty}\langle x\,|\,i\rangle\,\langle i\,|\,x'\rangle = \langle x\,|\,x'\rangle = \delta(x-x') \tag{1.2.10}$$

thus

$$\sum_{\mathrm{i}=1}^{\infty}\psi_i^*(x)\psi_i(x') = \sum_{\mathrm{i}=1}^{\infty}\langle x\,|\,i\rangle\,\langle i\,|\,x'\rangle = \delta(x-x') \tag{1.2.11}$$

c.

$$\int \mathrm{d}x\,\langle x'\,|\,x\rangle\,\langle x\,|\,a\rangle = \langle x'\,|\,a\rangle \tag{1.2.12}$$

thus

$$\int \mathrm{d}x\delta(x'-x)a(x) = a(x') \tag{1.2.13}$$

i.e.

$$\int \mathrm{d}x'\delta(x-x')a(x') = a(x) \tag{1.2.14}$$

d.

$$\langle x' \,|\, \mathcal{O} \,|\, a \rangle = \int \mathrm{d}x \, \langle x' \,|\, \mathcal{O} \,|\, x \rangle \, \langle x \,|\, a \rangle = \langle x' \,|\, b \rangle \tag{1.2.15}$$

$\therefore$

$$\mathcal{O}a(x') = \int \mathrm{d}x O(x', x) a(x) = b(x') \tag{1.2.16}$$

i.e.

$$b(x) = \mathcal{O}a(x) = \int \mathrm{d}x' O(x, x') a(x') \tag{1.2.17}$$

e.

$$\begin{aligned} O(x, x') = \langle x \,|\, \mathcal{O} \,|\, x' \rangle &= \langle x| \left(\sum_i |i\rangle \, \langle i| \right) \mathcal{O} \left(\sum_j |j\rangle \, \langle j| \right) |x'\rangle \\ &= \sum_{ij} \langle x \,|\, i \rangle \, \langle i \,|\, \mathcal{O} \,|\, j \rangle \, \langle j \,|\, x' \rangle \\ &= \sum_{ij} \psi_i(x) O_{ij} \psi_j^*(x') \end{aligned} \tag{1.2.18}$$

1.3 The Variation Method

1.3.1 The Variation Principle

Ex 1.18

$$\begin{aligned} \mathscr{E} &= \frac{\left\langle \tilde{\Phi} \,\middle|\, -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \delta(x) \,\middle|\, \tilde{\Phi} \right\rangle}{\left\langle \tilde{\Phi} \,\middle|\, \tilde{\Phi} \right\rangle} = \frac{N^2 \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{-\alpha x^2} \left[-\frac{1}{2}(-2\alpha + 4\alpha^2 x^2) - \delta(x) \right] \mathrm{e}^{-\alpha x^2}}{N^2 \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{-2\alpha x^2}} \\ &= \frac{\alpha \dfrac{\pi^{1/2}}{(2\alpha)^{1/2}} - 2\alpha^2 \dfrac{2\pi^{1/2}}{4(2\alpha)^{3/2}} - 1}{\dfrac{\pi^{1/2}}{(2\alpha)^{1/2}}} \\ &= \frac{\alpha \pi^{1/2} - \alpha^2 \dfrac{\pi^{1/2}}{(2\alpha)} - (2\alpha)^{1/2}}{\pi^{1/2}} \\ &= \alpha - \frac{1}{2}\alpha - \frac{(2\alpha)^{1/2}}{\pi^{1/2}} \\ &= \frac{1}{2}\alpha - \frac{(2\alpha)^{1/2}}{\pi^{1/2}} \end{aligned} \tag{1.3.1}$$

Let $\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\alpha} = 0$, we have

$$\frac{1}{2} - \frac{1}{(2\pi\alpha)^{1/2}} = 0 \,\Rightarrow\, \alpha = \frac{2}{\pi} \tag{1.3.2}$$

thus

$$\mathscr{E}_{min} = -\frac{1}{\pi} \tag{1.3.3}$$

Ex 1.19

$$
\begin{aligned}
\mathscr{E} = \frac{\left\langle \tilde{\Phi} \middle| -\frac{1}{2}\nabla^2 - \frac{1}{r} \middle| \tilde{\Phi} \right\rangle}{\left\langle \tilde{\Phi} \middle| \tilde{\Phi} \right\rangle} &= \frac{N^2 \cdot 4\pi \int_{-\infty}^{\infty} r^2 \mathrm{d}r\, \mathrm{e}^{-\alpha r^2} \left[-\frac{1}{2}(4\alpha^2 r^2 - 6\alpha) - \frac{1}{r} \right] \mathrm{e}^{-\alpha r^2}}{N^2 \cdot 4\pi \int_{-\infty}^{\infty} r^2 \mathrm{d}r\, \mathrm{e}^{-2\alpha r^2}} \\
&= \frac{-2\alpha^2 \frac{24\pi^{1/2}}{64(2\alpha)^{5/2}} + 3\alpha \frac{2\pi^{1/2}}{8(2\alpha)^{3/2}} - \frac{1}{2(2\alpha)}}{\frac{2\pi^{1/2}}{8(2\alpha)^{3/2}}} \\
&= -2\alpha^2 \frac{12}{8(2\alpha)} + 3\alpha - \frac{2(2\alpha)^{1/2}}{\pi^{1/2}} \\
&= \frac{3}{2}\alpha - \frac{2(2\alpha)^{1/2}}{\pi^{1/2}}
\end{aligned}
\tag{1.3.4}
$$

Let $\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}r} = 0$,

$$
\frac{3}{2} - \frac{2}{\sqrt{2\pi\alpha}} = 0 \Rightarrow \alpha = \frac{8}{9\pi} \tag{1.3.5}
$$

$$
\mathscr{E}_{min} = \frac{4}{3\pi} - \frac{8}{3\pi} = -\frac{4}{3\pi} \tag{1.3.6}
$$

Ex 1.20

$$
\begin{aligned}
\omega(\theta) = \mathbf{c}^\dagger \mathbf{O} \mathbf{c} &= \begin{pmatrix} \cos\theta & \sin\theta \end{pmatrix} \begin{pmatrix} O_{11}\cos\theta + O_{12}\sin\theta \\ O_{12}\cos\theta + O_{22}\sin\theta \end{pmatrix} \\
&= O_{11}\cos^2\theta + 2O_{12}\cos\theta\sin\theta + O_{22}\sin^2\theta
\end{aligned}
\tag{1.3.7}
$$

Let $\frac{\mathrm{d}\omega}{\mathrm{d}\theta} = 0$, thus

$$
O_{11}(-2\cos\theta\sin\theta) + O_{12} \cdot 2\cos 2\theta + O_{22} \cdot 2\sin\theta\cos\theta = 0 \tag{1.3.8}
$$

$$
(O_{22} - O_{11})\sin 2\theta + 2O_{12}\cos 2\theta = 0 \tag{1.3.9}
$$

$$
\theta = \frac{1}{2}\arctan\frac{2O_{12}}{O_{11} - O_{22}} \tag{1.3.10}
$$

$$
\omega = O_{11}\cos^2\theta + O_{12}\sin 2\theta + O_{22}\sin^2\theta \tag{1.3.11}
$$

which are exactly the results in Eq. (1.105) and Eq. (1.106a) in the textbook. We get the result because the trial vector $\mathbf{c}$ is the exact eigenvector of $\mathbf{O}$.

1.3.2 The Linear Variational Problem

Ex 1.21

a.

$$
\left\langle \tilde{\Phi}' \middle| \tilde{\Phi}' \right\rangle = 1 = \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \left\langle \Phi_\alpha \middle| \Phi_\beta \right\rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle \tag{1.3.12}
$$

Since $\left\langle \tilde{\Phi}' \middle| \Phi_0 \right\rangle = 0$, we have

$$
\sum_{\alpha=1}^{\infty}\sum_{\beta=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \left\langle \Phi_\alpha \middle| \Phi_\beta \right\rangle \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.13}
$$

thus

$$
\sum_{\alpha=1}^{\infty}\sum_{\beta=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \delta_{\alpha\beta} \left\langle \Phi_\beta \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.14}
$$

$$
\sum_{\alpha=1}^{\infty} \left\langle \tilde{\Phi}' \middle| \Phi_\alpha \right\rangle \left\langle \Phi_\alpha \middle| \tilde{\Phi}' \right\rangle = 1 \tag{1.3.15}
$$

$$\sum_{\alpha=1}^{\infty} \left| \left\langle \Phi_\alpha \,\middle|\, \tilde{\Phi}' \right\rangle \right|^2 = 1 \tag{1.3.16}$$

Similarly,

$$\left\langle \tilde{\Phi}' \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}' \right\rangle = \sum_{\alpha\beta} \left\langle \tilde{\Phi}' \,\middle|\, \Phi_\alpha \right\rangle \langle \Phi_\alpha \,|\, \mathscr{H} \,|\, \Phi_\beta \rangle \left\langle \Phi_\beta \,\middle|\, \tilde{\Phi}' \right\rangle = \sum_{\alpha=1}^{\infty} \sum_{\beta=1}^{\infty} \left\langle \tilde{\Phi}' \,\middle|\, \Phi_\alpha \right\rangle \langle \Phi_\alpha \,|\, \mathscr{H} \,|\, \Phi_\beta \rangle \left\langle \Phi_\beta \,\middle|\, \tilde{\Phi}' \right\rangle \tag{1.3.17}$$

From Eq. (1.170) from the textbook, we get

$$\langle \Phi_\alpha \,|\, \mathscr{H} \,|\, \Phi_\beta \rangle = \mathscr{E}_\alpha \delta_{\alpha\beta} \tag{1.3.18}$$

thus

$$\left\langle \tilde{\Phi}' \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}' \right\rangle = \sum_{\alpha=1}^{\infty} \left| \left\langle \Phi_\alpha \,\middle|\, \tilde{\Phi}' \right\rangle \right|^2 \mathscr{E}_\alpha \geq \sum_{\alpha=1}^{\infty} \left| \left\langle \Phi_\alpha \,\middle|\, \tilde{\Phi}' \right\rangle \right|^2 \mathscr{E}_1 = \mathscr{E}_1 \tag{1.3.19}$$

b.

$$\left\langle \tilde{\Phi}' \,\middle|\, \tilde{\Phi}' \right\rangle = 1 = \left(x^* \langle \tilde{\Phi}_0 | + y^* \langle \tilde{\Phi}_1 | \right) \left(x \, | \tilde{\Phi}_0 \rangle + y \, | \tilde{\Phi}_1 \rangle \right) = |x|^2 + |y|^2 \tag{1.3.20}$$

c.

$$\begin{aligned} \left\langle \tilde{\Phi}' \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}' \right\rangle &= |x|^2 \left\langle \tilde{\Phi}_0 \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}_0 \right\rangle + |y|^2 \left\langle \tilde{\Phi}_1 \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}_1 \right\rangle + x^* y \left\langle \tilde{\Phi}_0 \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}_1 \right\rangle + x y^* \left\langle \tilde{\Phi}_1 \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}_0 \right\rangle \\ &= E_1 - |x|^2 (E_1 - E_0) \end{aligned} \tag{1.3.21}$$

thus

$$\mathscr{E}_1 \leq \left\langle \tilde{\Phi}' \,\middle|\, \mathscr{H} \,\middle|\, \tilde{\Phi}' \right\rangle \leq E_1 - |x|^2 (E_1 - E_1) = E_1 \tag{1.3.22}$$

Ex 1.22

$$\begin{aligned} H_{11} &= \langle 1s \,|\, \mathscr{H} \,|\, 1s \rangle = -\frac{1}{2} + F \langle 1s \,|\, r\cos\theta \,|\, 1s \rangle = -\frac{1}{2} \\ H_{12} &= H_{21} = \langle 1s \,|\, \mathscr{H} \,|\, 2p_z \rangle = 0 + F \langle 1s \,|\, r\cos\theta \,|\, 2p_z \rangle = \frac{128\sqrt{2}\pi}{243} F \\ H_{22} &= \langle 2p_z \,|\, \mathscr{H} \,|\, 2p_z \rangle = -\frac{1}{8} + F \langle 2p_z \,|\, r\cos\theta \,|\, 2p_z \rangle = -\frac{1}{8} \end{aligned} \tag{1.3.23}$$

Suppose $\mathbf{c} = \begin{pmatrix} \cos p \\ \sin p \end{pmatrix}$, with the result of Ex 1.20, we have

$$p = \frac{1}{2} \arctan \frac{2H_{12}}{H_{11} - H_{22}} = -\frac{1}{2} \arctan \left(\frac{2048\sqrt{2}F}{729} \right) \tag{1.3.24}$$

thus

$$\mathscr{E}(F) = H_{11} \cos^2 p + H_{12} \sin 2p + H_{22} \sin^2 p = -\frac{1}{2} - \frac{262144}{177147} F^2 + \mathcal{O}(F^3) \tag{1.3.25}$$

$\therefore$

$$\alpha = 2 \times \frac{262144}{177147} = 2.96 \tag{1.3.26}$$

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2.2.1 Spin Orbitals and Spatial Orbitals

Ex 2.1 Consider $\langle \chi_k \,|\, \chi_m \rangle$. If $k = m$,

$$\langle \chi_{2i-1} \,|\, \chi_{2i-1} \rangle = \langle \psi_i^\alpha \,|\, \psi_i^\alpha \rangle \langle \alpha \,|\, \alpha \rangle = 1 \tag{2.2.1}$$

$$\langle \chi_{2i} \,|\, \chi_{2i} \rangle = \left\langle \psi_i^\beta \,\middle|\, \psi_i^\beta \right\rangle \langle \alpha \,|\, \alpha \rangle = 1 \tag{2.2.2}$$

thus

$$\langle \chi_k \,|\, \chi_k \rangle = 1 \tag{2.2.3}$$

If $k \neq m$, three cases may occur as below

$$\langle \chi_{2i-1} \,|\, \chi_{2j-1} \rangle = \left\langle \psi_i^\alpha \,\middle|\, \psi_j^\alpha \right\rangle \langle \alpha \,|\, \alpha \rangle = 0 \cdot 1 = 0 \qquad (i \neq j) \tag{2.2.4}$$

$$\langle \chi_{2i-1} \,|\, \chi_{2j} \rangle = \left\langle \psi_i^\alpha \,\middle|\, \psi_j^\beta \right\rangle \langle \alpha \,|\, \beta \rangle = S_{ij} \cdot 0 = 0 \tag{2.2.5}$$

$$\langle \chi_{2i} \,|\, \chi_{2j} \rangle = \left\langle \psi_i^\beta \,\middle|\, \psi_j^\beta \right\rangle \langle \beta \,|\, \beta \rangle = 0 \cdot 1 = 0 \qquad (i \neq j) \tag{2.2.6}$$

thus

$$\langle \chi_k \,|\, \chi_m \rangle = 0 \qquad (k \neq m) \tag{2.2.7}$$

Overall,

$$\langle \chi_k \,|\, \chi_m \rangle = \delta_{km} \tag{2.2.8}$$

2.2.2 Hartree Products

Ex 2.2

$$\begin{aligned} \mathscr{H}\Psi^{HP} &= \sum_{i=1}^{N} h(i)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N) \\ &= \underline{\varepsilon_i\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)} + \underline{\chi_i(\mathbf{x}_1)[\varepsilon_j\chi_j(\mathbf{x}_2)]\cdots\chi_k(\mathbf{x}_N)} + \cdots + \underline{\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots[\varepsilon_k\chi_k(\mathbf{x}_N)]} \\ &= (\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k)\Psi^{HP} \end{aligned} \tag{2.2.9}$$

2.2.3 Slater Determinants

Ex 2.3

$$\begin{aligned} \langle \Psi \,|\, \Psi \rangle &= \frac{1}{2}(\langle \chi_i \,|\, \chi_i \rangle \langle \chi_j \,|\, \chi_j \rangle - \langle \chi_i \,|\, \chi_j \rangle \langle \chi_j \,|\, \chi_i \rangle - \langle \chi_j \,|\, \chi_i \rangle \langle \chi_i \,|\, \chi_j \rangle + \langle \chi_j \,|\, \chi_j \rangle \langle \chi_i \,|\, \chi_i \rangle) \\ &= \frac{1}{2}(1 + 0 + 0 + 1) = 1 \end{aligned} \tag{2.2.10}$$

Ex 2.4 According to Ex. 2.2, we know that $\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)$ are an eigenfunction of $\mathscr{H}$ and has the eigenvalue $\varepsilon_i\varepsilon_j$. Similarly, we have the same conclusion for $\chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)$.
For the antisymmetrized wave function,

$$\begin{aligned} \langle \Psi \,|\, \mathscr{H} \,|\, \Psi \rangle &= \frac{1}{2}\left(\langle \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \,|\, \mathscr{H} \,|\, \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \rangle - \langle \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \,|\, \mathscr{H} \,|\, \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \rangle \right. \\ &\quad \left. - \langle \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \,|\, \mathscr{H} \,|\, \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \rangle + \langle \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \,|\, \mathscr{H} \,|\, \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \rangle\right) \\ &= \frac{1}{2}(\varepsilon_i + \varepsilon_j - 0 - 0 + \varepsilon_i + \varepsilon_j) \\ &= \varepsilon_i + \varepsilon_j \end{aligned} \tag{2.2.11}$$

Ex 2.5

$$\begin{aligned}\langle K \mid L\rangle &= \frac{1}{2}\left\langle \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \mid \chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) - \chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\right\rangle \\ &= \frac{1}{2}(\langle\chi_i \mid \chi_k\rangle\langle\chi_j \mid \chi_l\rangle - \langle\chi_i \mid \chi_l\rangle\langle\chi_j \mid \chi_k\rangle - \langle\chi_j \mid \chi_k\rangle\langle\chi_i \mid \chi_l\rangle + \langle\chi_j \mid \chi_l\rangle\langle\chi_i \mid \chi_k\rangle) \\ &= \frac{1}{2}(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik}) \\ &= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\end{aligned} \tag{2.2.12}$$

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H_2 Model

Ex 2.6

$$\langle\psi_1 \mid \psi_1\rangle = \frac{1}{2(1+S_{12})}(\langle\phi_1 \mid \phi_1\rangle + 2\langle\phi_1 \mid \phi_2\rangle + \langle\phi_2 \mid \phi_2\rangle) = \frac{2+2S_{12}}{2(1+S_{12})} = 1 \tag{2.2.13}$$

$$\langle\psi_2 \mid \psi_2\rangle = \frac{1}{2(1-S_{12})}(\langle\phi_1 \mid \phi_1\rangle - 2\langle\phi_1 \mid \phi_2\rangle + \langle\phi_2 \mid \phi_2\rangle) = \frac{2-2S_{12}}{2(1-S_{12})} = 1 \tag{2.2.14}$$

$$\langle\psi_1 \mid \psi_2\rangle = \frac{1}{2\sqrt{1+S_{12}}\sqrt{1-S_{12}}}(\langle\phi_1 \mid \phi_1\rangle - \langle\phi_2 \mid \phi_2\rangle) = 0 \tag{2.2.15}$$

2.2.6 Excited Determinants

2.2.7 Form of the Exact Wfn and CI

Ex 2.7 Size of full CI matrix

$$C_{72}^{42} = 164307576757973059488 \approx 1.64 \times 10^{20} \tag{2.2.16}$$

The number of singly excited determinants

$$42 \times 30 = 1260 \tag{2.2.17}$$

The number of doubly excited determinants

$$C_{42}^2 C_{30}^2 = 374535 \tag{2.2.18}$$

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H_2 Matrix Elements

Ex 2.8

$$\begin{aligned}\left\langle\Psi_{12}^{34} \,\middle|\, h(1) \,\middle|\, \Psi_{12}^{34}\right\rangle &= \frac{1}{2}\left\langle \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \mid h(1) \mid \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1)\right\rangle \\ &= \frac{1}{2}(\langle\chi_3 \mid h(1) \mid \chi_3\rangle - 0 - 0 + \langle\chi_4 \mid h(1) \mid \chi_4\rangle) \\ &= \frac{1}{2}(\langle\chi_3 \mid h(1) \mid \chi_3\rangle + \langle\chi_4 \mid h(1) \mid \chi_4\rangle)\end{aligned} \tag{2.3.1}$$

thus

$$\left\langle\Psi_{12}^{34} \,\middle|\, \mathcal{O}_1 \,\middle|\, \Psi_{12}^{34}\right\rangle = \langle 3 \mid h \mid 3\rangle + \langle 4 \mid h \mid 4\rangle \tag{2.3.2}$$

$$\begin{aligned}\left\langle\Psi_0 \,\middle|\, h(1) \,\middle|\, \Psi_{12}^{34}\right\rangle &= \frac{1}{2}\left\langle \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_2)\chi_1(\mathbf{x}_1) \mid h(1) \mid \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1)\right\rangle \\ &= \frac{1}{2}(0 - 0 - 0 + 0) \\ &= 0\end{aligned} \tag{2.3.3}$$

thus

$$\left\langle\Psi_0 \,\middle|\, \mathcal{O}_1 \,\middle|\, \Psi_{12}^{34}\right\rangle = 0 \tag{2.3.4}$$

Similarly, we get

$$\left\langle\Psi_{12}^{34} \,\middle|\, \mathcal{O}_1 \,\middle|\, \Psi_0\right\rangle = 0 \tag{2.3.5}$$

Ex 2.9 From Eq. (2.92) in textbook, we get

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_0 \rangle = \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,|\, 12 \rangle - \langle 12 \,|\, 21 \rangle \tag{2.3.6}$$

From Ex 2.8, we get

$$\left\langle \Psi_0 \,\middle|\, \mathcal{O}_1 \,\middle|\, \Psi_{12}^{34} \right\rangle = \left\langle \Psi_{12}^{34} \,\middle|\, \mathcal{O}_1 \,\middle|\, \Psi_0 \right\rangle = 0 \tag{2.3.7}$$

thus

$$\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \left\langle \Psi_0 \,\middle|\, \mathcal{O}_2 \,\middle|\, \Psi_{12}^{34} \right\rangle \\
&= \frac{1}{2} \left\langle \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \right\rangle \\
&= \langle 12 \,|\, 34 \rangle - \langle 12 \,|\, 43 \rangle
\end{aligned} \tag{2.3.8}$$

$$\begin{aligned}
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle &= \left\langle \Psi_{12}^{34} \,\middle|\, \mathcal{O}_2 \,\middle|\, \Psi_0 \right\rangle \\
&= \frac{1}{2} \left\langle \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_2)\chi_1(\mathbf{x}_1) \right\rangle \\
&= \langle 34 \,|\, 12 \rangle - \langle 34 \,|\, 21 \rangle
\end{aligned} \tag{2.3.9}$$

$$\begin{aligned}
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \left\langle \Psi_{12}^{34} \,\middle|\, h(1) + h(2) + \frac{1}{r_{12}} \,\middle|\, \Psi_{12}^{34} \right\rangle \\
&= 2 \times \frac{1}{2} \langle \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \,|\, h(1) \,|\, \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \rangle \\
&+ \frac{1}{2} \left\langle \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \chi_3(\mathbf{x}_1)\chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2)\chi_4(\mathbf{x}_1) \right\rangle \\
&= \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,|\, 34 \rangle - \langle 34 \,|\, 43 \rangle
\end{aligned} \tag{2.3.10}$$

2.3.2 Notations for 1- and 2-Electron Integrals

2.3.3 General Rules for Matrix Elements

Ex 2.10

$$\langle K \,|\, \mathscr{H} \,|\, K \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N \langle mn \,\|\, mn \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N ([mm|nn] - [mn|nm]) \tag{2.3.11}$$

When $m = n$,

$$[mm|mm] - [mm|mm] = 0 \tag{2.3.12}$$

thus

$$\langle K \,|\, \mathscr{H} \,|\, K \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_{n \neq m}^N ([mm|nn] - [mn|nm]) = \sum_m^N [m|h|m] + \sum_m^N \sum_{n>m}^N ([mm|nn] - [mn|nm]) \tag{2.3.13}$$

Ex 2.11

$$\begin{aligned}
\langle K \,|\, \mathscr{H} \,|\, K \rangle = \langle K \,|\, \mathcal{O}_1 + \mathcal{O}_2 \,|\, K \rangle &= \sum_m^N [m|h|m] + \sum_m^N \sum_{n>m}^N \langle mn \,\|\, mn \rangle \\
&= \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 3 \,|\, h \,|\, 3 \rangle + \langle 12 \,\|\, 12 \rangle + \langle 13 \,\|\, 13 \rangle + \langle 23 \,\|\, 23 \rangle
\end{aligned} \tag{2.3.14}$$

Ex 2.12

$$\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_0 \rangle &= \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,\|\, 12 \rangle \\
&= \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,|\, 12 \rangle - \langle 12 \,|\, 21 \rangle
\end{aligned} \tag{2.3.15}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle = \langle 12 \,\|\, 34 \rangle = \langle 12 \,|\, 34 \rangle - \langle 12 \,|\, 43 \rangle \tag{2.3.16}$$

$$\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle = \langle 34 \,\|\, 12 \rangle = \langle 34 \,|\, 12 \rangle - \langle 34 \,|\, 21 \rangle \tag{2.3.17}$$

$$\begin{aligned}
\left\langle \Psi_{12}^{34} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{12}^{34} \right\rangle &= \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,\|\, 34 \rangle \\
&= \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,|\, 34 \rangle - \langle 34 \,|\, 43 \rangle
\end{aligned} \tag{2.3.18}$$

Which are exactly the same with Ex 2.9.

Ex 2.13 if $a=b$, $r=s$

$$\langle \Psi_a^r \,|\, \mathcal{O} \,|\, \Psi_b^s \rangle = \langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, \Psi_a^r \rangle = \sum_c^N \langle c \,|\, h \,|\, c \rangle - \langle a \,|\, h \,|\, a \rangle + \langle r \,|\, h \,|\, r \rangle \tag{2.3.19}$$

if $a=b$, $r \neq s$

$$\langle \Psi_a^r \,|\, \mathcal{O} \,|\, \Psi_b^s \rangle = \langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, \Psi_a^s \rangle = \langle r \,|\, h \,|\, s \rangle \tag{2.3.20}$$

if $a \neq b$, $r=s$

$$\langle \Psi_a^r \,|\, \mathcal{O} \,|\, \Psi_b^s \rangle = \langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, \Psi_b^r \rangle = \langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, -(\Psi_a^r)_b^a \rangle = -\langle b \,|\, h \,|\, a \rangle \tag{2.3.21}$$

if $a \neq b$, $r \neq s$

$$\langle \Psi_a^r \,|\, \mathcal{O} \,|\, \Psi_b^s \rangle = \langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, (\Psi_a^r)_{rb}^{as} \rangle = 0 \tag{2.3.22}$$

Ex 2.14

$$^N E_0 = \sum_m^N \langle m \,|\, h \,|\, m \rangle + \sum_m^M \sum_{n>m}^M \langle mn \,\|\, mn \rangle \tag{2.3.23}$$

$$^{N-1} E_0 = \sum_{m\neq a}^N \langle m \,|\, h \,|\, m \rangle + \sum_{m\neq a}^M \sum_{n>m, n\neq a}^M \langle mn \,\|\, mn \rangle \tag{2.3.24}$$

$$^N E_0 - ^{N-1} E_0 = \langle a \,|\, h \,|\, a \rangle + \sum_{b\neq a}^N \langle ab \,\|\, ab \rangle \tag{2.3.25}$$

2.3.4 Derivation of the Rules for Matrix Elements

Ex 2.15

$$\begin{aligned} \langle \Psi \,|\, \mathscr{H} \,|\, \Psi \rangle &= \frac{1}{N!} \left\langle \sum_{n=1}^{N!} (-1)^{p_n} \mathscr{P}_n \{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \,\middle|\, \sum_{c=1}^N h(c) \,\middle|\, \sum_{m=1}^{N!} (-1)^{p_m} \mathscr{P}_m \{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \right\rangle \\ &= \frac{1}{N!} \sum_{n=1}^{N!} \sum_{m=1}^{N!} (-1)^{p_n+p_m} \sum_{c=1}^N \langle \mathscr{P}_n \{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \,|\, h(c) \,|\, \mathscr{P}_m \{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \rangle \end{aligned} \tag{2.3.26}$$

Since the integral inside equals 0 when $\mathscr{P}_n \neq \mathscr{P}_m$,

$$\langle \Psi \,|\, \mathscr{H} \,|\, \Psi \rangle = \frac{1}{N!} \sum_{n=1}^{N!} (-1)^{p_n+p_n} (\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k) = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k \tag{2.3.27}$$

Ex 2.16

$$\begin{aligned} \langle K \,|\, \mathscr{H} \,|\, L \rangle &= \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} \left\langle (-1)^{p_n} \mathscr{P}_n K^{HP} \,\middle|\, \mathscr{H} \,\middle|\, L \right\rangle \\ &= \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} \left\langle K^{HP} \,\middle|\, \mathscr{H} \,\middle|\, L \right\rangle \\ &= \frac{1}{\sqrt{N!}} \times N! \left\langle K^{HP} \,\middle|\, \mathscr{H} \,\middle|\, L \right\rangle \\ &= \sqrt{N!} \left\langle K^{HP} \,\middle|\, \mathscr{H} \,\middle|\, L \right\rangle \end{aligned} \tag{2.3.28}$$

2.3.5 Transition from Spin Orbitals to Spatial Orbitals

Ex 2.17

$$\begin{aligned} |1\rangle &= |\psi_1 \alpha\rangle \quad |2\rangle = |\psi_1 \beta\rangle \\ |3\rangle &= |\psi_2 \alpha\rangle \quad |4\rangle = |\psi_2 \beta\rangle \end{aligned} \tag{2.3.29}$$

thus

$$\begin{aligned} \mathbf{H} &= \begin{pmatrix} \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,|\, 12 \rangle - \langle 12 \,|\, 21 \rangle & \langle 12 \,|\, 34 \rangle - \langle 12 \,|\, 43 \rangle \\ \langle 34 \,|\, 12 \rangle - \langle 34 \,|\, 21 \rangle & \langle 3 \,|\, h \,|\, 3 \rangle + \langle 4 \,|\, h \,|\, 4 \rangle + \langle 34 \,|\, 34 \rangle - \langle 34 \,|\, 43 \rangle \end{pmatrix} \\ &= \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix} \end{aligned} \tag{2.3.30}$$

Ex 2.18

$$\begin{aligned}
|\langle ab \| rs\rangle|^2 &= (\langle ab\,|\,rs\rangle - \langle ab\,|\,sr\rangle)^*(\langle ab\,|\,rs\rangle - \langle ab\,|\,sr\rangle) \\
&= \langle rs\,|\,ab\rangle \langle ab\,|\,rs\rangle - \langle rs\,|\,ab\rangle \langle ab\,|\,sr\rangle - \langle sr\,|\,ab\rangle \langle ab\,|\,rs\rangle + \langle sr\,|\,ab\rangle \langle ab\,|\,sr\rangle \\
&= [ra|sb][ar|bs] - [ra|sb][as|br] - [sa|rb][ar|bs] + [sa|rb][as|br] \\
&= [ar|bs]^2 - 2[ar|bs][as|br] + [as|br]^2
\end{aligned} \tag{2.3.31}$$

Let's calculate $E_0^{(2)}$ term by term.

$$\begin{aligned}
\left(E_0^{(2)}\right)_1 &= \frac{1}{4}\sum_{abrs} \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4}\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{[ar|bs]^2 + [\bar{a}\bar{r}|bs]^2 + [ar|\bar{b}\bar{s}]^2 + [\bar{a}\bar{r}|\bar{b}\bar{s}]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{\langle ab\,|\,rs\rangle \langle rs\,|\,ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.32}$$

$$\begin{aligned}
\left(E_0^{(2)}\right)_2 &= \frac{1}{4}\sum_{abrs} \frac{-2[ar|bs][as|br]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\frac{1}{2}\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{[ar|bs][as|br] + [\bar{a}\bar{r}|\bar{b}\bar{s}][\bar{a}\bar{s}|\bar{b}\bar{r}]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{[ar|bs][as|br]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{\langle ab\,|\,rs\rangle \langle rs\,|\,ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.33}$$

$$\begin{aligned}
\left(E_0^{(2)}\right)_3 &= \frac{1}{4}\sum_{abrs} \frac{[as|br]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \frac{1}{4}\sum_{absr} \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_r} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{\langle ab\,|\,rs\rangle \langle rs\,|\,ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.34}$$

thus,

$$E_0^{(2)} = \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^{K} \frac{\langle ab\,|\,rs\rangle \left(2\langle rs\,|\,ab\rangle - \langle rs\,|\,ba\rangle\right)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{2.3.35}$$

2.3.6 Coulomb and Exchange Integrals

Ex 2.19

$$J_{ii} = (ii|ii) = K_{ii} \tag{2.3.36}$$

$$J_{ij}^* = \langle ij\,|\,ij\rangle^* = \langle ij\,|\,ij\rangle = J_{ij} \tag{2.3.37}$$

$$K_{ij}^* = \langle ij\,|\,ji\rangle^* = \langle ji\,|\,ij\rangle = \langle ij\,|\,ji\rangle = K_{ij} \tag{2.3.38}$$

$$J_{ij} = (ii|jj) = (jj|ii) = J_{ji} \tag{2.3.39}$$

$$K_{ij} = (ij|ji) = (ji|ij) = K_{ji} \tag{2.3.40}$$

Ex 2.20 For real spatial orbitals

$$K_{ij} = (ij|ji) = (ij|ij) = (ji|ji) \tag{2.3.41}$$

$$K_{ij} = \langle ij \,|\, ji\rangle = \langle ii \,|\, jj\rangle = \langle jj \,|\, ii\rangle \tag{2.3.42}$$

Ex 2.21

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix} \tag{2.3.43}$$

Ex 2.22

$$E_{\uparrow\downarrow}^{HP} = \left\langle \Psi_{\uparrow\downarrow}^{HP} \middle| h(1) + h(2) + \frac{1}{r_{12}} \middle| \Psi_{\uparrow\downarrow}^{HP} \right\rangle = (1|h|1) + (2|h|2) + (11|22) = h_{11} + h_{22} + J_{12} \tag{2.3.44}$$

$$E_{\downarrow\downarrow}^{HP} = \left\langle \Psi_{\downarrow\downarrow}^{HP} \middle| h(1) + h(2) + \frac{1}{r_{12}} \middle| \Psi_{\downarrow\downarrow}^{HP} \right\rangle = (1|h|1) + (2|h|2) + (11|22) = h_{11} + h_{22} + J_{12} \tag{2.3.45}$$

2.3.7 Pseudo-Classical Interpretation of Determinantal Energies

Ex 2.23 a.-g. can be obtained immediately with definition.

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

Ex 2.24 Since $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$, we have

$$(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)\,|K\rangle = 0 \tag{2.4.1}$$

for any $|K\rangle$.

Ex 2.25 Since $a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$, we have

$$(a_1 a_2^\dagger + a_2^\dagger a_1)\,|K\rangle = 0 \tag{2.4.2}$$

$$(a_1 a_1^\dagger + a_1^\dagger a_1)\,|K\rangle = |K\rangle \tag{2.4.3}$$

for any $|K\rangle$.

Ex 2.26

$$\langle \chi_i \,|\, \chi_j\rangle = \left\langle 0 \middle| a_i a_j^\dagger \middle| 0 \right\rangle = \left\langle 0 \middle| \delta_{ij} - a_j^\dagger a_i \middle| 0 \right\rangle = \delta_{ij} \tag{2.4.4}$$

where $|0\rangle$ is the vacuum state.

Ex 2.27 First, if $i \notin \{1, 2, \cdots, N\}$ or $j \notin \{1, 2, \cdots, N\}$,

$$\left\langle K \middle| a_i^\dagger a_j \middle| K \right\rangle = 0 \tag{2.4.5}$$

because inexistent electron cannot be annihilated.
Thus, $i, j \in \{1, 2, \cdots, N\}$, and

$$\left\langle K \middle| a_i^\dagger a_j \middle| K \right\rangle = \delta_{ij}\,\langle K \,|\, K\rangle - \left\langle K \middle| a_j a_i^\dagger \middle| K \right\rangle \tag{2.4.6}$$

$\left\langle K \middle| a_j a_i^\dagger \middle| K \right\rangle$ would be 0 because χ_i is created twice. Thus,

$$\left\langle K \middle| a_i^\dagger a_j \middle| K \right\rangle = \delta_{ij} \tag{2.4.7}$$

Overall, $\left\langle K \middle| a_i^\dagger a_j \middle| K \right\rangle = 1$ when $i = j$ and $i \in \{1, 2, \cdots, N\}$, but is 0 otherwise.

Ex 2.28

a. That's obvious since inexistent electron cannot be annihilated.

b. That's obvious since an electron cannot be created twice.

c.

$$
\begin{aligned}
a_r^\dagger a_a |\Psi_0\rangle &= a_r^\dagger a_a(-|\chi_a \cdots \chi_1 \chi_b \cdots \chi_N\rangle) \\
&= -a_r^\dagger |\cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= -|\chi_r \cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= |\chi_1 \cdots \chi_r \chi_b \cdots \chi_N\rangle \\
&= |\Psi_a^r\rangle
\end{aligned}
\tag{2.4.8}
$$

d. That's similar to 2.28.c.

e.

$$
\begin{aligned}
a_s^\dagger a_b a_r^\dagger a_a |\Psi_0\rangle &= a_s^\dagger a_b a_r^\dagger(-|\chi_2 \cdots \chi_1 \chi_b \cdots \chi_N\rangle) \\
&= -a_s^\dagger a_b |\chi_r \chi_2 \cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= -a_s^\dagger(-|\chi_2 \cdots \chi_1 \chi_r \cdots \chi_N\rangle) \\
&= |\chi_s \chi_2 \cdots \chi_1 \chi_r \cdots \chi_N\rangle \\
&= |\chi_1 \cdots \chi_r \chi_s \cdots \chi_N\rangle \\
&= |\Psi_{ab}^{rs}\rangle
\end{aligned}
\tag{2.4.9}
$$

$\therefore$

$$
|\Psi_{ab}^{rs}\rangle = a_s^\dagger a_b a_r^\dagger a_a |\Psi_0\rangle = a_s^\dagger(-a_r^\dagger a_b) a_a |\Psi_0\rangle = a_r^\dagger a_s^\dagger a_b a_a |\Psi_0\rangle \tag{2.4.10}
$$

f. That's similar to 2.28.e.

2.4.2 Second-Quantized Operators and Their Matrix Elements

Ex 2.29

$$
\begin{aligned}
\langle \Psi_0 \,|\, \mathcal{O}_1 \,|\, \Psi_0 \rangle &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \langle 0 | a_2 a_1 a_i^\dagger a_j a_1^\dagger a_2^\dagger |0\rangle \\
&= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \langle 0 | a_2 a_1 (\delta_{ij} - a_j^\dagger a_i) a_1^\dagger a_2^\dagger |0\rangle \\
&= \sum_{i} \langle i \,|\, h \,|\, i \rangle \langle 0 | a_2 a_1 a_1^\dagger a_2^\dagger |0\rangle - \sum_{ij} \langle i \,|\, h \,|\, j \rangle \langle 0 | a_2 a_1 a_j a_i^\dagger a_1^\dagger a_2^\dagger |0\rangle
\end{aligned}
\tag{2.4.11}
$$

The second terms must be 0 since $i \in 1, 2$.
Thus,

$$
\langle \Psi_0 \,|\, \mathcal{O}_1 \,|\, \Psi_0 \rangle = \sum_{i} \langle i \,|\, h \,|\, i \rangle \langle 0 | a_2 a_1 a_1^\dagger a_2^\dagger |0\rangle = \langle 1 \,|\, h \,|\, 1 \rangle + \langle 2 \,|\, h \,|\, 2 \rangle \tag{2.4.12}
$$

Ex 2.30

$$
\begin{aligned}
\langle \Psi_a^r \,|\, \mathcal{O}_1 \,|\, \Psi_0 \rangle &= \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_r a_i^\dagger a_j \,\middle|\, \Psi_0 \right\rangle = \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger (\delta_{ri} - a_i^\dagger a_r) a_j \,\middle|\, \Psi_0 \right\rangle \\
&= \sum_{j} \langle r \,|\, h \,|\, j \rangle \langle \Psi_0 \,|\, a_a^\dagger a_j \,|\, \Psi_0 \rangle - \sum_{ij} \langle i \,|\, h \,|\, j \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j \,\middle|\, \Psi_0 \right\rangle \\
&= \sum_{j} \langle r \,|\, h \,|\, j \rangle \langle \Psi_0 \,|\, (\delta_{aj} - a_j a_a^\dagger) \,|\, \Psi_0 \rangle \\
&= \langle r \,|\, h \,|\, a \rangle \langle \Psi_0 \,|\, \Psi_0 \rangle - \sum_{j} \langle r \,|\, h \,|\, j \rangle \langle \Psi_0 \,|\, a_j a_a^\dagger \,|\, \Psi_0 \rangle \\
&= \langle r \,|\, h \,|\, a \rangle
\end{aligned}
\tag{2.4.13}
$$

Ex 2.31

$$\langle \Psi_a^r \,|\, \mathcal{O}_2 \,|\, \Psi_0 \rangle = \frac{1}{2} \sum_{ijkl} \langle ij \,|\, kl \rangle \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \tag{2.4.14}$$

while

$$\begin{aligned}
\left\langle \Psi_0 \,\middle|\, a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle &= \left\langle \Psi_0 \,\middle|\, a_a^\dagger \delta_{ri} a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle - \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_r a_j^\dagger a_l a_k \,\middle|\, \Psi_0 \right\rangle \\
&= \delta_{ri} \Big(\left\langle \Psi_0 \,\middle|\, a_j^\dagger \delta_{ak} a_l \,\middle|\, \Psi_0 \right\rangle - \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k a_a^\dagger a_l \,\middle|\, \Psi_0 \right\rangle \Big) \\
&\quad - \Big(\left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger \delta_{rj} a_l a_k \,\middle|\, \Psi_0 \right\rangle - \left\langle \Psi_0 \,\middle|\, a_a^\dagger a_i^\dagger a_j^\dagger a_r a_l a_k \,\middle|\, \Psi_0 \right\rangle \Big) \\
&= \delta_{ri}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle - \delta_{ri}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \\
&\quad - \delta_{rj} \Big(\left\langle \Psi_0 \,\middle|\, a_i^\dagger \delta_{ak} a_l \,\middle|\, \Psi_0 \right\rangle - \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k a_a^\dagger a_l \,\middle|\, \Psi_0 \right\rangle \Big) + 0 \\
&= \delta_{ri}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle - \delta_{ri}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \\
&\quad - \delta_{rj}\delta_{ak} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l \,\middle|\, \Psi_0 \right\rangle + \delta_{rj}\delta_{al} \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle
\end{aligned} \tag{2.4.15}$$

According to Ex. 2.27, we have

$$\begin{aligned}
\langle \Psi_a^r \,|\, \mathcal{O}_2 \,|\, \Psi_0 \rangle &= \frac{1}{2} \Bigg(\sum_{jl} \langle rj \,|\, al \rangle \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_l \,\middle|\, \Psi_0 \right\rangle - \sum_{jk} \langle rj \,|\, ka \rangle \left\langle \Psi_0 \,\middle|\, a_j^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \\
&\qquad - \sum_{il} \langle ir \,|\, al \rangle \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_l \,\middle|\, \Psi_0 \right\rangle + \sum_{ik} \langle ir \,|\, ka \rangle \left\langle \Psi_0 \,\middle|\, a_i^\dagger a_k \,\middle|\, \Psi_0 \right\rangle \Bigg) \\
&= \frac{1}{2} \left(\sum_j^N \langle rj \,|\, aj \rangle - \sum_j^N \langle rj \,|\, ja \rangle - \sum_i^N \langle ir \,|\, ai \rangle + \sum_i^N \langle ir \,|\, ia \rangle \right) \\
&= \sum_j^N \langle rj \,|\, aj \rangle - \sum_j^N \langle rj \,|\, ja \rangle \\
&= \sum_j^N \langle rj \,\|\, aj \rangle
\end{aligned} \tag{2.4.16}$$

2.5 Spin-Adapted Configurations

2.5.1 Spin Operators

Ex 2.32

a)

$$\widehat{\mathbf{s}}_+ \,|\alpha\rangle = (\widehat{\mathbf{s}}_x + \mathrm{i}\,\widehat{\mathbf{s}}_y)\,|\alpha\rangle = \left(\frac{1}{2} + \mathrm{i}\,\frac{\mathrm{i}}{2}\right)|\beta\rangle = 0 \tag{2.5.1}$$

$$\widehat{\mathbf{s}}_+ \,|\beta\rangle = (\widehat{\mathbf{s}}_x + \mathrm{i}\,\widehat{\mathbf{s}}_y)\,|\beta\rangle = \left(\frac{1}{2} - \mathrm{i}\,\frac{\mathrm{i}}{2}\right)|\alpha\rangle = |\alpha\rangle \tag{2.5.2}$$

$$\widehat{\mathbf{s}}_- \,|\alpha\rangle = (\widehat{\mathbf{s}}_x - \mathrm{i}\,\widehat{\mathbf{s}}_y)\,|\alpha\rangle = \left(\frac{1}{2} - \mathrm{i}\,\frac{\mathrm{i}}{2}\right)|\beta\rangle = |\beta\rangle \tag{2.5.3}$$

$$\widehat{\mathbf{s}}_- \,|\beta\rangle = (\widehat{\mathbf{s}}_x - \mathrm{i}\,\widehat{\mathbf{s}}_y)\,|\beta\rangle = \left(\frac{1}{2} + \mathrm{i}\,\frac{\mathrm{i}}{2}\right)|\alpha\rangle = 0 \tag{2.5.4}$$

b)

$$\widehat{\mathbf{s}}_+ \,\widehat{\mathbf{s}}_- = (\widehat{\mathbf{s}}_x + \mathrm{i}\,\widehat{\mathbf{s}}_y)(\widehat{\mathbf{s}}_x - \mathrm{i}\,\widehat{\mathbf{s}}_y) = \widehat{\mathbf{s}}_x^2 + \widehat{\mathbf{s}}_y^2 + \mathrm{i}(\widehat{\mathbf{s}}_y\,\widehat{\mathbf{s}}_x - \widehat{\mathbf{s}}_x\,\widehat{\mathbf{s}}_y) = \widehat{\mathbf{s}}_x^2 + \widehat{\mathbf{s}}_y^2 + \widehat{\mathbf{s}}_z \tag{2.5.5}$$

$$\widehat{\mathrm{s}}_- \widehat{\mathrm{s}}_+ = (\widehat{\mathrm{s}}_x - \mathrm{i}\,\widehat{\mathrm{s}}_y)(\widehat{\mathrm{s}}_x + \mathrm{i}\,\widehat{\mathrm{s}}_y) = \widehat{\mathrm{s}}_x^2 + \widehat{\mathrm{s}}_y^2 + \mathrm{i}(\widehat{\mathrm{s}}_x \widehat{\mathrm{s}}_y - \widehat{\mathrm{s}}_y \widehat{\mathrm{s}}_x) = \widehat{\mathrm{s}}_x^2 + \widehat{\mathrm{s}}_y^2 - \widehat{\mathrm{s}}_z \tag{2.5.6}$$

thus,

$$\begin{aligned}\widehat{\mathrm{s}}^2 &= \widehat{\mathrm{s}}_x^2 + \widehat{\mathrm{s}}_y^2 + \widehat{\mathrm{s}}_z^2 = \widehat{\mathrm{s}}_+ \widehat{\mathrm{s}}_- - \widehat{\mathrm{s}}_z + \widehat{\mathrm{s}}_z^2 &(2.5.7)\\ &= \widehat{\mathrm{s}}_- \widehat{\mathrm{s}}_+ + \widehat{\mathrm{s}}_z + \widehat{\mathrm{s}}_z^2 &(2.5.8)\end{aligned}$$

Ex 2.33

$$\widehat{\mathrm{s}}^2 = \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix} \quad \widehat{\mathrm{s}}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \quad \widehat{\mathrm{s}}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \widehat{\mathrm{s}}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{2.5.9}$$

thus

$$\widehat{\mathrm{s}}_+ \widehat{\mathrm{s}}_- - \widehat{\mathrm{s}}_z + \widehat{\mathrm{s}}_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix} = \widehat{\mathrm{s}}^2 \tag{2.5.10}$$

$$\widehat{\mathrm{s}}_- \widehat{\mathrm{s}}_+ + \widehat{\mathrm{s}}_z + \widehat{\mathrm{s}}_z^2 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix} = \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix} = \widehat{\mathrm{s}}^2 \tag{2.5.11}$$

Ex 2.34

$$\begin{aligned}[\widehat{\mathrm{s}}^2, \widehat{\mathrm{s}}_z] &= [\widehat{\mathrm{s}}_+ \widehat{\mathrm{s}}_- - \widehat{\mathrm{s}}_z + \widehat{\mathrm{s}}_z^2, \widehat{\mathrm{s}}_z] \\ &= \widehat{\mathrm{s}}_+[\widehat{\mathrm{s}}_-, \widehat{\mathrm{s}}_z] + [\widehat{\mathrm{s}}_+, \widehat{\mathrm{s}}_z]\widehat{\mathrm{s}}_- - 0 + 0 \\ &= \widehat{\mathrm{s}}_+[\widehat{\mathrm{s}}_x - \mathrm{i}\,\widehat{\mathrm{s}}_y, \widehat{\mathrm{s}}_z] + [\widehat{\mathrm{s}}_x + \mathrm{i}\,\widehat{\mathrm{s}}_y, \widehat{\mathrm{s}}_z]\widehat{\mathrm{s}}_- \\ &= \widehat{\mathrm{s}}_+(-\mathrm{i}\,\widehat{\mathrm{s}}_y - \mathrm{i}\cdot\mathrm{i}\,\widehat{\mathrm{s}}_x) + (-\mathrm{i}\,\widehat{\mathrm{s}}_y + \mathrm{i}\cdot\mathrm{i}\,\widehat{\mathrm{s}}_x)\widehat{\mathrm{s}}_- \\ &= \widehat{\mathrm{s}}_+ \widehat{\mathrm{s}}_- - \widehat{\mathrm{s}}_+ \widehat{\mathrm{s}}_- \\ &= 0 \end{aligned} \tag{2.5.12}$$

Ex 2.35

$$\mathscr{H}\mathscr{A}\,|\Phi\rangle = \mathscr{A}\mathscr{H}\,|\Phi\rangle = \mathscr{A}E\,|\Phi\rangle = E\mathscr{A}\,|\Phi\rangle \tag{2.5.13}$$

thus $\mathscr{A}\,|\Phi\rangle$ is also an eigenfunction of $\mathscr{H}$ with eigenvalue E.

Ex 2.36

$$\langle\Psi_1\,|\,\mathscr{H}\mathscr{A}\,|\,\Psi_2\rangle = a_2\,\langle\Psi_1\,|\,\mathscr{H}\,|\,\Psi_2\rangle \tag{2.5.14}$$

Since $[\mathscr{A}, \mathscr{H}] = 0$ and $\mathscr{A}$ is Hermitian,

$$\langle\Psi_1\,|\,\mathscr{H}\mathscr{A}\,|\,\Psi_2\rangle = \langle\Psi_1\,|\,\mathscr{A}\mathscr{H}\,|\,\Psi_2\rangle = \left\langle\Psi_1\,\middle|\,\mathscr{A}^\dagger\mathscr{H}\,\middle|\,\Psi_2\right\rangle = a_1\,\langle\Psi_1\,|\,\mathscr{H}\,|\,\Psi_2\rangle \tag{2.5.15}$$

thus

$$(a_1 - a_2)\,\langle\Psi_1\,|\,\mathscr{H}\,|\,\Psi_2\rangle = 0 \tag{2.5.16}$$

Since $a_1 \neq a_2$,

$$\langle\Psi_1\,|\,\mathscr{H}\,|\,\Psi_2\rangle = 0 \tag{2.5.17}$$

Ex 2.37

$$\begin{aligned}\hat{\mathscr{S}}_z\,|\chi_i\chi_j\cdots\chi_k\rangle &= \hat{\mathscr{S}}_z\frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{p_n}\hat{\mathscr{P}}_n\{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \\ &= \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{p_n}\hat{\mathscr{P}}_n\{\hat{\mathscr{S}}_z\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \\ &= \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{p_n}\hat{\mathscr{P}}_n\left\{\sum_{i=1}^{N}\widehat{\mathrm{s}}_z(i)\chi_i(1)\chi_j(2)\cdots\chi_k(N)\right\}\end{aligned}$$

$$= \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \hat{\mathscr{P}}_n \left\{ \left(\frac{1}{2} N^\alpha - \frac{1}{2} N^\beta \right) \chi_i(1) \chi_j(2) \cdots \chi_k(N) \right\}$$

$$= \frac{1}{2}(N^\alpha - N^\beta) \left|\chi_i \chi_j \cdots \chi_k\right\rangle \tag{2.5.18}$$

2.5.2 Restricted Determinants and Spin-Adapted Configurations

Ex 2.38 From Ex 2.37, we have

$$\hat{\mathscr{S}}_z \left|\psi_i \bar{\psi}_i \psi_j \bar{\psi}_j \cdots\right\rangle = 0 \tag{2.5.19}$$

thus

$$\hat{\mathscr{S}}_z^2 \left|\psi_i \bar{\psi}_i \psi_j \bar{\psi}_j \cdots\right\rangle = 0 \tag{2.5.20}$$

While

$$\begin{aligned} \hat{\mathscr{S}}_+ \left|\psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots\right\rangle &= \hat{\mathscr{S}}_+ \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \hat{\mathscr{P}}_n \{\psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots\} \\ &= \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \hat{\mathscr{P}}_n \{\hat{\mathscr{S}}_+ \psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots\} \\ &= \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \hat{\mathscr{P}}_n \left\{ \sum_a^N \widehat{\mathbf{s}}_+(a) \psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots \right\} \\ &= \sum_a^N \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \hat{\mathscr{P}}_n \{\widehat{\mathbf{s}}_+(a) \psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots\} \end{aligned} \tag{2.5.21}$$

Since

$$\widehat{\mathbf{s}}_+(a) \psi_k(a) = 0 \quad \widehat{\mathbf{s}}_+(a) \bar{\psi}_k(a) = \psi_k(a) \tag{2.5.22}$$

$$\hat{\mathscr{S}}_+ \left|\psi_i \bar{\psi}_i \cdots \psi_k \bar{\psi}_k \cdots\right\rangle = \sum_a^N 0 = 0 \tag{2.5.23}$$

thus

$$\hat{\mathscr{S}}_- \hat{\mathscr{S}}_+ \left|\psi_i \bar{\psi}_i \psi_j \bar{\psi}_j \cdots\right\rangle = 0 \tag{2.5.24}$$

Therefore,

$$\hat{\mathscr{S}}^2 \left|\psi_i \bar{\psi}_i \psi_j \bar{\psi}_j \cdots\right\rangle = (\hat{\mathscr{S}}_- \hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2) \left|\psi_i \bar{\psi}_i \psi_j \bar{\psi}_j \cdots\right\rangle = 0 \tag{2.5.25}$$

Ex 2.39

-

$$\begin{aligned} \hat{\mathscr{S}}^2 \left|{}^1\Psi_1^2\right\rangle &= (\hat{\mathscr{S}}_- \hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2) \frac{1}{2} (\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\ &= \frac{1}{2} (\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2))(\hat{\mathscr{S}}_- \hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned} \tag{2.5.26}$$

$\because$

$$\hat{\mathscr{S}}_- \hat{\mathscr{S}}_+ (\alpha(1)\beta(2) - \beta(1)\alpha(2)) = \hat{\mathscr{S}}_- (\alpha(1)\alpha(2) - \alpha(1)\alpha(2)) = 0 \tag{2.5.27}$$

$$\hat{\mathscr{S}}_z (\alpha(1)\beta(2) - \beta(1)\alpha(2)) = [1/2 + (-1/2)]\alpha(1)\beta(2) - [-1/2 + 1/2]\beta(1)\alpha(2) = 0 \tag{2.5.28}$$

$\therefore$

$$\hat{\mathscr{S}}^2 \left|{}^1\Psi_1^2\right\rangle = 0 \tag{2.5.29}$$

thus $\left|{}^1\Psi_1^2\right\rangle$ is singlet.

•

$$\begin{aligned}\hat{\mathscr{S}}^2 \left|{}^3\Psi_1^2\right\rangle &= (\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)\frac{1}{2}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ &= \frac{1}{2}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \qquad (2.5.30)\end{aligned}$$

$\because$

$$\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = \hat{\mathscr{S}}_-(\alpha(1)\alpha(2) + \alpha(1)\alpha(2)) = 2(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \qquad (2.5.31)$$

$$\hat{\mathscr{S}}_z(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = [1/2 + (-1/2)]\alpha(1)\beta(2) + [-1/2 + 1/2]\beta(1)\alpha(2) = 0 \qquad (2.5.32)$$

$\therefore$

$$\hat{\mathscr{S}}^2 \left|{}^3\Psi_1^2\right\rangle = 2 \left|{}^3\Psi_1^2\right\rangle \qquad (2.5.33)$$

i.e. $S = 1$,
thus $\left|{}^3\Psi_1^2\right\rangle$ is triplet.

•

$$\begin{aligned}\hat{\mathscr{S}}^2 \left|\Psi_1^{\bar{2}}\right\rangle &= (\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)\frac{-1}{\sqrt{2}}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))\beta(1)\beta(2) \\ &= \frac{-1}{\sqrt{2}}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)\beta(1)\beta(2) \qquad (2.5.34)\end{aligned}$$

$\because$

$$\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+\beta(1)\beta(2) = \hat{\mathscr{S}}_-(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = 2\beta(1)\beta(2) \qquad (2.5.35)$$

$$\hat{\mathscr{S}}_z\beta(1)\beta(2) = -\beta(1)\beta(2) \qquad (2.5.36)$$

$$\hat{\mathscr{S}}_z^2\beta(1)\beta(2) = \beta(1)\beta(2) \qquad (2.5.37)$$

$$(2.5.38)$$

$\therefore$

$$\hat{\mathscr{S}}^2 \left|\Psi_1^{\bar{2}}\right\rangle = 2 \left|\Psi_1^{\bar{2}}\right\rangle \qquad (2.5.39)$$

i.e. $S = 1$,
thus $\left|\Psi_1^{\bar{2}}\right\rangle$ is triplet.

•

$$\begin{aligned}\hat{\mathscr{S}}^2 \left|\Psi_{\bar{1}}^2\right\rangle &= (\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)\frac{1}{\sqrt{2}}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))\alpha(1)\alpha(2) \\ &= \frac{1}{\sqrt{2}}(\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2)\alpha(1)\alpha(2) \qquad (2.5.40)\end{aligned}$$

$\because$

$$\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+\alpha(1)\alpha(2) = 0 \qquad (2.5.41)$$

$$\hat{\mathscr{S}}_z\alpha(1)\alpha(2) = \alpha(1)\alpha(2) \qquad (2.5.42)$$

$$\hat{\mathscr{S}}_z^2\alpha(1)\alpha(2) = \alpha(1)\alpha(2) \qquad (2.5.43)$$

$$(2.5.44)$$

$\therefore$

$$\hat{\mathscr{S}}^2 \left|\Psi_{\bar{1}}^2\right\rangle = 2 \left|\Psi_{\bar{1}}^2\right\rangle \qquad (2.5.45)$$

i.e. $S = 1$,
thus $\left|\Psi_{\bar{1}}^2\right\rangle$ is triplet.

Ex 2.40

•

$$\begin{aligned}\left\langle {}^1\Psi_1^2 \,\middle|\, \mathscr{H} \,\middle|\, {}^1\Psi_1^2 \right\rangle &= \frac{1}{4}\left\langle \psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1) \,\middle|\, \mathscr{H} \,\middle|\, \psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1) \right\rangle \\ &\quad \left\langle \alpha(1)\beta(2) - \beta(1)\alpha(2) \,\middle|\, \alpha(1)\beta(2) - \beta(1)\alpha(2) \right\rangle \\ &= \frac{1}{4}((1|h|1) + (2|h|2) + (11|22) + (12|21) + (21|12) + (2|h|2) + (1|h|1) + (22|11))(1 - 0 - 0 + 1) \\ &= h_{11} + h_{22} + J_{12} + K_{12} \end{aligned} \tag{2.5.46}$$

•

$$\begin{aligned}\left\langle {}^3\Psi_1^2 \,\middle|\, \mathscr{H} \,\middle|\, {}^3\Psi_1^2 \right\rangle &= \frac{1}{4}\left\langle \psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1) \,\middle|\, \mathscr{H} \,\middle|\, \psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1) \right\rangle \\ &\quad \left\langle \alpha(1)\beta(2) + \beta(1)\alpha(2) \,\middle|\, \alpha(1)\beta(2) + \beta(1)\alpha(2) \right\rangle \\ &= \frac{1}{4}((1|h|1) + (2|h|2) + (11|22) - (12|21) - (21|12) + (2|h|2) + (1|h|1) + (22|11))(1 + 0 + 0 + 1) \\ &= h_{11} + h_{22} + J_{12} - K_{12} \end{aligned} \tag{2.5.47}$$

2.5.3 Unrestricted Determinants

Ex 2.41

a.

$$\begin{aligned}\hat{\mathscr{S}}^2 \left| K \right\rangle &= \left(\hat{\mathscr{S}}_-\hat{\mathscr{S}}_+ + \hat{\mathscr{S}}_z + \hat{\mathscr{S}}_z^2\right)\frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2)\alpha(1)\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\beta(1)\alpha(2)\right) \\ &= \frac{1}{\sqrt{2}}\psi_1^\alpha(1)\psi_1^\beta(2)\left(\hat{\mathscr{S}}_-\alpha(1)\alpha(2) + 0 + 0\right) - \psi_1^\beta(1)\psi_1^\alpha(2)\left(\hat{\mathscr{S}}_-\alpha(1)\alpha(2) + 0 + 0\right) \\ &= \frac{1}{\sqrt{2}}\left(\psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\right)(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ &= \frac{1}{\sqrt{2}}\left[\psi_1^\alpha(1)\psi_1^\beta(2)\alpha(1)\beta(2) + \psi_1^\alpha(1)\psi_1^\beta(2)\beta(1)\alpha(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\alpha(1)\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\beta(1)\alpha(2)\right] \\ &= \left| K \right\rangle + \frac{1}{\sqrt{2}}\left[\psi_1^\alpha(1)\psi_1^\beta(2)\beta(1)\alpha(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\alpha(1)\beta(2)\right] \end{aligned} \tag{2.5.48}$$

thus, $\left| K \right\rangle$ being an eigenfunction of $\hat{\mathscr{S}}^2$ requires

$$\psi_1^\alpha(1)\psi_1^\beta(2)\beta(1)\alpha(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\alpha(1)\beta(2) = k\left| K \right\rangle \tag{2.5.49}$$

which requires

$$\psi_1^\alpha = \psi_1^\beta \tag{2.5.50}$$

b.

$$\begin{aligned}\left\langle K \,\middle|\, \hat{\mathscr{S}}^2 \,\middle|\, K \right\rangle &= \frac{1}{2}\left\langle \psi_1^\alpha(1)\psi_1^\beta(2)\alpha(1)\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2)\beta(1)\alpha(2) \,\middle|\, (\psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2))(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \right\rangle \\ &= \frac{1}{2}\left\langle \psi_1^\alpha(1)\psi_1^\beta(2) \,\middle|\, \psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2) \right\rangle - \left\langle \psi_1^\beta(1)\psi_1^\alpha(2) \,\middle|\, \psi_1^\alpha(1)\psi_1^\beta(2) - \psi_1^\beta(1)\psi_1^\alpha(2) \right\rangle \\ &= \frac{1}{2}\left[\left(1 - \left|S_{11}^{\alpha\beta}\right|^2\right) - \left(\left|S_{11}^{\alpha\beta}\right|^2 - 1\right)\right] \\ &= 1 - \left|S_{11}^{\alpha\beta}\right|^2 \end{aligned} \tag{2.5.51}$$

Modern Quantum Chemistry, Szabo & Ostlund
HW

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Contents

3 The Hartree-Fock Approximation

3.1 The HF Equations

3.1.1 The Coulomb and Exchange Operators

3.1.2 The Fock Operator

Ex 3.1

$$\begin{aligned}
\left\langle \chi_i \middle| \hat{f} \middle| \chi_j \right\rangle &= \left\langle \chi_i(1) \middle| h(1) + \sum_b [\mathscr{J}_b(1) - \mathscr{K}_b(1)] \middle| \chi_j(1) \right\rangle \\
&= [i|h|j] + \sum_{b\neq j} \left[\left\langle \chi_i(1)\chi_b(2) \middle| \frac{1}{r_{12}} \middle| \chi_b(2)\chi_j(1) \right\rangle - \left\langle \chi_i(1)\chi_b(2) \middle| \frac{1}{r_{12}} \middle| \chi_b(1)\chi_j(2) \right\rangle \right] \\
&= [i|h|j] + \sum_{b\neq j} ([ij|bb] - [ib|bj]) \qquad (3.1.1)
\end{aligned}$$

Since

$$[ij|jj] - [ij|jj] = 0 \qquad (3.1.2)$$

we have

$$\begin{aligned}
\left\langle \chi_i \middle| \hat{f} \middle| \chi_j \right\rangle &= \langle i \,|\, h \,|\, j \rangle + \sum_b (\langle ib \,|\, jb \rangle - \langle ib \,|\, bj \rangle) \\
&= \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle \qquad (3.1.3)
\end{aligned}$$

3.2 Derivation of the HF Equations

3.2.1 Functional Variation

3.2.2 Minimization of the Energy of a Single Determinant

Ex 3.2 Take the complex conjugate of

$$\mathscr{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) \qquad (3.2.1)$$

we have

$$\mathscr{L}[\{\chi_\alpha\}]^* = E_0[\{\chi_\alpha\}]^* - \sum_a^N \sum_b^N \varepsilon_{ba}^*([a|b]^* - \delta_{ab}^*) \qquad (3.2.2)$$

i.e.

$$\mathscr{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) \qquad (3.2.3)$$

thus

$$\sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) = \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) = \sum_b^N \sum_a^N \varepsilon_{ab}^*([a|b] - \delta_{ba}) \qquad (3.2.4)$$

$\therefore$

$$\varepsilon_{ba} = \varepsilon_{ab}^* \qquad (3.2.5)$$

Ex 3.3 $\because$

$$\begin{aligned}
[\delta\chi_a|h|\chi_a] &= [\chi_a|h|\delta\chi_a]^* && (3.2.6) \\
[\chi_a\delta\chi_a|\chi_b\chi_b] &= [\delta\chi_a\chi_a|\chi_b\chi_b]^* && (3.2.7) \\
[\chi_a\chi_a|\chi_b\delta\chi_b] &= [\chi_a\chi_a|\delta\chi_b\chi_b]^* && (3.2.8) \\
[\chi_a\chi_b|\chi_b\delta\chi_a] &= [\chi_b\delta\chi_a|\chi_a\chi_b] = [\delta\chi_a\chi_b|\chi_b\chi_a]^* && (3.2.9) \\
[\chi_a\chi_b|\delta\chi_b\chi_a] &= [\delta\chi_b\chi_a|\chi_a\chi_b] = [\chi_a\delta\chi_b|\chi_b\chi_a]^* && (3.2.10)
\end{aligned}$$

$\therefore$

$$\delta E_0 = \sum_a^N [\delta\chi_a|h|\chi_a] + \frac{1}{2}\sum_a^N\sum_b^N ([\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b])$$
$$- \frac{1}{2}\sum_a^N\sum_b^N ([\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a]) + \text{complex conjugates} \tag{3.2.11}$$

while

$$\sum_a^N\sum_b^N [\chi_a\chi_a|\delta\chi_b\chi_b] = \sum_b^N\sum_a^N [\chi_b\chi_b|\delta\chi_a\chi_a] = \sum_a^N\sum_b^N [\delta\chi_a\chi_a|\chi_b\chi_b] \tag{3.2.12}$$
$$\sum_a^N\sum_b^N [\chi_a\chi_b|\delta\chi_b\chi_a] = \sum_b^N\sum_a^N [\chi_b\chi_a|\delta\chi_a\chi_b] = \sum_a^N\sum_b^N [\delta\chi_a\chi_b|\chi_b\chi_a] \tag{3.2.13}$$

thus

$$\delta E_0 = \sum_a^N [\delta\chi_a|h|\chi_a] + \sum_a^N\sum_b^N ([\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a]) + \text{complex conjugates} \tag{3.2.14}$$

3.2.3 The Canonical HF Equations

3.3 Interpretation of Solutions to the HF Equations

3.3.1 Orbital Energies and Koopmans' Theorem

Ex 3.4

$$f_{ij} = \langle \chi_i \,|\, f \,|\, \chi_j \rangle = \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle \tag{3.3.1}$$

$$\begin{aligned} f_{ji}^* &= \langle \chi_j \,|\, f \,|\, \chi_i \rangle^* = \langle j \,|\, h \,|\, i \rangle^* + \sum_b \langle jb \,\|\, ib \rangle^* \\ &= \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle \\ &= f_{ij} \end{aligned} \tag{3.3.2}$$

thus the Fock operator is Hermitian.

Ex 3.5

$$\begin{aligned} \text{IP} &= ^{N-2} E - E_0 \\ &= \sum_{a\neq c,d} \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_{a\neq c,d}\sum_{b\neq c,d} \langle ab \,\|\, ab \rangle - \left[\sum_a \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_a\sum_b \langle ab \,\|\, ab \rangle\right] \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \frac{1}{2}\sum_{a\neq c,d} \langle ac \,\|\, ac \rangle - \frac{1}{2}\sum_{a\neq c,d} \langle ad \,\|\, ad \rangle - \frac{1}{2}\sum_{b\neq c,d} \langle cb \,\|\, cb \rangle - \frac{1}{2}\sum_{b\neq c,d} \langle db \,\|\, db \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \sum_{a\neq c,d} \langle ac \,\|\, ac \rangle - \sum_{a\neq c,d} \langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \left(\sum_{a\neq c} \langle ac \,\|\, ac \rangle - \langle dc \,\|\, dc \rangle\right) - \left(\sum_{a\neq d} \langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle\right) - \langle cd \,\|\, cd \rangle \\ &= -\varepsilon_c - \varepsilon_d + \langle cd \,|\, cd \rangle - \langle cd \,|\, dc \rangle \end{aligned} \tag{3.3.3}$$

Ex 3.6

$$
\begin{aligned}
{}^{N}E_0 - {}^{N+1}E^r &= \sum_a \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_a \sum_b \langle ab \,\|\, ab \rangle \\
&\quad - \left[\sum_a \langle a \,|\, h \,|\, a \rangle + \langle r \,|\, h \,|\, r \rangle + \frac{1}{2}\sum_a \sum_b \langle ab \,\|\, ab \rangle + \frac{1}{2}\sum_b \langle rb \,\|\, rb \rangle + \frac{1}{2}\sum_a \langle ar \,\|\, ar \rangle \right] \\
&= -\langle r \,|\, h \,|\, r \rangle - \frac{1}{2}\sum_b \langle rb \,\|\, rb \rangle - \frac{1}{2}\sum_b \langle br \,\|\, br \rangle \\
&= -\langle r \,|\, h \,|\, r \rangle - \sum_b \langle rb \,\|\, rb \rangle
\end{aligned} \tag{3.3.4}
$$

3.3.2 Brillouin's Theorem

3.3.3 The HF Hamiltonian

Ex 3.7 Suppose $\mathscr{H}_0$ commutes with $\mathscr{P}_n$,

$$
\begin{aligned}
\mathscr{H}_0 \,|\Psi_0\rangle &= \mathscr{H}_0 \frac{1}{\sqrt{N!}} \sum_n^{N!} (-1)^{p_n} \mathscr{P}_n \left\{ \sum_i^N f(i) \chi_j(1) \cdots \chi_k(N) \right\} \\
&= \frac{1}{\sqrt{N!}} \sum_n^{N!} (-1)^{p_n} \mathscr{P}_n \{ (\varepsilon_j + \cdots + \varepsilon_k) \chi_j(1) \cdots \chi_k(N) \} \\
&= \sum_a \varepsilon_a
\end{aligned} \tag{3.3.5}
$$

Now we show $\mathscr{H}_0$ commutes with $\mathscr{P}_n$, for example, $\mathscr{P}_{ab}$

$$
\mathscr{P}_{ab}\mathscr{H}_0 = \mathscr{P}_{ab}(\cdots + f(a) + \cdots + f(b) + \cdots) = (\cdots + f(b) + \cdots + f(a) + \cdots)\mathscr{P}_{ab} = \mathscr{H}_0 \mathscr{P}_{ab} \tag{3.3.6}
$$

Ex 3.8

$$
\mathscr{V} = \sum_i^N \sum_{j>i}^N \mathscr{O}_2 - \sum_i^N \sum_b^N [\mathscr{G}_b(i) - \mathscr{K}_b(i)] \tag{3.3.7}
$$

thus

$$
\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_0 \rangle &= \sum_i^N \sum_{j>i}^N \langle \Psi_0 \,|\, \mathscr{O}_2 \,|\, \Psi_0 \rangle - \sum_i^N \sum_b^N [\langle \Psi_0 \,|\, \mathscr{G}_b(i) - \mathscr{K}_b(i) \,|\, \Psi_0 \rangle] \\
&= \frac{1}{2} \sum_a^N \sum_b^N \langle ab \,\|\, ab \rangle - \sum_i^N \sum_b^N [\langle ib \,|\, ib \rangle - \langle ib \,|\, bi \rangle] \\
&= -\frac{1}{2} \sum_a^N \sum_b^N \langle ab \,\|\, ab \rangle
\end{aligned} \tag{3.3.8}
$$

3.4 Restricted Closed-shell HF: The Roothaan Equations

3.4.1 Closed-shell HF: Restricted Spin Orbitals

Ex 3.9

$$
\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_b^N (\langle ib \,|\, ib \rangle - \langle ib \,|\, bi \rangle) \\
&= (i|h|i) + \sum_c^{N/2} (\langle ic \,|\, ic \rangle - \langle ic \,|\, ci \rangle) + \sum_{\bar{c}}^{N/2} (\langle i\bar{c} \,|\, i\bar{c} \rangle - \langle i\bar{c} \,|\, \bar{c}i \rangle)
\end{aligned} \tag{3.4.1}
$$

Assume χ_j has α spin, since assuming α or β is identical

$$
\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_c^{N/2} \left[(ic|ic)\langle\alpha\,|\,\alpha\rangle\langle\alpha\,|\,\alpha\rangle - (ic|ci)\langle\alpha\,|\,\alpha\rangle\langle\alpha\,|\,\alpha\rangle\right] + \sum_c^{N/2} \left[(ic|ic)\langle\alpha\,|\,\alpha\rangle\langle\beta\,|\,\beta\rangle - (ic|ci)\langle\alpha\,|\,\beta\rangle\langle\beta\,|\,\alpha\rangle\right] \\
&= (i|h|i) + \sum_c^{N/2} \left[2(ic|ic) - (ic|ci)\right] \\
&= (i|h|i) + \sum_n^{N/2} (2J_{ib} - K_{ib})
\end{aligned}
\tag{3.4.2}
$$

3.4.2 Introduction of a Basis: The Roothaan Equations

Ex 3.10

$$
\begin{aligned}
(\mathbf{C}^\dagger \mathbf{S} \mathbf{C})_{\mu\nu} &= \sum_i \sum_j C^\dagger_{\mu i} S_{ij} C_{j\nu} \\
&= \sum_i \sum_j C^*_{i\mu} \langle \phi_i\,|\,\phi_j\rangle C_{j\nu} \\
&= \langle \phi_\mu\,|\,\phi_\nu\rangle \\
&= \delta_{\mu\nu}
\end{aligned}
\tag{3.4.3}
$$

thus

$$
\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.4}
$$

3.4.3 The Charge Density

Ex 3.11

$$
\begin{aligned}
\rho(\mathbf{r}) &= \langle \Psi_0\,|\,\hat{\rho}(\mathbf{r})\,|\,\Psi_0\rangle \\
&= \sum_i^N \frac{1}{N!} \sum_I^{N!} \sum_J^{N!} (-1)^{p_I} (-1)^{p_J} \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \hat{\mathscr{P}}_I \{\chi_1(1) \cdots \chi_N(N)\}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathscr{P}}_J \{\chi_1(1) \cdots \chi_N(N)\}
\end{aligned}
\tag{3.4.5}
$$

Since $\{\chi_m\}$ are orthogonal,

$$
\begin{aligned}
\rho(\mathbf{r}) &= \sum_i^N \frac{1}{N!} \sum_I^{N!} \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \hat{\mathscr{P}}_I \{\chi_1(1) \cdots \chi_N(N)\}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathscr{P}}_I \{\chi_1(1) \cdots \chi_N(N)\} \\
&= \sum_i^N \frac{1}{N!} (N-1)! \sum_s^N \int \mathrm{d}\mathbf{x}_i \chi_s^*(\mathbf{x}_i) \delta(\mathbf{r}_i - \mathbf{r}) \chi_s(\mathbf{x}_i) \\
&= \sum_i^N \frac{1}{N} \cdot 2 \sum_s^{N/2} \int \mathrm{d}\mathbf{r}_i \phi_s(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}) \phi_s(\mathbf{r}_i) \\
&= \sum_i^N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= 2 \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r})
\end{aligned}
\tag{3.4.6}
$$

Ex 3.12 From Ex 3.10, we have

$$
\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.7}
$$

i.e.

$$\sum_i^K \sum_j^K C_{i\mu}^* S_{ij} C_{j\nu} = \delta_{\mu\nu} \tag{3.4.8}$$

thus

$$\begin{aligned}
(\mathbf{PSP})_{\mu\sigma} &= \sum_\nu^K \sum_\lambda^K P_{\mu\nu} S_{\nu\lambda} P_{\lambda\sigma} \\
&= 4 \sum_\nu^K \sum_\lambda^K \sum_a^{N/2} C_{\mu a} C_{\nu a}^* S_{\nu\lambda} \sum_b^{N/2} C_{\lambda b} C_{\sigma b}^* \\
&= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \left(\sum_\nu^K \sum_\lambda^K C_{\nu a}^* S_{\nu\lambda} C_{\lambda b} \right) C_{\sigma b}^* \\
&= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \delta_{ab} C_{\sigma b}^* \\
&= 4 \sum_a^{N/2} C_{\mu a} C_{\sigma a}^* \\
&= 2 P_{\mu\sigma}
\end{aligned} \tag{3.4.9}$$

thus

$$\mathbf{PSP} = 2\mathbf{P} \tag{3.4.10}$$

Ex 3.13 Eq. 3.122 shows

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2} \int \mathrm{d}\mathbf{r}_2 \psi_a^*(\mathbf{r}_2)(2 - \hat{\mathscr{P}}_{12}) r_{12}^{-1} \psi_a(\mathbf{r}_2) \tag{3.4.11}$$

thus

$$\begin{aligned}
f(\mathbf{r}_1) &= h(\mathbf{r}_1) + \sum_a^{N/2} \int \mathrm{d}\mathbf{r}_2 \sum_\sigma C_{\sigma a}^* \phi_\sigma^*(\mathbf{r}_2)(2 - \hat{\mathscr{P}}_{12}) r_{12}^{-1} \sum_\lambda C_{\lambda a} \phi_\lambda(\mathbf{r}_2) \\
&= h(\mathbf{r}_1) + \sum_\sigma \sum_\lambda \left(\sum_a^{N/2} C_{\sigma a}^* C_{\lambda a} \right) \int \mathrm{d}\mathbf{r}_2 \phi_\sigma^*(\mathbf{r}_2)(2 - \hat{\mathscr{P}}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \\
&= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\sigma,\lambda} P_{\lambda\sigma} \int \mathrm{d}\mathbf{r}_2 \phi_\sigma^*(\mathbf{r}_2)(2 - \hat{\mathscr{P}}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2)
\end{aligned} \tag{3.4.12}$$

3.4.4 Expression for the Fock Matrix

Ex 3.14 In expression $(\mu\nu|\lambda\sigma)$, there are three interchangeable pairs, i.e. $\mu \leftrightarrow \nu$, $\lambda \leftrightarrow \sigma$, and $\mu\nu \leftrightarrow \lambda\sigma$. Thus $(\mu\nu|\lambda\sigma)$ has an 8-fold symmetry. Similarly, $(\mu\mu|\lambda\sigma), (\mu\nu|\mu\lambda), (\mu\nu|\mu\nu), (\mu\mu|\sigma\sigma)$ has 2-fold symmetry, and $(\mu\mu|\mu\nu), (\mu\mu|\mu\mu)$ has 1-fold symmetry.
Therefore, the number of unique 2e integrals is

expression	number	$K = 100$
$(\mu\nu\|\lambda\sigma)$	$K(K-1)(K-2)(K-3)/8$	11763675
$(\mu\mu\|\lambda\sigma)$	$K(K-1)(K-2)/2$	485100
$(\mu\nu\|\mu\lambda)$	$K(K-1)(K-2)/2$	485100
$(\mu\nu\|\mu\nu)$	$K(K-1)/2$	4950
$(\mu\mu\|\sigma\sigma)$	$K(K-1)/2$	4950
$(\mu\mu\|\mu\nu)$	$K(K-1)$	9900
$(\mu\mu\|\mu\mu)$	K	100

thus the total number is 12 753 775.

3.4.5 Orthogonalization of the Basis

Ex 3.15 $\because$

$$\mathbf{U}^\dagger\mathbf{S}\mathbf{U} = \mathbf{s} \tag{3.4.13}$$

$\therefore$

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s} \tag{3.4.14}$$

i.e.

$$\sum_\nu S_{\mu\nu}U_{\nu i} = U_{\mu i}s_i \tag{3.4.15}$$

thus

$$\sum_\mu U_{\mu i}^* \sum_\nu S_{\mu\nu}U_{\nu i} = \sum_\mu U_{\mu i}^* U_{\mu i}s_i \tag{3.4.16}$$

$$\sum_\mu \sum_\nu U_{\mu i}^* \langle \phi_\mu \mid \phi_\nu \rangle U_{\nu i} = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.17}$$

Suppose

$$\phi_i' = \sum_\nu U_{\nu i}\phi_\nu \tag{3.4.18}$$

thus

$$\langle \phi_i' \mid \phi_i' \rangle = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.19}$$

$\because$

$$\langle \phi_i' \mid \phi_i' \rangle > 0 \qquad |U_{\mu i}|^2 > 0 \tag{3.4.20}$$

$\therefore$

$$s_i > 0 \tag{3.4.21}$$

Ex 3.16

- (3.174)

Since (ϕ, ϕ', ψ are row vectors)

$$\boldsymbol{\psi} = \boldsymbol{\phi}\mathbf{C} \tag{3.4.22}$$

$$\boldsymbol{\psi} = \boldsymbol{\phi}'\mathbf{C}' = \boldsymbol{\phi}\mathbf{X}\mathbf{C}' \tag{3.4.23}$$

we have

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \tag{3.4.24}$$

i.e.

$$\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C} \tag{3.4.25}$$

- (3.177)

$$\begin{aligned}
F'_{\mu\nu} &= \langle \phi'_\mu \mid f \mid \phi'_\nu \rangle \\
&= \left\langle \sum_i \phi_i X_{i\mu} \middle| f \middle| \sum_j \phi_j X_{j\nu} \right\rangle \\
&= \sum_i \sum_j X_{i\mu}^* X_{j\nu} \langle \phi_i \mid f \mid \phi_j \rangle \\
&= \sum_i \sum_j X_{i\mu}^* F_{ij} X_{j\nu}
\end{aligned} \tag{3.4.26}$$

i.e.

$$\mathbf{F}' = \mathbf{X}^\dagger\mathbf{F}\mathbf{X} \tag{3.4.27}$$

3.4.6 The SCF Procedure

3.4.7 Expectation Values and Population Analysis

Ex 3.17 From (3.148) in the textbook, we get

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{a}^{N/2}[2(\mu\nu|aa) - (\mu a|a\nu)] \tag{3.4.28}$$

thus

$$\begin{aligned}
E_0 &= \sum_{a}^{N/2}[2h_{aa} + \sum_{b}^{N/2}(2J_{ab} - K_{ab})] \\
&= 2\sum_{a}^{N/2}(a|h|a) + \sum_{a}^{N/2}\sum_{b}^{N/2}[2(aa|bb) - (ab|ba)] \\
&= 2\sum_{a}^{N/2}\sum_{\mu}\sum_{\nu}C_{\mu a}^{*}C_{\nu a}(\mu|h|\nu) + \sum_{a}^{N/2}\sum_{b}^{N/2}\left[2\sum_{\mu}\sum_{\nu}C_{\mu a}^{*}C_{\nu a}(\mu\nu|bb) - \sum_{\mu}\sum_{\nu}C_{\mu a}^{*}C_{\nu a}(\mu b|b\nu)\right] \\
&= \sum_{\mu}\sum_{\nu}P_{\nu\mu}H_{\mu\nu}^{\text{core}} + \frac{1}{2}\sum_{b}^{N/2}\sum_{\mu}\sum_{\nu}[2P_{\nu\mu}(\mu\nu|bb) - P_{\nu\mu}(\mu b|b\nu)] \\
&= \sum_{\mu}\sum_{\nu}P_{\nu\mu}[H_{\mu\nu}^{\text{core}} + \frac{1}{2}G_{\mu\nu}] \\
&= \frac{1}{2}\sum_{\mu}\sum_{\nu}P_{\nu\mu}[H_{\mu\nu}^{\text{core}} + F_{\mu\nu}]
\end{aligned} \tag{3.4.29}$$

Ex 3.18 For symmetrically orthogonalized basis,

$$\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C} \tag{3.4.30}$$

thus

$$\begin{aligned}
P'_{\mu\nu} &= 2\sum_{a}^{N/2}C'_{\mu a}C'^{*}_{\nu a} \\
&= 2\sum_{a}^{N/2}\sum_{i}S_{\mu i}^{1/2}C_{ia}\sum_{j}S_{\nu j}^{1/2*}C_{ja}^{*} \\
&= \sum_{i}\sum_{j}S_{\mu i}^{1/2}\left(2\sum_{a}^{N/2}C_{ia}C_{ja}^{*}\right)S_{\nu j}^{1/2*} \\
&= \sum_{i}\sum_{j}S_{\mu i}^{1/2}P_{ij}S_{\nu j}^{1/2*} \\
&= \sum_{i}\sum_{j}S_{\mu i}^{1/2}P_{ij}S_{j\nu}^{1/2}
\end{aligned} \tag{3.4.31}$$

i.e.

$$\mathbf{P}' = \mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2} \tag{3.4.32}$$

thus

$$\sum_{\mu}(\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2})_{\mu\mu} = \sum_{\mu}\mathbf{P}'_{\mu\mu} \tag{3.4.33}$$

3.5 Model Calculations on H_2 and HeH^+

3.5.1 The $1s$ Minimal STO-3G Basis Set

Ex 3.19

$$\begin{aligned}
\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_B) &= \left(\frac{2\alpha}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \left(\frac{2\beta}{\pi}\right)^{3/4} \mathrm{e}^{-\beta|\mathbf{r}-\mathbf{R}_B|^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2-\beta|\mathbf{r}-\mathbf{R}_B|^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \exp\Big(-\Big[(\alpha+\beta)|\mathbf{r}|^2 - 2\mathbf{r}\cdot(\alpha\mathbf{R}_A+\beta\mathbf{R}_B) + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\Big]\Big)
\end{aligned} \tag{3.5.1}$$

Let

$$p = \alpha+\beta \qquad \mathbf{R}_P = \frac{\alpha\mathbf{R}_A+\beta\mathbf{R}_B}{\alpha+\beta} \tag{3.5.2}$$

we have

$$\begin{aligned}
\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_B) &= \left(\frac{2\alpha}{\pi}\frac{\beta}{\pi}\right)^{3/4} \exp\Big(-\Big[p|\mathbf{r}|^2 - 2\mathbf{r}\cdot(p\mathbf{R}_P) + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\Big]\Big) \\
&= \left(\frac{2\alpha}{\pi}\frac{2\beta}{\pi}\right)^{3/4} \exp\Big(-\Big[p|\mathbf{r}-\mathbf{R}_P|^2 - p|\mathbf{R}_P|^2 + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\Big]\Big) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \left(\frac{2p}{\pi}\right)^{3/4} \mathrm{e}^{-p|\mathbf{r}-\mathbf{R}_P|^2} \exp\Big(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\Big)
\end{aligned} \tag{3.5.3}$$

Let

$$\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r}-\mathbf{R}_B) = K_{AB}\left(\frac{2p}{\pi}\right)^{3/4} \mathrm{e}^{-p|\mathbf{r}-\mathbf{R}_P|^2} \tag{3.5.4}$$

thus

$$\begin{aligned}
K_{AB} &= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\Big(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\Big) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\Big(\frac{1}{p}(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B) - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\Big) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\Big(\frac{1}{p}\Big(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B - p\alpha|\mathbf{R}_A|^2 - p\beta|\mathbf{R}_B|^2\Big)\Big) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\Big(\frac{1}{p}\Big(-\alpha\beta|\mathbf{R}_A|^2 - \alpha\beta|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B\Big)\Big) \\
&= \left(\frac{2\alpha\beta}{p\pi}\right)^{3/4} \exp\Big(-\frac{\alpha\beta}{p}|\mathbf{R}_A-\mathbf{R}_B|^2\Big)
\end{aligned} \tag{3.5.5}$$

Ex 3.20 At $r=0$,

$$\phi_{1s}^{\mathrm{CGF}}(\zeta=1.0, \text{STO-1G}) = 0.267\,656 \tag{3.5.6}$$

$$\phi_{1s}^{\mathrm{CGF}}(\zeta=1.0, \text{STO-2G}) = 0.389\,383 \tag{3.5.7}$$

$$\phi_{1s}^{\mathrm{CGF}}(\zeta=1.0, \text{STO-3G}) = 0.454\,986 \tag{3.5.8}$$

while

$$\phi_{1s}^{\mathrm{SF}}(\zeta=1.0) = \frac{1}{\sqrt{\pi}} = 0.564\,19 \tag{3.5.9}$$

3.5.2 STO-3G H_2

Ex 3.21

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(0.270\,950) \tag{3.5.10}$$

Since $\alpha = \alpha_{(\zeta=1.0)} \times \zeta^2$,

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.24, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(0.416\,613) \tag{3.5.11}$$

thus

$$\begin{aligned}
S_{12} &= K_{AB}\left(\frac{2\cdot 2\alpha}{\pi}\right)^{3/4}\int \mathrm{d}\mathbf{r}\,\mathrm{e}^{-2\alpha|\mathbf{r}-\mathbf{R}_P|^2} \\
&= \left(\frac{2\alpha}{2\pi}\right)^{3/4}\mathrm{e}^{-\frac{\alpha}{2}R^2}\left(\frac{2\cdot 2\alpha}{\pi}\right)^{3/4}\int \mathrm{d}\mathbf{r}\,\mathrm{e}^{-2\alpha|\mathbf{r}-\mathbf{R}_A|^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/2}\mathrm{e}^{-\frac{\alpha}{2}R^2}\,4\pi\int \mathrm{d}r r^2\,\mathrm{e}^{-2\alpha r^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/2}\mathrm{e}^{-\frac{\alpha}{2}R^2}\,4\pi\frac{\sqrt{\pi}}{8\sqrt{2}\alpha^{3/2}} \\
&= \mathrm{e}^{-\frac{\alpha}{2}R^2}
\end{aligned} \tag{3.5.12}$$

At $R = 1.4, \alpha = 0.416\,613$,

$$S_{12} = 0.6648 \tag{3.5.13}$$

Ex 3.22 Let

$$\psi_1 = c_1(\phi_1 + \phi_2) \qquad \psi_2 = c_2(\phi_1 - \phi_2) \tag{3.5.14}$$

$$\begin{aligned}
1 &= \langle \phi_1 \,|\, \psi_1 \rangle = c_1^2(S_{11} + S_{12} + S_{21} + S_{22}) \\
&= c_1^2(2 + 2S_{12})
\end{aligned} \tag{3.5.15}$$

$\therefore$

$$c_1 = [2(1 + S_{12})]^{-1/2} \tag{3.5.16}$$

$$\begin{aligned}
1 &= \langle \phi_2 \,|\, \psi_2 \rangle = c_2^2(S_{11} - S_{12} - S_{21} + S_{22}) \\
&= c_2^2(2 - 2S_{12})
\end{aligned} \tag{3.5.17}$$

$\therefore$

$$c_2 = [2(1 - S_{12})]^{-1/2} \tag{3.5.18}$$

Ex 3.23 Suppose

$$\psi_1 = c_1(\phi_1 + \phi_2) \qquad \psi_2 = c_2(\phi_1 - \phi_2) \tag{3.5.19}$$

thus

$$\mathbf{H}^{\mathrm{core}}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \tag{3.5.20}$$

$$\begin{pmatrix} H_{11}^{\mathrm{core}} & H_{12}^{\mathrm{core}} \\ H_{21}^{\mathrm{core}} & H_{22}^{\mathrm{core}} \end{pmatrix}\begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix}\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{3.5.21}$$

$$\begin{pmatrix} (H_{11}^{\mathrm{core}} + H_{12}^{\mathrm{core}})c_1 & (H_{11}^{\mathrm{core}} - H_{12}^{\mathrm{core}})c_2 \\ (H_{21}^{\mathrm{core}} + H_{22}^{\mathrm{core}})c_1 & (H_{21}^{\mathrm{core}} - H_{22}^{\mathrm{core}})c_2 \end{pmatrix} = \begin{pmatrix} (S_{11} + S_{12})c_1\varepsilon_1 & (S_{11} - S_{12})c_2\varepsilon_2 \\ (S_{21} + S_{22})c_1\varepsilon_1 & (S_{21} - S_{22})c_2\varepsilon_2 \end{pmatrix} \tag{3.5.22}$$

$\therefore$

$$\begin{cases} \varepsilon_1 = (H_{11}^{\mathrm{core}} + H_{12}^{\mathrm{core}})/(1 + S_{12}) \\ \varepsilon_2 = (H_{11}^{\mathrm{core}} - H_{12}^{\mathrm{core}})/(1 - S_{12}) \end{cases} \tag{3.5.23}$$

$$\varepsilon_1 = (-1.1204 - 0.9584)/(1 + 0.6593) = -1.2528 \tag{3.5.24}$$

$$\varepsilon_2 = (-1.1204 + 0.9584)/(1 - 0.6593) = -0.4755 \tag{3.5.25}$$

Ex 3.24

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a}C_{\nu a}^* = 2C_{\mu 1}C_{\nu 1}^* \tag{3.5.26}$$

$\therefore$

$$\begin{aligned}
\mathbf{P} &= 2\begin{pmatrix} C_{11}C_{11}^* & C_{11}C_{21}^* \\ C_{21}C_{11}^* & C_{21}C_{21}^* \end{pmatrix} \\
&= 2\begin{pmatrix} [2(1+S_{12})]^{-1/2}[2(1+S_{12})]^{-1/2} & [2(1+S_{12})]^{-1/2}[2(1+S_{12})]^{-1/2} \\ [2(1+S_{12})]^{-1/2}[2(1+S_{12})]^{-1/2} & [2(1+S_{12})]^{-1/2}[2(1+S_{12})]^{-1/2} \end{pmatrix} \\
&= (1+S_{12})^{-1}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}
\end{aligned} \tag{3.5.27}$$

For $H_2{}^+$,

$$\mathbf{P}_{H_2{}^+} = \frac{1}{2}(1+S_{12})^{-1}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{3.5.28}$$

Ex 3.25

$$\begin{aligned}
F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right] \\
&= H_{\mu\nu}^{\text{core}} + (1+S_{12})^{-1}\sum_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right]
\end{aligned} \tag{3.5.29}$$

$\therefore$

$$\begin{aligned}
F_{11} &= H_{11}^{\text{core}} + (1+S_{12})^{-1}\left[(11|11) - \frac{1}{2}(11|11) + (11|21) - \frac{1}{2}(11|21) + (11|12) - \frac{1}{2}(12|11) + (11|22) - \frac{1}{2}(12|21)\right] \\
&= H_{11}^{\text{core}} + (1+S_{12})^{-1}\left[\frac{1}{2}(11|11) + (11|21) + (11|22) - \frac{1}{2}(12|21)\right]
\end{aligned} \tag{3.5.30}$$

$$\begin{aligned}
F_{11} = F_{22} &= -1.1204 + (1+0.6593)^{-1}\left(\frac{1}{2}\times 0.7746 + 0.4441 + 0.5697 - \frac{1}{2}\times 0.2970\right) \\
&= -0.3655
\end{aligned} \tag{3.5.31}$$

$$\begin{aligned}
F_{12} &= H_{12}^{\text{core}} + (1+S_{12})^{-1}\left[(12|11) - \frac{1}{2}(11|12) + (12|21) - \frac{1}{2}(11|22) + (12|12) - \frac{1}{2}(12|12) + (12|22) - \frac{1}{2}(12|22)\right] \\
&= H_{12}^{\text{core}} + (1+S_{12})^{-1}\left[(11|12) - \frac{1}{2}(11|22) + \frac{3}{2}(12|12)\right]
\end{aligned} \tag{3.5.32}$$

$$\begin{aligned}
F_{12} = F_{21} &= -0.9584 + (1+0.6593)^{-1}\left(0.4441 - \frac{1}{2}\times 0.5697 + \frac{3}{2}\times 0.2970\right) \\
&= -0.5939
\end{aligned} \tag{3.5.33}$$

Ex 3.26 Similar to the procedure in Ex 3.23, we get

$$\varepsilon_1 = \frac{F_{11}+F_{12}}{1+S_{12}} = \frac{-0.3655-0.5939}{1+0.6593} = -0.5782 \tag{3.5.34}$$

$$\varepsilon_2 = \frac{F_{11}-F_{12}}{1-S_{12}} = \frac{-0.3655+0.5939}{1-0.6593} = 0.6703 \tag{3.5.35}$$

Ex 3.27

$$
\begin{aligned}
E_0 &= \sum_{\mu\nu} \frac{1}{2} P_{\nu\mu}(H^{\text{core}}_{\mu\nu} + F_{\mu\nu}) \\
&= \frac{1}{2}\frac{1}{1+S_{12}}(H^{\text{core}}_{11} + F_{11} + H^{\text{core}}_{12} + F_{12} + H^{\text{core}}_{21} + F_{21} + H^{\text{core}}_{22} + F_{22}) \\
&= \frac{H^{\text{core}}_{11} + F_{11} + H^{\text{core}}_{12} + F_{12}}{1+S_{12}} \\
&= \frac{-1.1204 - 0.3655 - 0.9584 - 0.5939}{1+0.6593} \\
&= -1.8310
\end{aligned} \tag{3.5.36}
$$

$$
E_{tot} = E_0 + \frac{1}{R} = -1.1167 \tag{3.5.37}
$$

3.5.3 An SCF Calculation on STO-3G HeH$^+$

Ex 3.28

$$
\begin{aligned}
\mathbf{X}^\dagger_{\text{Schmidt}}\mathbf{S}\mathbf{X}_{\text{Schmidt}} &= \begin{pmatrix} 1 & 0 \\ -S_{12}/\sqrt{1-S_{12}^2} & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\
&= \begin{pmatrix} 1 & S_{12} \\ 0 & \sqrt{1-S_{12}^2} \end{pmatrix} \begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\
&= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\end{aligned} \tag{3.5.38}
$$

thus the Schmidt transformation produces orthonormal basis.

Ex 3.29

$$
E_0(R\to\infty) = \frac{1}{2}\sum_\mu\sum_\nu P_{\nu\mu}(R\to\infty)[2H^{\text{core}}_{\mu\nu} + G_{\mu\nu}] \tag{3.5.39}
$$

where

$$
P_{\nu\mu}(R\to\infty) = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \tag{3.5.40}
$$

$$
\begin{aligned}
G_{\mu\nu} &= \sum_\lambda\sum_\sigma P_{\lambda\sigma}(R\to\infty)\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right] \\
&= 2\left[(\mu\nu|\phi_1\phi_1) - \frac{1}{2}(\mu\phi_1|\phi_1\nu)\right]
\end{aligned} \tag{3.5.41}
$$

thus

$$
\begin{aligned}
E_0(R\to\infty) &= \frac{1}{2}\sum_\mu\sum_\nu P_{\nu\mu}(R\to\infty)[2H^{\text{core}}_{\mu\nu} + G_{\mu\nu}] \\
&= \frac{1}{2}\times 2[2H^{\text{core}}_{11} + G_{11}] \\
&= 2(T_{11} + V^1_{11}) + 2\left[(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)\right] \\
&= 2T_{11} + 2V^1_{11} + (\phi_1\phi_1|\phi_1\phi_1)
\end{aligned} \tag{3.5.42}
$$

3.6 Polyatomic Basis Sets

3.6.1 Contracted Gaussian Functions

3.6.2 Minimal Basis Sets: STO-3G

3.6.3 Double Zeta Basis Sets: 4-31G

Ex 3.30 The outer basis function

$$
\phi''_{1s}(\mathbf{r}) = g_{1s}(0.298073, \mathbf{r}) \tag{3.6.1}
$$

The inner basis function

$$\phi'_{1s}(\mathbf{r}) = N[0.46954g_{1s}(1.242567, \mathbf{r}) + 0.15457g_{1s}(5.782948, \mathbf{r}) + 0.02373g_{1s}(38.47497, \mathbf{r})] \tag{3.6.2}$$

Renormalize it, we get

$$N = 1.689 \tag{3.6.3}$$

thus

$$\phi'_{1s}(\mathbf{r}) = 0.79330g_{1s}(1.242567, \mathbf{r}) + 0.26115g_{1s}(5.782948, \mathbf{r}) + 0.04009g_{1s}(38.47497, \mathbf{r}) \tag{3.6.4}$$

3.6.4 Polarized Basis Sets: 6-31G* and 6-31G**

Ex 3.31

	C	H	total
STO-3G	5	1	36
4-31G	9	2	66
6-31G* (Cartesian)	15	2	102
6-31G** (Cartesian)	15	5	120

3.7 Some Illustrative Closed-shell Calculations

3.7.1 Total Energies

Ex 3.32
Reaction I

basis	ΔE/ a.u.	ΔE/(kcal/mol)	
STO-3G	-0.061	-38.28	exoergic
4-31G	-0.069	-43.30	
6-31G*	-0.045	-28.24	
6-31G**	-0.055	-34.51	
HF-limit	-0.051	-32.00	

Reaction II

basis	ΔE/ a.u.	ΔE/(kcal/mol)	
STO-3G	0.186	116.72	endoergic
4-31G	-0.114	-71.54	exoergic
6-31G*	-0.088	-55.22	
6-31G**	-0.095	-59.61	
HF-limit	-0.097	-60.87	

The contribution of zero-point vibrations to the energy change of reaction I would be $-0.37\,\text{kcal/mol}$, to the energy change of reaction II would be $17.78\,\text{kcal/mol}$. Thus the effect of zero-point vibrations should not be ignored.

3.7.2 Ionization Potentials

3.7.3 Equilibrium Geometries

3.7.4 Population Analysis and Dipole Moments

3.8 Unrestricted Open-shell HF: The Pople-Nesbet Equations

3.8.1 Open-shell HF: Unrestricted Spin Orbitals

Ex 3.33

$$\begin{aligned}
f^{\alpha}(1) &= \int \mathrm{d}\omega_1 \alpha^*(\omega_1)\left[h(1) + \sum_a \int \mathrm{d}\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1}(1-\hat{\mathscr{P}}_{12})\chi_a(2)\right]\alpha(\omega_1) \\
&= h(1) + \sum_a^{N_\alpha}\left[\int \mathrm{d}\omega_1 \alpha^*(\omega_1)\int \mathrm{d}\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1}\chi_a(2)\alpha(\omega_1) - \int \mathrm{d}\omega_1 \alpha^*(\omega_1)\int \mathrm{d}\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1}\chi_a(1)\alpha(\omega_2)\right] \\
&\quad + \sum_a^{N_\beta}\left[\int \mathrm{d}\omega_1 \alpha^*(\omega_1)\int \mathrm{d}\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1}\chi_a(2)\alpha(\omega_1) - \int \mathrm{d}\omega_1 \alpha^*(\omega_1)\int \mathrm{d}\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1}\chi_a(1)\alpha(\omega_2)\right] \\
&= h(1) + \sum_a^{N_\alpha}\left[\int \mathrm{d}\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_2) - \int \mathrm{d}\mathbf{r}_2 \int \mathrm{d}\omega_2 \int \mathrm{d}\omega_1 \alpha^*(\omega_1)\alpha^*(\omega_2)\psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_1)\alpha(\omega_1)\alpha(\omega_2)\right] \\
&\quad + \sum_a^{N_\beta}\left[\int \mathrm{d}\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\beta}(\mathbf{r}_2) - \int \mathrm{d}\mathbf{r}_2 \int \mathrm{d}\omega_2 \int \mathrm{d}\omega_1 \alpha^*(\omega_1)\beta^*(\omega_2)\psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\beta}(\mathbf{r}_1)\beta(\omega_1)\alpha(\omega_2)\right] \\
&= h(1) + \sum_a^{N_\alpha}\left[\int \mathrm{d}\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_2) - \int \mathrm{d}\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\alpha}(\mathbf{r}_1)\right] + \sum_a^{N_\beta}\left[\int \mathrm{d}\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1}\psi_a^{\beta}(\mathbf{r}_2) - 0\right] \\
&= h(1) + \sum_a^{N_\alpha}\left[J_a^{\alpha}(1) - K_a^{\alpha}(1)\right] + \sum_a^{N_\beta} J_a^{\beta}(1)
\end{aligned} \tag{3.8.1}$$

Ex 3.34

$$\begin{aligned}
E_0 &= \sum_a h_{aa} + \frac{1}{2}\sum_a^{N_\alpha}\sum_b^{N_\alpha}(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \sum_a^{N_\alpha}\sum_b^{N_\beta} J_{ab}^{\alpha\beta} \\
&= h_{11}^{\alpha} + h_{22}^{\alpha} + h_{11}^{\alpha} + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}
\end{aligned} \tag{3.8.2}$$

Ex 3.35

$$\begin{aligned}
\varepsilon_i^{\alpha} &= (\psi_i^{\alpha}(1)|h(1) + \sum_a^{N_\alpha}\left[J_a^{\alpha}(1) - K_a^{\alpha}(1)\right] + \sum_a^{N_\beta} J_a^{\beta}(1)|\psi_i^{\alpha}(1)) \\
&= h_{ii}^{\alpha} + \sum_a^{N_\alpha}\left[J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}\right] + \sum_a^{N_\beta} J_{ia}^{\alpha\beta}
\end{aligned} \tag{3.8.3}$$

$$\begin{aligned}
\varepsilon_i^{\beta} &= (\psi_i^{\beta}(1)|h(1) + \sum_a^{N_\alpha}\left[J_a^{\beta}(1) - K_a^{\beta}(1)\right] + \sum_a^{N_\beta} J_a^{\alpha}(1)|\psi_i^{\beta}(1)) \\
&= h_{ii}^{\beta} + \sum_a^{N_\alpha}\left[J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}\right] + \sum_a^{N_\beta} J_{ia}^{\beta\alpha}
\end{aligned} \tag{3.8.4}$$

Since

$$E_0 = \sum_a h_{aa} + \frac{1}{2}\sum_a^{N_\alpha}\sum_b^{N_\alpha}(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2}\sum_a^{N_\beta}\sum_b^{N_\beta}(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N_\alpha}\sum_b^{N_\beta} J_{ab}^{\alpha\beta} \tag{3.8.5}$$

we have

$$E_0 = \sum_i^{N_\alpha} \varepsilon_i^\alpha + \sum_i^{N_\beta} \varepsilon_i^\beta - \frac{1}{2}\sum_i^{N_\alpha}\sum_a^{N_\alpha}(J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) - \frac{1}{2}\sum_i^{N_\beta}\sum_a^{N_\beta}(J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) - \sum_i^{N_\beta}\sum_a^{N_\alpha} J_{ia}^{\beta\alpha} \tag{3.8.6}$$

3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

3.8.3 Unrestricted Density Matrices

Ex 3.36

$$\int \mathrm{d}\mathbf{r}\rho^S(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\big[\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})\big] \tag{3.8.7}$$

$$= N_\alpha - N_\beta \tag{3.8.8}$$

Since

$$\left\langle \hat{\mathscr{S}}_z \right\rangle = \frac{1}{2}(N_\alpha - N_\beta) \tag{3.8.9}$$

we get

$$\int \mathrm{d}\mathbf{r}\rho^S(\mathbf{r}) = 2\left\langle \hat{\mathscr{S}}_z \right\rangle \tag{3.8.10}$$

Ex 3.37

$$\begin{aligned}
\rho^\alpha(\mathbf{r}) &= \sum_a^{N_\alpha} \psi_a^{\alpha*}(\mathbf{r})\psi_a^\alpha(\mathbf{r}) \\
&= \sum_a^{N_\alpha}\sum_\nu C_{\nu a}^{\alpha*}\phi_\nu^*(\mathbf{r})\sum_\mu C_{\mu a}^\alpha \phi_\mu(\mathbf{r}) \\
&= \sum_\nu\sum_\mu\left[\sum_a^{N_\alpha} C_{\nu a}^{\alpha*}C_{\mu a}^\alpha\right]\phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r})
\end{aligned} \tag{3.8.11}$$

Let

$$P_{\mu\nu}^\alpha = \sum_a^{N_\alpha} C_{\nu a}^{\alpha*}C_{\mu a}^\alpha \tag{3.8.12}$$

thus

$$\rho^\alpha(\mathbf{r}) = \sum_\nu\sum_\mu P_{\mu\nu}^\alpha \phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r}) \tag{3.8.13}$$

The formulation for β spin is similar.

Ex 3.38

$$\begin{aligned}
\langle \mathscr{O}_1 \rangle &= \sum_i^N \langle \chi_i \,|\, h \,|\, \chi_i \rangle \\
&= \sum_i^{N_\alpha}(\psi_i^\alpha|h|\psi_i^\alpha) + \sum_i^{N_\beta}(\psi_i^\beta|h|\psi_i^\beta) \\
&= \sum_i^{N_\alpha}\sum_\nu\sum_\mu C_{\nu a}^{\alpha*}(\phi_\nu|h|\phi_\mu)C_{\mu a}^\alpha + \sum_i^{N_\beta}\sum_\nu\sum_\mu C_{\nu a}^{\beta*}(\phi_\nu|h|\phi_\mu)C_{\mu a}^\beta \\
&= \sum_\nu\sum_\mu P_{\mu\nu}^\alpha(\phi_\nu|h|\phi_\mu) + \sum_\nu\sum_\mu P_{\mu\nu}^\beta(\phi_\nu|h|\phi_\mu) \\
&= \sum_\nu\sum_\mu P_{\mu\nu}^T(\phi_\nu|h|\phi_\mu)
\end{aligned} \tag{3.8.14}$$

Ex 3.39

$$
\begin{aligned}
\left\langle \hat{\rho}^S \right\rangle &= \left\langle \Psi_0 \,\middle|\, \hat{\rho}^S \,\middle|\, \Psi_0 \right\rangle \\
&= \frac{1}{N!} \sum_{i,j}^{N!} (-1)^{p_i} (-1)^{p_j} \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\} \sum_m^N 2\delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathscr{P}}_j \{\chi_1(1) \cdots \chi_N(N)\} \\
&= \frac{2}{N!} \sum_i^{N!} \sum_m^N \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\} \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\} \\
&= \frac{2}{N} \sum_s^N \sum_m^N \int \mathrm{d}\mathbf{x}_m \chi_s^*(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \chi_s(m) \\
&= \frac{2}{N} \sum_m^N \left[\sum_s^{N_\alpha} \int \mathrm{d}\mathbf{r}_m \psi_s^{\alpha *}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\alpha(m) + \sum_s^{N_\beta} \int \mathrm{d}\mathbf{r}_m \psi_s^{\beta *}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\beta(m) \right] \\
&= \frac{2}{N} \sum_m^N \left[\frac{1}{2} \sum_s^{N_\alpha} \int \mathrm{d}\mathbf{r}_m \psi_s^{\alpha *}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\alpha(m) - \frac{1}{2} \sum_s^{N_\beta} \int \mathrm{d}\mathbf{r}_m \psi_s^{\beta *}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\beta(m) \right] \\
&= \frac{2}{N} N \left[\frac{1}{2} \sum_s^{N_\alpha} \psi_s^{\alpha *}(\mathbf{R}) \psi_s^\alpha(\mathbf{R}) - \frac{1}{2} \sum_s^{N_\beta} \psi_s^{\beta *}(\mathbf{R}) \psi_s^\beta(\mathbf{R}) \right] \\
&= 2 \left[\frac{1}{2} \rho^\alpha(\mathbf{R}) - \frac{1}{2} \rho^\beta(\mathbf{R}) \right] \\
&= \rho^S(\mathbf{R})
\end{aligned} \tag{3.8.15}
$$

where

$$
\begin{aligned}
\rho^S(\mathbf{R}) &= \sum_\nu \sum_\mu P_{\nu\mu}^S \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R}) \\
&= \sum_\nu (\mathbf{P}^S \mathbf{A})_{\nu\nu} \\
&= \operatorname{tr}\bigl(\mathbf{P}^S \mathbf{A}\bigr)
\end{aligned} \tag{3.8.16}
$$

3.8.4 Expression for the Fock Matrices

3.8.5 Solution of the Unrestricted SCF Equations

Ex 3.40

$$
\begin{aligned}
E_0 &= \sum_a^{N_\alpha} h_{aa}^\alpha + \sum_a^{N_\beta} h_{aa}^\beta + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_a^{N_\beta} \sum_b^{N_\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta} \\
&= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha H_{\mu\nu}^{\text{core}} + \sum_\mu \sum_\nu P_{\nu\mu}^\beta H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\alpha P_{\sigma\lambda}^\alpha [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] \\
&\quad + \frac{1}{2} \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\beta P_{\sigma\lambda}^\beta [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\alpha P_{\sigma\lambda}^\beta (\mu\nu|\lambda\sigma) \\
&= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\alpha [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\beta (\mu\nu|\lambda\sigma) \right\} \\
&\quad + \sum_\mu \sum_\nu P_{\nu\mu}^\beta \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\beta [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\alpha (\mu\nu|\lambda\sigma) \right\} \\
&= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^\alpha (\mu\sigma|\lambda\nu)] \right\} \\
&\quad + \sum_\mu \sum_\nu P_{\nu\mu}^\beta \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^\beta (\mu\sigma|\lambda\nu)] \right\}
\end{aligned}
$$

$$\tag{3.8.17}$$

while

$$F^{\alpha}_{\mu\nu} = H^{\text{core}}_{\mu\nu} + \sum_{\lambda}\sum_{\sigma}\left[P^{T}_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^{\alpha}_{\lambda\sigma}(\mu\lambda|\sigma\nu)\right] \tag{3.8.18}$$

$$F^{\beta}_{\mu\nu} = H^{\text{core}}_{\mu\nu} + \sum_{\lambda}\sum_{\sigma}\left[P^{T}_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^{\beta}_{\lambda\sigma}(\mu\lambda|\sigma\nu)\right] \tag{3.8.19}$$

thus

$$\begin{aligned} E_0 &= \sum_{\mu}\sum_{\nu}\left\{P^{\alpha}_{\nu\mu}\left[\frac{1}{2}H^{\text{core}}_{\mu\nu} + \frac{1}{2}F^{\alpha}_{\mu\nu}\right] + P^{\beta}_{\nu\mu}\left[\frac{1}{2}H^{\text{core}}_{\mu\nu} + \frac{1}{2}F^{\beta}_{\mu\nu}\right]\right\} \\ &= \frac{1}{2}\sum_{\mu}\sum_{\nu}\left[P^{T}_{\nu\mu}H^{\text{core}}_{\mu\nu} + P^{\alpha}_{\nu\mu}F^{\alpha}_{\mu\nu} + P^{\beta}_{\nu\mu}F^{\beta}_{\mu\nu}\right] \end{aligned} \tag{3.8.20}$$

3.8.6 Illustrative Unrestricted Calculations

Ex 3.41

$$\begin{aligned} \left\langle \hat{\mathscr{S}}^2 \right\rangle &= \left\langle c_1{}^2\Psi + c_2{}^4\Psi \,\middle|\, \hat{\mathscr{S}}^2 \,\middle|\, c_1{}^2\Psi + c_2{}^4\Psi \right\rangle \\ &= \frac{3}{4}c_1^2 + \frac{15}{4}c_2^2 \\ &= \frac{3}{4}(1-c_2^2) + \frac{15}{4}c_2^2 \\ &= \frac{3}{4} + 3c_2^2 \end{aligned} \tag{3.8.21}$$

thus

basis	$\left\langle \hat{\mathscr{S}}^2 \right\rangle$	c_2	contamination/%
STO-3G	0.7652	0.07118	0.5067
4-31G	0.7622	0.06377	0.4067
6-31G*	0.7618	0.06272	0.3933
6-31G**	0.7614	0.06164	0.3800

3.8.7 The Dissociation Problem and Its Unrestricted Solution

Ex 3.42

$$\langle \psi_1^{\alpha} \,|\, \psi_1^{\alpha} \rangle = \langle \cos\theta\psi_1 + \sin\theta\psi_2 \,|\, \cos\theta\psi_1 + \sin\theta\psi_2 \rangle = \cos\theta^2 + \sin\theta^2 = 1 \tag{3.8.22}$$

$$\langle \psi_2^{\alpha} \,|\, \psi_2^{\alpha} \rangle = \langle -\sin\theta\psi_1 + \cos\theta\psi_2 \,|\, -\sin\theta\psi_1 + \cos\theta\psi_2 \rangle = \sin\theta^2 + \cos\theta^2 = 1 \tag{3.8.23}$$

$$\langle \psi_1^{\alpha} \,|\, \psi_2^{\alpha} \rangle = \langle \cos\theta\psi_1 + \sin\theta\psi_2 \,|\, -\sin\theta\psi_1 + \cos\theta\psi_2 \rangle = -\cos\theta\sin\theta + \sin\theta\cos\theta = 0 \tag{3.8.24}$$

thus $\{\psi_1^{\alpha}, \psi_2^{\alpha}\}$ is orthonormal.
Similarly conclusion can be derived for β orbitals.

Ex 3.43 For $R = 1.4$,

$$\begin{aligned} \eta &= \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{(\varepsilon_2 - 2J_{12} + K_{12}) - (\varepsilon_1 - J_{11}) + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{0.6703 + 0.5782 + 0.6746 + 0.6975 - 3\times 0.6636 + 3\times 0.1813}{0.6746 + 0.6975 - 2\times 0.6636 + 4\times 0.1813} notag \quad (3.8.25) \\ &= 1.524 > 1 \quad (3.8.26) \end{aligned}$$

thus unrestricted solution does not exist for this case.
For $R = 4.0$,

$$\begin{aligned}\eta &= \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{0.0916 + 0.2542 + 0.5026 + 0.5259 - 3 \times 0.5121 + 3 \times 0.2651}{0.5026 + 0.5259 - 2 \times 0.5121 + 4 \times 0.2651} notag \qquad (3.8.27) \\ &= 0.5948 \qquad (3.8.28)\end{aligned}$$

$$\theta = \arccos(\sqrt{\eta}) = 0.6900 = 39.53° \tag{3.8.29}$$

Ex 3.44

$$\begin{aligned}\lim_{R\to\infty} |\Psi_0\rangle &= \frac{1}{2}\left[|\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle - \sqrt{2}\,|{}^3\Psi_1^2\rangle\right] \\ &= \frac{1}{2}\big[|\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle - \big(|\psi_1\bar{\psi}_2\rangle - |\psi_2\bar{\psi}_1\rangle\big)\big] \\ &= \frac{1}{2}\left[\frac{1}{2}\,|(\phi_1+\phi_2)(\bar{\phi}_1+\bar{\phi}_2)\rangle - \frac{1}{2}\,|(\phi_1-\phi_2)(\bar{\phi}_1-\bar{\phi}_2)\rangle - \left(\frac{1}{2}\,|(\phi_1+\phi_2)(\bar{\phi}_1-\bar{\phi}_2)\rangle - \frac{1}{2}\,|(\phi_1-\phi_2)(\bar{\phi}_1+\bar{\phi}_2)\rangle\right)\right] \\ &= \frac{1}{4}\big(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big) - \frac{1}{4}\big(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big) \\ &\quad - \frac{1}{4}\big[\big(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle - |\phi_2\bar{\phi}_2\rangle\big) - \big(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle - |\phi_2\bar{\phi}_2\rangle\big)\big] \\ &= \frac{1}{2}\big(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle\big) - \frac{1}{4}\big(-2\,|\phi_1\bar{\phi}_2\rangle + 2\,|\phi_2\bar{\phi}_1\rangle\big) \\ &= |\phi_1\bar{\phi}_2\rangle \qquad (3.8.30)\end{aligned}$$

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Contents

4 Configuration Interaction

4.1 Multiconfigurational Wave Functions and the Structure of Full CI Matrix

4.1.1 Intermediate Normalization and an Expression for the Correlation Energy

Ex 4.1 If $a \notin \{c, d, e\}$ and $r \notin \{t, u, v\}$,

$$\left\langle \Psi_a^r \middle| \mathscr{H} \middle| \Psi_{cde}^{tuv} \right\rangle = 0 \tag{4.1.1}$$

Let's suppose $a = e$, thus

$$\left\langle \Psi_a^r \middle| \mathscr{H} \middle| \Psi_{cde}^{tuv} \right\rangle = \left\langle \Psi_a^r \middle| \mathscr{H} \middle| \Psi_{acd}^{vtu} \right\rangle \tag{4.1.2}$$

if $r \neq v$, this term will still be zero, thus

$$\sum_{c<d<e,t<u<v} c_{cde}^{tuv} \left\langle \Psi_a^r \middle| \mathscr{H} \middle| \Psi_{cde}^{tuv} \right\rangle = \sum_{c<d,t<u} c_{acd}^{rtu} \left\langle \Psi_a^r \middle| \mathscr{H} \middle| \Psi_{acd}^{rtu} \right\rangle \tag{4.1.3}$$

Ex 4.2

$$\begin{vmatrix} -E_{\text{corr}} & K_{12} \\ K_{12} & 2\Delta - E_{\text{corr}} \end{vmatrix} = 0 \tag{4.1.4}$$

$$-E_{\text{corr}}(2\Delta - E_{\text{corr}}) - K_{12}^2 = 0 \tag{4.1.5}$$

$$E_{\text{corr}} = \frac{2\Delta \pm \sqrt{4\Delta^2 + 4K_{12}^2}}{2} = \Delta \pm \sqrt{\Delta^2 + K_{12}^2} \tag{4.1.6}$$

choosing the lowest eigenvalue,

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} \tag{4.1.7}$$

Ex 4.3 At $R = 1.4$,

$$\begin{aligned} \Delta &= \varepsilon_2 - \varepsilon_1 + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12} \\ &= 0.6703 + 0.5782 + \frac{1}{2}(0.6746 + 0.6975) - 2 \times 0.6636 + 0.1813 \\ &= 0.78865 \end{aligned} \tag{4.1.8}$$

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} = 0.78865 - \sqrt{0.78865^2 + 0.1813^2} = -0.020571 \tag{4.1.9}$$

$$c = \frac{E_{\text{corr}}}{K_{12}} = \frac{-0.020571}{0.1813} = -0.1135 \tag{4.1.10}$$

As $R \to \infty$, $\varepsilon_2 - \varepsilon_1 \to 0$, all 2e integrals $\to \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$, thus

$$\lim_{R\to\infty} \Delta = 0 + \lim_{R\to\infty} \left[\frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}\right] = 0 \tag{4.1.11}$$

$$\lim_{R\to\infty} E_{\text{corr}} = -\lim_{R\to\infty} K_{12} \tag{4.1.12}$$

$$\lim_{R\to\infty} c = \lim_{R\to\infty} \frac{E_{\text{corr}}}{K_{12}} = -1 \tag{4.1.13}$$

As $R \to \infty$, the full CI wave function will be

$$|\Phi_0\rangle = |\Psi_0\rangle - |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle \tag{4.1.14}$$

Since

$$\psi_1 = \frac{1}{\sqrt{2(1 + S_{12})}}(\phi_1 + \phi_2) \tag{4.1.15}$$

$$\psi_2 = \frac{1}{\sqrt{2(1 - S_{12})}}(\phi_1 - \phi_2) \tag{4.1.16}$$

we get

$$|\psi_1\bar{\psi}_1\rangle = \frac{1}{2(1+S_{12})}\big(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big) \tag{4.1.17}$$

$$|\psi_2\bar{\psi}_2\rangle = \frac{1}{2(1-S_{12})}\big(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big) \tag{4.1.18}$$

As $R \to \infty$, $S_{12} \to 0$, thus

$$|\Phi_0\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle = |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle \tag{4.1.19}$$

Renormalize it, we get

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}\big(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle\big) \tag{4.1.20}$$

4.2 Doubly Exited CI

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

Ex 4.4

$$\gamma_{ij} = \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_1' \chi_i^*(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')\chi_j(\mathbf{x}_1') \tag{4.4.1}$$

$$\begin{aligned}
\gamma_{ji}^* &= \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_1' \chi_j(\mathbf{x}_1)\gamma^*(\mathbf{x}_1, \mathbf{x}_1')\chi_i^*(\mathbf{x}_1') \\
&= \int \mathrm{d}\mathbf{x}_1' \mathrm{d}\mathbf{x}_1 \chi_j(\mathbf{x}_1')\gamma^*(\mathbf{x}_1', \mathbf{x}_1)\chi_i^*(\mathbf{x}_1) \\
&= \int \mathrm{d}\mathbf{x}_1' \mathrm{d}\mathbf{x}_1 \chi_j(\mathbf{x}_1')\gamma(\mathbf{x}_1, \mathbf{x}_1')\chi_i^*(\mathbf{x}_1) \\
&= \gamma_{ij}
\end{aligned} \tag{4.4.2}$$

$\therefore \boldsymbol{\gamma}$ is Hermitian.

Ex 4.5

$$\begin{aligned}
\langle \Phi \mid \Phi \rangle &= \frac{1}{N}\int \mathrm{d}\mathbf{x}_1 \gamma(\mathbf{x}_1, \mathbf{x}_1) \\
&= \frac{1}{N}\int \mathrm{d}\mathbf{x}_1 \sum_{ij} \chi_i(\mathbf{x}_1)\gamma_{ij}\chi_j^*(\mathbf{x}_1) \\
&= \frac{1}{N}\sum_{ij}\left[\int \mathrm{d}\mathbf{x}_1 \chi_j^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\right]\gamma_{ij} \\
&= \frac{1}{N}\sum_{ij}\delta_{ji}\gamma_{ij} \\
&= \frac{1}{N}\,\mathrm{tr}\,\boldsymbol{\gamma}
\end{aligned} \tag{4.4.3}$$

thus

$$\mathrm{tr}\,\boldsymbol{\gamma} = N \tag{4.4.4}$$

Ex 4.6

a.

$$\begin{aligned}\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle &= \sum_i \langle \Phi \mid h(\mathbf{x}_1) \mid \Phi \rangle \\ &= N \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) h(\mathbf{x}_1) \Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \\ &= N \frac{1}{N} \int \mathrm{d}\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1} \\ &= \int \mathrm{d}\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1} \end{aligned} \tag{4.4.5}$$

b.

$$\begin{aligned}\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle &= \int \mathrm{d}\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1} \\ &= \int \mathrm{d}\mathbf{x}_1 [h(\mathbf{x}_1) \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1} \\ &= \sum_{ij} \left[\int \mathrm{d}\mathbf{x}_1 \chi_j^*(\mathbf{x}_1) h(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \right] \gamma_{ij} \\ &= \sum_{ij} h_{ji} \gamma_{ij} \\ &= \sum_j (\mathbf{h}\boldsymbol{\gamma})_{jj} \\ &= \mathrm{tr}(\mathbf{h}\boldsymbol{\gamma}) \end{aligned} \tag{4.4.6}$$

Ex 4.7

a.

$$\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle = \sum_{ij} \langle i \mid h \mid j \rangle \left\langle \Phi \,\middle|\, a_i^+ a_j \,\middle|\, \Phi \right\rangle \tag{4.4.7}$$

while

$$\langle \Phi \mid \mathscr{O}_1 \mid \Phi \rangle = \sum_{ij} h_{ij} \gamma_{ji} \tag{4.4.8}$$

$\therefore$

$$\gamma_{ji} = \left\langle \Phi \,\middle|\, a_i^+ a_j \,\middle|\, \Phi \right\rangle \tag{4.4.9}$$

i.e.

$$\gamma_{ij} = \left\langle \Phi \,\middle|\, a_j^+ a_i \,\middle|\, \Phi \right\rangle \tag{4.4.10}$$

b.

$$\gamma_{ij}^{\mathrm{HF}} = \left\langle \Psi_0 \,\middle|\, a_j^+ a_i \,\middle|\, \Psi_0 \right\rangle \tag{4.4.11}$$

If i is unoccupied, thus $\gamma_{ij}^{\mathrm{HF}} = 0$ as we cannot annihilate electrons from it. If j is unoccupied, $\gamma_{ij}^{\mathrm{HF}} = \delta_{ij} - \left\langle \Psi_0 \,\middle|\, a_i a_j^+ \,\middle|\, \Psi_0 \right\rangle = \delta_{ij} - \delta_{ij} = 0$.
Otherwise, when i, j are occupied, it's clear that $\gamma_{ij}^{\mathrm{HF}} = \delta_{ij}$.
Thus,

$$\gamma_{ij}^{\mathrm{HF}} = \begin{cases} \delta_{ij} & i, j \text{ are occupied} \\ 0 & \text{otherwise} \end{cases} \tag{4.4.12}$$

Ex 4.8

a. Since

$$|^1\Phi_0\rangle = c_0\,|\psi_1\bar{\psi}_1\rangle + \sum_{r=2}^{K} c_1^r \frac{1}{\sqrt{2}}\big(|\psi_1\bar{\psi}_r\rangle + |\psi_r\bar{\psi}_1\rangle\big) + \frac{1}{2}\sum_{r=2}^{K}\sum_{s=2}^{K} c_{11}^{rs}\frac{1}{\sqrt{2}}\big(|\psi_r\bar{\psi}_s\rangle + |\psi_s\bar{\psi}_r\rangle\big) \tag{4.4.13}$$

we can write

$$|^1\Phi_0\rangle = \sum_i^K\sum_j^K C_{ij}\,|\psi_i\bar{\psi}_j\rangle \tag{4.4.14}$$

When one or two of i,j equals 1, it is clear that $C_{ij} = C_{ji}$. Otherwise, $c_{11}^{rs} = c_{11}^{sr}$. Thus, $\mathbf{C}$ is symmetric.

b.

$$\begin{aligned}
\gamma(\mathbf{x}_1,\mathbf{x}_1') &= 2\int \mathrm{d}\mathbf{x}_2 \sum_{ij} C_{ij}\frac{1}{\sqrt{2}}\big(\psi_i(\mathbf{x}_1)\bar{\psi}_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar{\psi}_j(\mathbf{x}_1)\big)\sum_{kl} C_{kl}^*\frac{1}{\sqrt{2}}\big(\psi_k^*(\mathbf{x}_1')\bar{\psi}_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar{\psi}_l^*(\mathbf{x}_1')\big)\\
&= \sum_{ij}\sum_{kl} C_{ij}C_{kl}^*\int \mathrm{d}\mathbf{x}_2\big(\psi_i(\mathbf{x}_1)\bar{\psi}_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar{\psi}_j(\mathbf{x}_1)\big)\big(\psi_k^*(\mathbf{x}_1')\bar{\psi}_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar{\psi}_l^*(\mathbf{x}_1')\big)\\
&= \sum_{ij}\sum_{kl} C_{ij}C_{kl}^*\big[\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1')\delta_{jl} + \bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}_1')\delta_{ik}\big]\\
&= \sum_{ij}\sum_{k} C_{ij}C_{kj}^*\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1') + \sum_{ij}\sum_{l} C_{ij}C_{il}^*\bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}_1')\\
&= \sum_{ik}(\mathbf{C}\mathbf{C}^\dagger)_{ik}\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1') + \sum_{jl}(\mathbf{C}^\dagger\mathbf{C})_{lj}\bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}_1')\\
&= \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\psi_i(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1') + \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ji}\bar{\psi}_i(\mathbf{x}_1)\bar{\psi}_j^*(\mathbf{x}_1')\\
&= \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\big[\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')\big]
\end{aligned} \tag{4.4.15}$$

c.

$$\mathbf{d} = \mathbf{U}^\dagger\mathbf{C}\mathbf{U} \tag{4.4.16}$$

$$\mathbf{d}^\dagger = (\mathbf{U}^\dagger\mathbf{C}\mathbf{U})^\dagger = \mathbf{U}^\dagger\mathbf{C}^\dagger\mathbf{U} \tag{4.4.17}$$

Since $\mathbf{U}$ is unitary

$$\mathbf{d}^2 = \mathbf{d}\mathbf{d}^\dagger = \mathbf{U}^\dagger\mathbf{C}\mathbf{U}\mathbf{U}^\dagger\mathbf{C}^\dagger\mathbf{U} = \mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U} \tag{4.4.18}$$

d. Since

$$\psi_k = \sum_i U_{ik}^\dagger\zeta_i \tag{4.4.19}$$

$$\begin{aligned}
\gamma(\mathbf{x}_1,\mathbf{x}_1') &= \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\big[\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')\big]\\
&= \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\left[\sum_k U_{ki}^\dagger\zeta_k(1)\sum_l U_{lj}^{\dagger *}\zeta_l^*(1') + \sum_k U_{ki}^\dagger\bar{\zeta}_k(1)\sum_l U_{lj}^{\dagger *}\bar{\zeta}_l^*(1')\right]\\
&= \sum_k\sum_l\sum_{ij} U_{ki}^\dagger(\mathbf{C}\mathbf{C}^\dagger)_{ij}U_{jl}\big[\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')\big]\\
&= \sum_k\sum_l(\mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U})_{kl}\big[\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')\big]\\
&= \sum_k\sum_l d_k^2\delta_{kl}\big[\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')\big]\\
&= \sum_k d_k^2\big[\zeta_k(1)\zeta_k^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_k^*(1')\big]
\end{aligned} \tag{4.4.20}$$

e.

$$
\begin{aligned}
|{}^1\Phi_0\rangle &= \sum_i^K \sum_j^K C_{ij} \, |\psi_i \bar{\psi}_j\rangle \\
&= \sum_i^K \sum_j^K C_{ij} \left| \left(\sum_k U_{ki}^\dagger \zeta_k \right) \left(\sum_l U_{lj}^\dagger \bar{\zeta}_l \right) \right\rangle \\
&= \sum_i^K \sum_j^K \sum_k \sum_l U_{ki}^\dagger C_{ij} U_{jl} \, |\zeta_k \bar{\zeta}_l\rangle \\
&= \sum_k \sum_l d_k \delta_{kl} \, |\zeta_k \bar{\zeta}_l\rangle \\
&= \sum_k d_k \, |\zeta_k \bar{\zeta}_k\rangle
\end{aligned} \tag{4.4.21}
$$

4.5 The MCSCF and the GVB Methods

Ex 4.9

a.

$$
\begin{aligned}
\langle u \,|\, u \rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A + b\psi_B \,|\, a\psi_A + b\psi_B \rangle \\
&= \frac{1}{a^2+b^2} (a^2+b^2) \\
&= 1
\end{aligned} \tag{4.5.1}
$$

$$
\begin{aligned}
\langle v \,|\, v \rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A - b\psi_B \,|\, a\psi_A - b\psi_B \rangle \\
&= \frac{1}{a^2+b^2} (a^2+b^2) \\
&= 1
\end{aligned} \tag{4.5.2}
$$

$$
\begin{aligned}
\langle u \,|\, v \rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A + b\psi_B \,|\, a\psi_A - b\psi_B \rangle \\
&= \frac{a^2-b^2}{a^2+b^2}
\end{aligned} \tag{4.5.3}
$$

b.

$$
\begin{aligned}
|\Psi_{\text{GVB}}\rangle &= [2(1+S^2)]^{-1/2} [u(1)v(2) + u(2)v(1)] 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&= \left[2 + 2\left(\frac{a^2-b^2}{a^2+b^2} \right)^2 \right]^{-1/2} (a^2+b^2)^{-1} \\
&\quad \times [(a\psi_A(1) + b\psi_B(1))(a\psi_A(2) - b\psi_B(2)) + (a\psi_A(2) + b\psi_B(2))(a\psi_A(1) - b\psi_B(1))] \\
&\quad \times 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&= \left[2(a^2+b^2)^2 + 2\big(a^2-b^2\big)^2 \right]^{-1/2} [2a^2\psi_A(1)\psi_A(2) - 2b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&= \left[4(a^4+b^4) \right]^{-1/2} [2a^2\psi_A(1)\psi_A(2) - 2b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&= \big(a^4+b^4\big)^{-1/2} [a^2\psi_A(1)\psi_A(2) - b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]
\end{aligned} \tag{4.5.4}
$$

i.e.

$$
\begin{aligned}
|\Psi_{\text{GVB}}\rangle &= \big(a^4+b^4\big)^{-1/2} a^2 \times 2^{-1/2} \psi_A(1)\psi_A(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&\quad - \big(a^4+b^4\big)^{-1/2} b^2 \times 2^{-1/2} \psi_B(1)\psi_B(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\
&= \big(a^4+b^4\big)^{-1/2} a^2 \, |\psi_A \bar{\psi}_A\rangle - \big(a^4+b^4\big)^{-1/2} b^2 \, |\psi_B \bar{\psi}_B\rangle
\end{aligned} \tag{4.5.5}
$$

thus $|\Psi_{\mathrm{GVB}}\rangle$ is identical to $|\Psi^{\mathrm{MCSCF}}\rangle$.

4.6 Truncated CI and the Size-consistency Problem

Ex 4.10

$$\begin{aligned}\langle\Psi_0\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 1_2\bar{1}_2\,\|\,2_1\bar{2}_1\rangle \\ &= \langle 1_2\bar{1}_2\,|\,2_1\bar{2}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_1 2_1\rangle \\ &= [1_2 2_1|\bar{1}_2\bar{2}_1] - [1_2\bar{2}_1|\bar{1}_2 2_1] \\ &= (1_2 2_1|1_2 2_1) \\ &= 0\end{aligned} \tag{4.6.1}$$

$$\begin{aligned}\langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 1_1\bar{1}_1\rangle \\ &= \langle 1_2\bar{1}_2\,\|\,1_1\bar{1}_1\rangle \\ &= \langle 1_2\bar{1}_2\,|\,1_1\bar{1}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{1}_1 1_1\rangle \\ &= [1_2 1_1|\bar{1}_2\bar{1}_1] - [1_2\bar{1}_1|\bar{1}_2 1_1] \\ &= (1_2 1_1|1_2 1_1) \\ &= 0\end{aligned} \tag{4.6.2}$$

$$\begin{aligned}\langle 1_1\bar{1}_1 2_2\bar{2}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 2_2\bar{2}_2\,\|\,2_1\bar{2}_1\rangle \\ &= \langle 2_2\bar{2}_2\,|\,2_1\bar{2}_1\rangle - \langle 2_2\bar{2}_2\,|\,\bar{2}_1 2_1\rangle \\ &= [2_2 2_1|\bar{2}_2\bar{2}_1] - [2_2\bar{2}_1|\bar{2}_2 2_1] \\ &= (2_2 2_1|2_2 2_1) \\ &= 0\end{aligned} \tag{4.6.3}$$

Ex 4.11

$$\frac{{}^N E_{\mathrm{corr}}(\mathrm{DCI})}{N} = \frac{\Delta - (\Delta^2 + N K_{12}^2)^{1/2}}{N} \tag{4.6.4}$$

From Ex 4.3, we get $\Delta = 0.78865$, $K_{12} = 0.1813$, thus

N	${}^N E_{\mathrm{corr}}(\mathrm{DCI})/N$
1	-0.02057
10	-0.01864
100	-0.01188

Ex 4.12

a. In addition to the matrix elements obtained in Eq. 4.56 in the textbook, we need to calculate the rest, i.e. those involving $|2_1\bar{2}_1 2_2\bar{2}_2\rangle$.

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle = 0 \tag{4.6.5}$$

$$\begin{aligned}\langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle &= \langle 1_2\bar{1}_2\,\|\,2_2\bar{2}_2\rangle \\ &= \langle 1_2\bar{1}_2\,|\,2_2\bar{2}_2\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_2 2_2\rangle \\ &= [1_2 2_2|\bar{1}_2\bar{2}_2] - [1_2\bar{2}_2|\bar{1}_2 2_2] \\ &= (12|12) \\ &= K_{12}\end{aligned} \tag{4.6.6}$$

$$\begin{aligned}\langle 1_1\bar{1}_1 2_2\bar{2}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle &= \langle 1_1\bar{1}_1\,\|\,2_1\bar{2}_1\rangle \\ &= \langle 1_1\bar{1}_1\,|\,2_1\bar{2}_1\rangle - \langle 1_1\bar{1}_1\,|\,\bar{2}_1 2_1\rangle \\ &= [1_1 2_1|\bar{1}_1\bar{2}_1] - [1_1\bar{2}_1|\bar{1}_1 2_1] \\ &= (12|12) \\ &= K_{12}\end{aligned} \tag{4.6.7}$$

$$\langle 2_1\bar{2}_1 2_2\bar{2}_2 \,|\, \mathscr{H} - E_0 \,|\, 2_1\bar{2}_1 2_2\bar{2}_2\rangle = 4h_{22} + 2J_{22} - 4h_{11} - 2J_{11} \\ = 4\Delta \tag{4.6.8}$$

thus the full CI equation is

$$\begin{pmatrix} 0 & K_{12} & K_{12} & 0 \\ K_{12} & 2\Delta & 0 & K_{12} \\ K_{12} & 0 & 2\Delta & K_{12} \\ 0 & K_{12} & K_{12} & 4\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = {}^2E_{\text{corr}} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} \tag{4.6.9}$$

e. Directly solve the full CI equation (see `4-11,12.nb`), we get the lowest eigenvalue

$$^2E_{\text{corr}} = 2[\Delta - \sqrt{\Delta^2 + K_{12}^2}] \tag{4.6.10}$$

Ex 4.13

$$\begin{aligned} ^1E_{\text{corr}}(\text{exact}) &= \Delta - \sqrt{\Delta^2 + K_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \\ &\approx \Delta - \Delta\left(1 + \frac{1}{2}\frac{K_{12}^2}{\Delta^2}\right) \\ &\approx -\frac{1}{2}\frac{K_{12}^2}{\Delta} \end{aligned} \tag{4.6.11}$$

$$\begin{aligned} ^NE_{\text{corr}}(\text{DCI}) &= \Delta - \sqrt{\Delta^2 + NK_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{NK_{12}^2}{\Delta^2}} \\ &\approx \Delta - \Delta\left(1 + \frac{1}{2}\frac{NK_{12}^2}{\Delta^2}\right) \\ &\approx -\frac{1}{2}\frac{NK_{12}^2}{\Delta} \end{aligned} \tag{4.6.12}$$

Ex 4.14

a.

$$\begin{aligned} ^NE_{\text{corr}}(\text{DCI}) &= \Delta - \sqrt{\Delta^2 + NK_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{NK_{12}^2}{\Delta^2}} \\ &= \Delta - \Delta\left(1 + \frac{1}{2}\frac{NK_{12}^2}{\Delta^2} - \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^4} + \cdots\right) \\ &= -\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots \end{aligned} \tag{4.6.13}$$

b.

$$c_0^2 = \frac{1}{1 + Nc_1^2} \tag{4.6.14}$$

thus

$$1 - c_0^2 = \frac{Nc_1^2}{1 + Nc_1^2} \tag{4.6.15}$$

c.

$$
\begin{aligned}
c_1 &= \frac{K_{12}}{{}^N E_{\text{corr}}(\text{DCI}) - 2\Delta} \\
&= \frac{K_{12}}{-\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} - 2\Delta + \cdots} \\
&= \frac{1}{-\frac{1}{2}\frac{NK_{12}}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^3}{\Delta^3} - 2\frac{\Delta}{K_{12}} + \cdots} \\
&= -\frac{1}{2}\frac{K_{12}}{\Delta} + \cdots
\end{aligned} \tag{4.6.16}
$$

d.

$$
\Delta E_{\text{Davidson}} = (1 - c_0^2)\ {}^N E_{\text{corr}}(\text{DCI}) \tag{4.6.17}
$$

$$
\begin{aligned}
&= \frac{N(-K_{12}/2\Delta)^2}{1 + N(-K_{12}/2\Delta)^2}\left(-\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots\right) \\
&= N\frac{K_{12}^2}{4\Delta^2}\left(-\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots\right) \\
&= -\frac{N^2K_{12}^4}{8\Delta^3} + \cdots
\end{aligned} \tag{4.6.18}
$$

e.

$$
\begin{aligned}
\Delta E_{\text{Davidson}} &= (1 - c_0^2)\ {}^N E_{\text{corr}}(\text{DCI}) \\
&= \frac{Nc_1^2}{1 + Nc_1^2} NK_{12}c_1 \\
&= \frac{N^2K_{12}c_1^3}{1 + Nc_1^2}
\end{aligned} \tag{4.6.19}
$$

while

$$
c_1 = {}^N E_{\text{corr}}(\text{DCI})/NK_{12} \tag{4.6.20}
$$

thus

$$
\begin{aligned}
\Delta E_{\text{Davidson}} &= \frac{N^2K_{12}c_1^3}{1 + Nc_1^2} \\
&= \frac{[{}^N E_{\text{corr}}(\text{DCI})]^3/NK_{12}^2}{1 + [{}^N E_{\text{corr}}(\text{DCI})]^2/NK_{12}^2} \\
&= \frac{[{}^N E_{\text{corr}}(\text{DCI})]^3}{NK_{12}^2 + [{}^N E_{\text{corr}}(\text{DCI})]^2}
\end{aligned} \tag{4.6.21}
$$

Since

$$
{}^N E_{\text{corr}}(\text{DCI}) = \Delta - \sqrt{\Delta^2 + NK_{12}^2} \tag{4.6.22}
$$

$$
{}^N E_{\text{corr}}(\text{exact}) = N\left[\Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \tag{4.6.23}
$$

The values of ${}^N E_{\mathrm{corr}}(\mathrm{DCI})$, ${}^N E_{\mathrm{corr}}(\mathrm{exact})$, $\Delta E_{\mathrm{Davidson}}$ for $N = 1, \cdots, 20, 100$ are as follows.

N	${}^N E_{\mathrm{corr}}(\mathrm{DCI})$	${}^N E_{\mathrm{corr}}(\mathrm{exact})$	$\Delta E_{\mathrm{Davidson}}$
1	-0.020571	-0.020571	-0.0002615
2	-0.040632	-0.041142	-0.0009954
3	-0.060219	-0.061713	-0.0021360
4	-0.079364	-0.082284	-0.0036282
5	-0.098095	-0.102855	-0.0054259
6	-0.116439	-0.123426	-0.0074900
7	-0.134419	-0.143997	-0.0097872
8	-0.152055	-0.164567	-0.0122891
9	-0.169367	-0.185138	-0.0149711
10	-0.186371	-0.205709	-0.0178120
11	-0.203084	-0.22628	-0.0207933
12	-0.219519	-0.246851	-0.0238991
13	-0.235691	-0.267422	-0.0271151
14	-0.251612	-0.287993	-0.0304291
15	-0.267292	-0.308564	-0.0338301
16	-0.282743	-0.329135	-0.0373084
17	-0.297975	-0.349706	-0.0408554
18	-0.312996	-0.370277	-0.0444636
19	-0.327814	-0.390848	-0.0481262
20	-0.342439	-0.411419	-0.0518370
100	-1.188450	-2.057090	-0.3571950

The values and errors of DCI energies and DCI energies with Davidson correction are as follows.

N	${}^N E_{\mathrm{corr}}(\mathrm{DCI})/{}^N E_{\mathrm{corr}}(\mathrm{exact})$	Error/%	$[{}^N E_{\mathrm{corr}}(\mathrm{DCI}) + \Delta E_{\mathrm{Davidson}}]/{}^N E_{\mathrm{corr}}(\mathrm{exact})$	Error/%
1	1.0000	0.00	1.0127	-1.27
2	0.9876	1.24	1.0118	-1.18
3	0.9758	2.42	1.0104	-1.04
4	0.9645	3.55	1.0086	-0.86
5	0.9537	4.63	1.0065	-0.65
6	0.9434	5.66	1.0041	-0.41
7	0.9335	6.65	1.0015	-0.15
8	0.9240	7.60	0.9986	0.14
9	0.9148	8.52	0.9957	0.43
10	0.9060	9.40	0.9926	0.74
11	0.8975	10.25	0.9894	1.06
12	0.8893	11.07	0.9861	1.39
13	0.8813	11.87	0.9827	1.73
14	0.8737	12.63	0.9793	2.07
15	0.8662	13.38	0.9759	2.41
16	0.8591	14.10	0.9724	2.76
17	0.8521	14.79	0.9689	3.11
18	0.8453	15.47	0.9654	3.46
19	0.8387	16.13	0.9619	3.81
20	0.8323	16.77	0.9583	4.17
100	0.5777	42.23	0.7514	24.86

f. From data of Saxe et al., we get

$$E_{\text{corr}}(\text{DCI}) = -0.139340 \qquad c_0 = 0.97938 \tag{4.6.24}$$

thus

$$\begin{aligned}\Delta E_{\text{Davidson}} &= (1 - c_0^2) E_{\text{corr}}(\text{DCI}) \\ &= (1 - 0.97938^2) \times (-76.129178) \\ &= -0.005687\end{aligned} \tag{4.6.25}$$

thus

	correlation energy	error wrt full CI
DCI + Davidson	-0.145027	0.003181
DQCI	-0.145859	0.002349
Full CI	-0.148208	0

Ex 4.15

$$\begin{aligned}\langle \Psi_0 \,|\, \Phi_0 \rangle &= \prod_{i=1}^{N} \Big[(1 + c^2)^{-1/2} \langle 1_i \bar{1}_i \,|\, 1_i \bar{1}_i \rangle + c(1 + c^2)^{-1/2} \langle 1_i \bar{1}_i \,|\, 2_i \bar{2}_i \rangle \Big] \\ &= (1 + c^2)^{-N/2}\end{aligned} \tag{4.6.26}$$

Since

$$c = \frac{{}^1E_{\text{corr}}}{K_{12}} = \frac{-0.020571}{0.1813} = -0.1135 \tag{4.6.27}$$

we get

N	$\langle \Psi_0 \,\vert\, \Phi_0 \rangle$
1	0.9936
10	0.9380
100	0.5273

Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

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Contents

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

$$\begin{aligned}
{}^1E_{\text{corr}}(\text{FO}) &= \frac{|\langle 1\bar{1} \,\|\, 2\bar{2}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} \\
&= \frac{\left|\langle 1\bar{1} \,|\, 2\bar{2}\rangle - \langle 1\bar{1} \,|\, \bar{2}2\rangle\right|^2}{2\varepsilon_1 - 2\varepsilon_2} \\
&= \frac{\left|[12|\bar{1}\bar{2}] - [1\bar{2}|\bar{1}2]\right|^2}{2\varepsilon_1 - 2\varepsilon_2} \\
&= \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
\end{aligned} \tag{5.1.1}$$

b.

$$\begin{aligned}
{}^1E_{\text{corr}} &= \Delta - \Delta\sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \\
&= \Delta - \Delta\left(1 + \frac{K_{12}^2}{2\Delta^2}\right) \\
&= -\frac{K_{12}^2}{2\Delta}) \\
&\approx \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
\end{aligned} \tag{5.1.2}$$

Ex 5.2 From Eq. 5.9a and 5.9b in the textbook, we get

$$\sum_{t<u} c_{1_i\bar{1}_i}^{tu} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle = e_{1_i\bar{1}_i} \tag{5.1.3}$$

$$\left\langle \Psi_{1_i\bar{1}_i}^{rs} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi_{1_i\bar{1}_i}^{rs} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle c_{1_i\bar{1}_i}^{tu} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{rs} \tag{5.1.4}$$

$\therefore$

$$c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle = e_{1_i\bar{1}_i} \tag{5.1.5}$$

$$\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle c_{1_i\bar{1}_i}^{tu} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \tag{5.1.6}$$

(5.1.5) gives

$$K_{12} c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i} \tag{5.1.7}$$

(5.1.6) gives

$$K_{12} + \sum_{jk} \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_j\bar{2}_k} \right\rangle c_{1_i\bar{1}_i}^{2_j\bar{2}_k} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \tag{5.1.8}$$

Since

$$\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_j\bar{2}_k} \right\rangle c_{1_i\bar{1}_i}^{2_j\bar{2}_k} = \begin{cases} 2\Delta & j = k = i \\ 0 & j = k \neq i \\ 0 & i = j =\neq k \end{cases} \tag{5.1.9}$$

we have

$$K_{12} + 2\Delta c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \tag{5.1.10}$$

Ex 5.3

$$
\begin{aligned}
{}^2E_{\text{corr}}(\text{FO}) &= \sum_i \frac{|\langle 1_i\bar{1}_i \,\|\, 2_i\bar{2}_i\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} \\
&= 2\times\frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)} \\
&= \frac{K_{12}^2}{(\varepsilon_1-\varepsilon_2)}
\end{aligned} \tag{5.1.11}
$$

5.1.1 Invariance under Unitary Transformations: An Example

Ex 5.4

$$
\begin{aligned}
|a\bar{a}b\bar{b}\rangle &= 2^{-1/2}\big(|1_1\bar{a}b\bar{b}\rangle + |1_2\bar{a}b\bar{b}\rangle\big) \\
&= 2^{-1}\big(|1_1\bar{1}_1b\bar{b}\rangle + |1_1\bar{1}_2b\bar{b}\rangle + |1_2\bar{1}_1b\bar{b}\rangle + |1_2\bar{1}_2b\bar{b}\rangle\big) \\
&= 2^{-2}(|1_1\bar{1}_11_1\bar{1}_1\rangle - |1_1\bar{1}_11_1\bar{1}_2\rangle - |1_1\bar{1}_11_2\bar{1}_1\rangle + |1_1\bar{1}_11_2\bar{1}_2\rangle \\
&\quad + |1_1\bar{1}_21_1\bar{1}_1\rangle - |1_1\bar{1}_21_1\bar{1}_2\rangle - |1_1\bar{1}_21_2\bar{1}_1\rangle + |1_1\bar{1}_21_2\bar{1}_2\rangle \\
&\quad + |1_2\bar{1}_11_1\bar{1}_1\rangle - |1_2\bar{1}_11_1\bar{1}_2\rangle - |1_2\bar{1}_11_2\bar{1}_1\rangle + |1_2\bar{1}_11_2\bar{1}_2\rangle \\
&\quad + |1_2\bar{1}_21_1\bar{1}_1\rangle - |1_2\bar{1}_21_1\bar{1}_2\rangle - |1_2\bar{1}_21_2\bar{1}_1\rangle + |1_2\bar{1}_21_2\bar{1}_2\rangle) \\
&= 2^{-2}(2\,|1_1\bar{1}_11_1\bar{1}_1\rangle + 2\,|1_1\bar{1}_11_2\bar{1}_2\rangle - 2\,|1_1\bar{1}_21_1\bar{1}_2\rangle - 2\,|1_1\bar{1}_21_2\bar{1}_1\rangle) \\
&= 2^{-2}(2\,|1_1\bar{1}_11_2\bar{1}_2\rangle - 2\,|1_1\bar{1}_11_2\bar{1}_2\rangle) \\
&= |1_1\bar{1}_11_2\bar{1}_2\rangle
\end{aligned} \tag{5.1.12}
$$

Ex 5.5

$$
\begin{aligned}
\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{a}}^{**}\rangle &= 2^{-1/2}\big(\big\langle\Psi_0\,\big|\,\mathscr{H}\,\big|\,\Psi_{a\bar{a}}^{r\bar{r}}\big\rangle + \big\langle\Psi_0\,\big|\,\mathscr{H}\,\big|\,\Psi_{a\bar{a}}^{s\bar{s}}\big\rangle\big) \\
&= 2^{-1/2}\left(2\times\frac{1}{2}K_{12}\right) \\
&= 2^{-1/2}K_{12}
\end{aligned} \tag{5.1.13}
$$

$$
\begin{aligned}
\langle\Psi_{a\bar{a}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{a}}^{**}\rangle &= 2^{-1}(\big\langle\Psi_{a\bar{a}}^{r\bar{r}}\,\big|\,\mathscr{H}-E_0\,\big|\,\Psi_{a\bar{a}}^{r\bar{r}}\big\rangle + \big\langle\Psi_{a\bar{a}}^{r\bar{r}}\,\big|\,\mathscr{H}-E_0\,\big|\,\Psi_{a\bar{a}}^{s\bar{s}}\big\rangle \\
&\quad + \big\langle\Psi_{a\bar{a}}^{s\bar{s}}\,\big|\,\mathscr{H}-E_0\,\big|\,\Psi_{a\bar{a}}^{r\bar{r}}\big\rangle + \big\langle\Psi_{a\bar{a}}^{s\bar{s}}\,\big|\,\mathscr{H}-E_0\,\big|\,\Psi_{a\bar{a}}^{s\bar{s}}\big\rangle) \\
&= 2^{-1}\Bigg[\left(2h_{11}+2h_{22}+\frac{1}{2}J_{11}+\frac{1}{2}J_{22}+2J_{12}-K_{12}\right)-(4h_{11}+2J_{11}) \\
&\quad + \frac{1}{2}J_{22}+\frac{1}{2}J_{22} \\
&\quad + \left(2h_{11}+2h_{22}+\frac{1}{2}J_{11}+\frac{1}{2}J_{22}+2J_{12}-K_{12}\right)-(4h_{11}+2J_{11})\Bigg] \\
&= 2^{-1}\left(-2h_{11}+2h_{22}-\frac{3}{2}J_{11}+J_{22}+2J_{12}-K_{12}\right)\times 2 \\
&= -2h_{11}+2h_{22}-\frac{3}{2}J_{11}+J_{22}+2J_{12}-K_{12}
\end{aligned} \tag{5.1.14}
$$

Since

$$
\varepsilon_2-\varepsilon_1 = h_{22}-h_{11}+2J_{12}-K_{12}-J_{11} \tag{5.1.15}
$$

we have

$$
\langle\Psi_{a\bar{a}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{a}}^{**}\rangle = 2(\varepsilon_2-\varepsilon_1)-2J_{12}+K_{12}+\frac{1}{2}J_{11}+J_{22} \tag{5.1.16}
$$

Ex 5.6 Since

$$|\Psi_{a\bar{b}}^{**}\rangle = 2^{-1/2}(|\Psi_{a\bar{b}}^{r\bar{s}}\rangle + |\Psi_{a\bar{b}}^{s\bar{r}}\rangle) \tag{5.1.17}$$

$$\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{**} \right\rangle &= 2^{-1/2}\left(\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{r\bar{s}} \right\rangle + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{s\bar{r}} \right\rangle\right) \\
&= 2^{-1/2}\left(\left\langle a\bar{b} \,\middle\|\, r\bar{s} \right\rangle + \left\langle a\bar{b} \,\middle\|\, s\bar{r} \right\rangle\right) \\
&= 2^{-1/2}((ar|bs) + (as|br)) \\
&= 2^{-1/2}K_{12}
\end{aligned} \tag{5.1.18}$$

$$\begin{aligned}
\left\langle \Psi_{a\bar{b}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{**} \right\rangle &= 2^{-1}(\left\langle \Psi_{a\bar{b}}^{r\bar{s}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{r\bar{s}} \right\rangle + \left\langle \Psi_{a\bar{b}}^{r\bar{s}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{s\bar{r}} \right\rangle \\
&\quad + \left\langle \Psi_{a\bar{b}}^{s\bar{r}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{r\bar{s}} \right\rangle + \left\langle \Psi_{a\bar{b}}^{s\bar{r}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{s\bar{r}} \right\rangle) \\
&= 2^{-1}\Bigg[\left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11}) \\
&\quad + \frac{1}{2}J_{22} + \frac{1}{2}J_{22} \\
&\quad + \left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11})\Bigg] \\
&= \ldots \\
&= 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \equiv 2\Delta'
\end{aligned} \tag{5.1.19}$$

Thus the equations determining $e_{a\bar{b}}$ are identical to that of $e_{a\bar{a}}$. Similarly, $e_{\bar{a}b}$ shares the same equations with them.
$\therefore\ e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$.

Ex 5.7

a. As shown in Ex 5.5, 5.6

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{**} \rangle = \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{**} \right\rangle = \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{\bar{a}b}^{**} \rangle = 2^{-1/2}K_{12} \tag{5.1.20}$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = \left\langle \Psi_{a\bar{b}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{a\bar{b}}^{**} \right\rangle = \langle \Psi_{\bar{a}b}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{\bar{a}b}^{**} \rangle = 2\Delta' \tag{5.1.21}$$

Similarly, we get

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle = 2^{-1/2}K_{12} \tag{5.1.22}$$

$$\left\langle \Psi_{b\bar{b}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle = 2\Delta' \tag{5.1.23}$$

For the rest,

$$\begin{aligned}
\left\langle \Psi_{a\bar{a}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle &= 2^{-1}(\left\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{r\bar{r}} \right\rangle + \left\langle \Psi_{a\bar{a}}^{r\bar{r}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{s\bar{s}} \right\rangle \\
&\quad + \left\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{r\bar{r}} \right\rangle + \left\langle \Psi_{a\bar{a}}^{s\bar{s}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{s\bar{s}} \right\rangle) \\
&= 2^{-1}\left[\left\langle b\bar{b} \,\middle\|\, a\bar{a} \right\rangle + 0 + 0 + \left\langle b\bar{b} \,\middle\|\, a\bar{a} \right\rangle\right] \\
&= (ab|ab) \\
&= \frac{1}{2}J_{11}
\end{aligned} \tag{5.1.24}$$

$$
\begin{aligned}
\langle \Psi_{a\bar{a}}^{**} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle &= 2^{-1}(\langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{s\bar{r}} \rangle \\
&\quad + \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{s\bar{r}} \rangle) \\
&= 2^{-1}\left[\langle \bar{r}\bar{b} \| \bar{a}\bar{s} \rangle - \langle r\bar{b} \| s\bar{a} \rangle + \langle s\bar{b} \| r\bar{a} \rangle - \langle \bar{s}\bar{b} \| \bar{a}\bar{r} \rangle\right] \\
&= 2^{-1}[(ra|bs) - (rs|ba) - (rs|ba) - (sr|ba) + (sa|br) - (sr|ba)] \\
&= 2^{-1}[(ra|bs) + (sa|br) - 4(ab|sr)] \\
&= 2^{-1}\left[2 \times \frac{1}{2}K_{12} - 4 \times \frac{1}{2}J_{12}\right] \\
&= \frac{1}{2}K_{12} - J_{12}
\end{aligned} \tag{5.1.25}
$$

Similarly, we get

$$
\langle \Psi_{a\bar{b}}^{**} | \mathscr{H} - E_0 | \Psi_{\bar{a}b}^{**} \rangle = \frac{1}{2}J_{11} \tag{5.1.26}
$$

$$
\langle \Psi_{a\bar{a}}^{**} | \mathscr{H} - E_0 | \Psi_{\bar{a}b}^{**} \rangle = \langle \Psi_{b\bar{b}}^{**} | \mathscr{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle = \langle \Psi_{b\bar{b}}^{**} | \mathscr{H} - E_0 | \Psi_{\bar{a}b}^{**} \rangle = \frac{1}{2}K_{12} - J_{12} \tag{5.1.27}
$$

thus the DCI equation is

$$
\begin{pmatrix}
0 & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} \\
2^{-1/2}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\
2^{-1/2}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\
2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\
2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta'
\end{pmatrix}
\begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}
= {}^2E_{\text{corr}}(\text{DCI})
\begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{5.1.28}
$$

b. By solving the DCI equation above (see `5-7.nb`), we get

$$
{}^2E_{\text{corr}}(\text{DCI}) = \frac{2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12}) - \sqrt{16(2^{-1/2}K_{12})^2 + [2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12})]^2}}{2} \tag{5.1.29}
$$

and

$$
c_1 = c_2 = c_3 = c_4 = \frac{2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12}) + \sqrt{16(2^{-1/2}K_{12})^2 + [2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12})]^2}}{8 \times 2^{-1/2}K_{12}} \tag{5.1.30}
$$

Since

$$
2\Delta' = 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \tag{5.1.31}
$$

$$
2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \tag{5.1.32}
$$

we have

$$
2\Delta = 2\Delta' + \frac{1}{2}J_{11} - 2J_{12} + K_{12} \tag{5.1.33}
$$

$\therefore$

$$
\begin{aligned}
{}^2E_{\text{corr}}(\text{DCI}) &= \frac{2\Delta - \sqrt{8K_{12}^2 + (2\Delta)^2}}{2} \\
&= \Delta - \sqrt{2K_{12}^2 + \Delta^2}
\end{aligned} \tag{5.1.34}
$$

$$
\begin{aligned}
c_1 = c_2 = c_3 = c_4 &= \frac{2\Delta + \sqrt{8K_{12}^2 + (2\Delta)^2}}{4\sqrt{2}K_{12}} \\
&= \frac{\Delta + \sqrt{2K_{12}^2 + \Delta^2}}{2\sqrt{2}K_{12}}
\end{aligned} \tag{5.1.35}
$$

Ex 5.8

$$
\begin{aligned}
E_{\text{corr}}(\text{FO}) &= \sum_{A<B}\sum_{R<S} \frac{|\langle AB \,\|\, RS\rangle|^2}{\varepsilon_A+\varepsilon_B-\varepsilon_R-\varepsilon_S} \\
&= \frac{|\langle a\bar{a}\,\|\,r\bar{r}\rangle|^2+|\langle a\bar{a}\,\|\,r\bar{s}\rangle|^2+|\langle a\bar{a}\,\|\,s\bar{r}\rangle|^2+|\langle a\bar{a}\,\|\,s\bar{s}\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} + \frac{\left|\langle a\bar{b}\,\|\,r\bar{r}\rangle\right|^2+\left|\langle a\bar{b}\,\|\,r\bar{s}\rangle\right|^2+\left|\langle a\bar{b}\,\|\,s\bar{r}\rangle\right|^2+\left|\langle a\bar{b}\,\|\,s\bar{s}\rangle\right|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} \\
&\quad + \frac{|\langle b\bar{a}\,\|\,r\bar{r}\rangle|^2+|\langle b\bar{a}\,\|\,r\bar{s}\rangle|^2+|\langle b\bar{a}\,\|\,s\bar{r}\rangle|^2+|\langle b\bar{a}\,\|\,s\bar{s}\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} + \frac{\left|\langle b\bar{b}\,\|\,r\bar{r}\rangle\right|^2+\left|\langle b\bar{b}\,\|\,r\bar{s}\rangle\right|^2+\left|\langle b\bar{b}\,\|\,s\bar{r}\rangle\right|^2+\left|\langle b\bar{b}\,\|\,s\bar{s}\rangle\right|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} \\
&= \frac{|(ar|ar)|^2+|(ar|as)|^2+|(as|ar)|^2+|(as|as)|^2}{2(\varepsilon_1-\varepsilon_2)} + \frac{|(ar|br)|^2+|(ar|bs)|^2+|(as|br)|^2+|(as|bs)|^2}{2(\varepsilon_1-\varepsilon_2)} \\
&\quad + \frac{|(br|ar)|^2+|(br|as)|^2+|(bs|ar)|^2+|(bs|as)|^2}{2(\varepsilon_1-\varepsilon_2)} + \frac{|(br|br)|^2+|(br|bs)|^2+|(bs|br)|^2+|(bs|bs)|^2}{2(\varepsilon_1-\varepsilon_2)} \\
&= \frac{\left|\frac{1}{2}K_{12}\right|^2+0+0+\left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1-\varepsilon_2)} + \frac{0+\left|\frac{1}{2}K_{12}\right|^2+\left|\frac{1}{2}K_{12}\right|^2+0}{2(\varepsilon_1-\varepsilon_2)} \\
&\quad + \frac{0+0+\left|\frac{1}{2}K_{12}\right|^2+\left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1-\varepsilon_2)} + \frac{\left|\frac{1}{2}K_{12}\right|^2+0+0+\left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1-\varepsilon_2)} \\
&= \frac{2K_{12}^2}{2(\varepsilon_1-\varepsilon_2)}
\end{aligned}
\tag{5.1.36}
$$

Ex 5.9

a.

$$
\begin{aligned}
{}^2E_{\text{corr}}(\text{EN(L)}) &= -\frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle\right|^2}{\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \,\middle|\, \mathscr{H}-E_0 \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle} - \frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle\right|^2}{\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \,\middle|\, \mathscr{H}-E_0 \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle} \\
&= -\frac{K_{12}^2}{2\Delta}\times 2 \\
&= -\frac{K_{12}^2}{\Delta}
\end{aligned}
\tag{5.1.37}
$$

b.

$$
\begin{aligned}
{}^2E_{\text{corr}}(\text{EN(D)}) &= e_{a\bar{a}}+e_{b\bar{b}}+e_{a\bar{b}}+e_{\bar{a}b} \\
&= 2e_{a\bar{a}}+2e_{a\bar{b}} \\
&= -2\frac{|\langle \Psi_0 \mid \mathscr{H} \mid \Psi_{a\bar{a}}^{**}\rangle|^2}{\langle \Psi_{a\bar{a}}^{**} \mid \mathscr{H}-E_0 \mid \Psi_{a\bar{a}}^{**}\rangle} - 2\frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{a\bar{b}}^{**}\right\rangle\right|^2}{\left\langle \Psi_{a\bar{b}}^{**} \,\middle|\, \mathscr{H}-E_0 \,\middle|\, \Psi_{a\bar{b}}^{**}\right\rangle} \\
&= -2\frac{\left|2^{-1/2}K_{12}\right|^2}{2\Delta'} - 2\frac{\left|2^{-1/2}K_{12}\right|^2}{2\Delta'} \\
&= -\frac{K_{12}^2}{2\Delta'}\times 2 \\
&= -\frac{K_{12}^2}{\Delta'}
\end{aligned}
\tag{5.1.38}
$$

c.

$$
\begin{aligned}
{}^2E_{\text{corr}}^{\text{singlet}}(\text{EN(D)}) &= e_{a\bar{a}}+e_{b\bar{b}}+e_{ab}^{\text{singlet}} \\
&= -\frac{K_{12}^2}{2\Delta'} - \frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^B\Psi_{ab}^{rs}\right\rangle\right|^2}{\langle {}^B\Psi_{ab}^{rs} \mid \mathscr{H}-E_0 \mid {}^B\Psi_{ab}^{rs}\rangle} \\
&= -\frac{K_{12}^2}{2\Delta'} - \frac{K_{12}^2}{2\Delta''}
\end{aligned}
\tag{5.1.39}
$$

d.

$$^2E_{\text{corr}}(\text{EN(L)}) = -0.04168 \tag{5.1.40}$$
$$^2E_{\text{corr}}(\text{EN(D)}) = -0.02755 \tag{5.1.41}$$
$$^2E_{\text{corr}}^{\text{singlet}}(\text{EN(D)}) = -0.02585 \tag{5.1.42}$$

thus EN pairs is not invariant to unitary transformations.

Ex 5.10 From Ex 5.7,

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{**} \rangle = \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle = 2^{-1/2} K_{12} \tag{5.1.43}$$
$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = \left\langle \Psi_{b\bar{b}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle = 2\Delta' \tag{5.1.44}$$
$$\left\langle \Psi_{a\bar{a}}^{**} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{b\bar{b}}^{**} \right\rangle = \frac{1}{2} J_{11} \tag{5.1.45}$$

From Eq 5.42 in the textbook,

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, {}^B\Psi_{ab}^{rs} \right\rangle = K_{12} \tag{5.1.46}$$
$$\left\langle {}^B\Psi_{ab}^{rs} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, {}^B\Psi_{ab}^{rs} \right\rangle = 2\Delta'' \tag{5.1.47}$$

and

$$\begin{aligned}
\left\langle \Psi_{a\bar{a}}^{**} \,\middle|\, \mathscr{H} \,\middle|\, {}^B\Psi_{ab}^{rs} \right\rangle &= 2^{-3/2} \left\langle \Psi_{a\bar{a}}^{r\bar{r}} + \Psi_{a\bar{a}}^{s\bar{s}} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{a}b}^{\bar{s}r} + \Psi_{\bar{a}b}^{\bar{r}s} + \Psi_{a\bar{b}}^{r\bar{s}} + \Psi_{a\bar{b}}^{s\bar{r}} \right\rangle \\
&= 2^{-3/2} \left(-\langle \bar{r}b \,\|\, \bar{s}a \rangle + \langle rb \,\|\, as \rangle + \left\langle \bar{r}\bar{b} \,\middle\|\, \bar{a}\bar{s} \right\rangle - \left\langle r\bar{b} \,\middle\|\, s\bar{a} \right\rangle + \langle sb \,\|\, ar \rangle - \langle \bar{s}b \,\|\, \bar{r}a \rangle - \left\langle s\bar{b} \,\middle\|\, r\bar{a} \right\rangle + \left\langle \bar{s}\bar{b} \,\middle\|\, \bar{a}\bar{r} \right\rangle \right) \\
&= 2^{-3/2} (-8(rs|ba) + 2(ra|bs) + 2(sa|br)) \\
&= 2^{-3/2} \left(-8 \times \frac{1}{2} J_{12} + 4 \times \frac{1}{2} K_{12} \right) \\
&= 2^{-1/2} (K_{12} - 2J_{12})
\end{aligned} \tag{5.1.48}$$

similarly,

$$\left\langle \Psi_{b\bar{b}}^{**} \,\middle|\, \mathscr{H} \,\middle|\, {}^B\Psi_{ab}^{rs} \right\rangle = 2^{-1/2} (\times K_{12} - 2J_{12}) \tag{5.1.49}$$

thus the DCI equation is

$$\begin{pmatrix} 0 & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & K_{12} \\ 2^{-1/2}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & 2^{-1/2}(K_{12} - 2J_{12}) \\ 2^{-1/2}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & 2^{-1/2}(K_{12} - 2J_{12}) \\ K_{12} & 2^{-1/2}(K_{12} - 2J_{12}) & 2^{-1/2}(K_{12} - 2J_{12}) & 2\Delta'' \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = {}^2E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} \tag{5.1.50}$$

by solving the DCI equation,

$$^2E_{\text{corr}}(\text{DCI}) = \Delta - \sqrt{\Delta^2 + 2K_{12}^2} \tag{5.1.51}$$

5.1.2 Some Illustrative Calculations

5.2 Coupled-pair Theories

5.2.1 The Coupled-cluster Approximation

5.2.2 The Cluster Expansion of the Wave Function

Ex 5.11 Eq. 5.49 gives

$$\begin{aligned}
|\Phi_0\rangle &= |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} |2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} |1_1\bar{1}_1 2_2\bar{2}_2\rangle + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} |2_1\bar{2}_1 2_2\bar{2}_2\rangle \\
&= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} a_{\bar{1}_1} a_{1_1} \right] |1_1\bar{1}_1 1_2\bar{1}_2\rangle
\end{aligned} \tag{5.2.1}$$

while

$$
\begin{aligned}
&\exp\Big(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\Big) |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\
&= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right)^2 + \cdots\right] |1_1\bar{1}_1 1_2\bar{1}_2\rangle
\end{aligned}
\tag{5.2.2}
$$

since we cannot annihilate or create any orbital twice, the terms over 3rd power must be zero, thus

$$
\begin{aligned}
&\exp\Big(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\Big) |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\
&= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right)^2\right] |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\
&= \Bigg[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1}\right)^2 + \left(c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}\right)^2 \\
&\quad + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1} a_{1_1} a_{\bar{1}_2} a_{1_2}\Bigg] |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\
&= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1} a_{1_1} a_{\bar{1}_2} a_{1_2}\right] |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\
&= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1} a_{1_1} a_{\bar{1}_2} a_{1_2}\right] |1_1\bar{1}_1 1_2\bar{1}_2\rangle
\end{aligned}
\tag{5.2.3}
$$

5.2.3 Linear CCA and the Coupled-Electron Pair Approximation

Ex 5.12

a. The diagonal elements of $\mathbf{D}$ is

$$
\mathbf{D}_{rasb,rasb} = \langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs} \rangle \tag{5.2.4}
$$

thus

$$
\begin{aligned}
E_{\text{corr}} &= -\mathbf{B}^\dagger \mathbf{D}^{-1} \mathbf{B} \\
&= -\sum_{a<b}\sum_{r<s} \frac{\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs}\rangle^\dagger \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs}\rangle}{\langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs}\rangle} \\
&= -\sum_{a<b}\sum_{r<s} \frac{|\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{ab}^{rs}\rangle|^2}{\langle \Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs}\rangle}
\end{aligned}
\tag{5.2.5}
$$

which matches Eq. 5.15 and 5.16.

b. localized orbitals:
From Ex 4.12, we get

$$
\mathbf{B} = \begin{pmatrix} K_{12} \\ K_{12} \end{pmatrix} \tag{5.2.6}
$$

$$
\mathbf{D} = \begin{pmatrix} 2\Delta & 0 \\ 0 & 2\Delta \end{pmatrix} \tag{5.2.7}
$$

thus

$$
\begin{aligned}
E_{\text{corr}}(\text{L-CCA(L)}) &= -\mathbf{B}^\dagger \mathbf{D}^{-1} \mathbf{B} \\
&= -\frac{K_{12}^2}{\Delta}
\end{aligned}
\tag{5.2.8}
$$

delocalized orbitals:
From Ex 5.7, we get

$$
\mathbf{B} = \begin{pmatrix} 2^{-1/2} K_{12} \\ 2^{-1/2} K_{12} \\ 2^{-1/2} K_{12} \\ 2^{-1/2} K_{12} \end{pmatrix} \tag{5.2.9}
$$

$$
\mathbf{D} = \begin{pmatrix} 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \tag{5.2.10}
$$

thus

$$
\begin{aligned}
E_{\text{corr}}(\text{L-CCA(D)}) &= -\mathbf{B}^{\dagger}\mathbf{D}^{-1}\mathbf{B} \\
&= -\frac{K_{12}^2}{\Delta}
\end{aligned} \tag{5.2.11}
$$

5.2.4 Some Illustrative Calculations

5.3 Many-electron Theories with Single Particle Hamiltonians

Ex 5.13

$$
C = \frac{-H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2H_{12}} \tag{5.3.1}
$$

$$
\begin{aligned}
\varepsilon_1 &= H_{11} + H_{12}C \\
&= H_{11} + \frac{-H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2} \\
&= \frac{H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2}
\end{aligned} \tag{5.3.2}
$$

while the eigenvalues of the matrix is

$$
\frac{H_{11} + H_{22} \pm \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2} \tag{5.3.3}
$$

5.3.1 The Relaxation Energy via CI, IEPA, CEPA and CCA

Ex 5.14

a.

$$
\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_b^s \rangle &= \left\langle \Psi_0 \,\middle|\, \sum_i [h_0(i) + v(i)] \,\middle|\, \Psi_b^s \right\rangle \\
&= v_{bs}
\end{aligned} \tag{5.3.4}
$$

b. Similarly

$$
\langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_0 \rangle = v_{ra} \tag{5.3.5}
$$

c.

$$
\begin{aligned}
\langle \Psi_a^r \,|\, \mathscr{H} - E_0 \,|\, \Psi_b^s \rangle &= \langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_b^s \rangle - E_0 \langle \Psi_a^r \,|\, \Psi_b^s \rangle \\
&= \begin{cases} 0 + 0 & a \neq b, r \neq s \\ v_{rs} + 0 & a = b, r \neq s \\ -v_{ba} + 0 & a \neq b, r = s \\ E_0 + \varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa} - E_0 & a = b, r = s \end{cases} \\
&= \begin{cases} 0 & a \neq b, r \neq s \\ v_{rs} & a = b, r \neq s \\ -v_{ba} & a \neq b, r = s \\ \varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa} & a = b, r = s \end{cases}
\end{aligned} \tag{5.3.6}
$$

d. Since we cannot create or annihilate an orbital twice,

$$
\langle \Psi_a^r \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs} \rangle = \begin{cases} v_{bs} & a \neq b, r \neq s \\ 0 & \text{otherwise} \end{cases} \tag{5.3.7}
$$

Ex 5.15

a.

$$\begin{aligned}
|\Phi_0\rangle &= a_1b_1\cdot 0 + a_1b_2\,|\chi_1^{(0)}\chi_2^{(0)}\rangle + a_1b_3\,|\chi_1^{(0)}\chi_3^{(0)}\rangle + a_1b_4\,|\chi_1^{(0)}\chi_4^{(0)}\rangle \\
&\quad + a_2b_1\,|\chi_2^{(0)}\chi_1^{(0)}\rangle + a_2b_2\cdot 0 + a_2b_3\,|\chi_2^{(0)}\chi_3^{(0)}\rangle + a_2b_4\,|\chi_2^{(0)}\chi_4^{(0)}\rangle \\
&\quad + a_3b_1\,|\chi_3^{(0)}\chi_1^{(0)}\rangle + a_3b_2\,|\chi_3^{(0)}\chi_2^{(0)}\rangle + a_3b_3\cdot 0 + a_3b_4\,|\chi_3^{(0)}\chi_4^{(0)}\rangle \\
&\quad + a_4b_1\,|\chi_4^{(0)}\chi_1^{(0)}\rangle + a_4b_2\,|\chi_4^{(0)}\chi_2^{(0)}\rangle + a_4b_3\,|\chi_4^{(0)}\chi_3^{(0)}\rangle + a_4b_4\cdot 0 \\
&= (a_1b_2 - a_2b_1)\,|\chi_1^{(0)}\chi_2^{(0)}\rangle + (a_1b_3 - a_3b_1)\,|\chi_1^{(0)}\chi_3^{(0)}\rangle + (a_1b_4 - a_4b_1)\,|\chi_1^{(0)}\chi_4^{(0)}\rangle \\
&\quad - (a_2b_3 - a_3b_2)\,|\chi_3^{(0)}\chi_2^{(0)}\rangle - (a_2b_4 - a_4b_2)\,|\chi_4^{(0)}\chi_2^{(0)}\rangle + (a_3b_4 - a_4b_3)\,|\chi_3^{(0)}\chi_4^{(0)}\rangle
\end{aligned} \tag{5.3.8}$$

thus, with intermediate normalization

$$\begin{aligned}
|\Phi_0\rangle &= |\Psi_0\rangle + \frac{a_1b_3 - a_3b_1}{a_1b_2 - a_2b_1}\,|\Psi_2^3\rangle + \frac{a_1b_4 - a_4b_1}{a_1b_2 - a_2b_1}\,|\Psi_2^4\rangle \\
&\quad - \frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1}\,|\Psi_1^3\rangle - \frac{a_2b_4 - a_4b_2}{a_1b_2 - a_2b_1}\,|\Psi_1^4\rangle + \frac{a_3b_4 - a_4b_3}{a_1b_2 - a_2b_1}\,|\Psi_{12}^{34}\rangle
\end{aligned} \tag{5.3.9}$$

$$\begin{aligned}
c_1^3c_2^4 - c_1^4c_2^3 &= -\frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1}\frac{a_1b_4 - a_4b_1}{a_1b_2 - a_2b_1} + \frac{a_2b_4 - a_4b_2}{a_1b_2 - a_2b_1}\frac{a_1b_3 - a_3b_1}{a_1b_2 - a_2b_1} \\
&= \frac{a_2a_4b_1b_3 + a_1a_3b_2b_4 - a_2a_3b_1b_4 - a_1a_4b_2b_3}{(a_1b_2 - a_2b_1)^2} \\
&= \frac{(a_1b_2 - a_2b_1)(a_3b_4 - a_4b_3)}{(a_1b_2 - a_2b_1)^2} \\
&= \frac{a_3b_4 - a_4b_3}{a_1b_2 - a_2b_1} \\
&= c_{12}^{34}
\end{aligned} \tag{5.3.10}$$

b.

$$\mathbf{U}_{AA}^{-1} = \frac{1}{\det(\mathbf{U}_{AA})}\begin{pmatrix} b_2 & -b_1 \\ -a_2 & a_1 \end{pmatrix} \tag{5.3.11}$$

$$\begin{aligned}
(\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1})_{11} &= \frac{1}{\det(\mathbf{U}_{AA})}(a_3b_2 - b_3a_2) \\
&= -\frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1} \\
&= c_1^3
\end{aligned} \tag{5.3.12}$$

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

Ex 5.16

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \tag{5.3.13}$$

the eigenvalues are

$$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta \tag{5.3.14}$$

while from Eq. 5.131, we get

$$\varepsilon_i = \alpha + 2\beta\cos\frac{\pi i}{3} \quad (i = 0, \pm 1, \pm 2, 3) \tag{5.3.15}$$

i.e.

$$\{\varepsilon_i\} = \{\alpha + 2\beta, \alpha + \beta, \alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta, \} \tag{5.3.16}$$

which is identical to those eigenvalues.
The total energy is

$$\begin{aligned}\mathscr{E}_0 &= 2(\alpha + 2\beta + \alpha + \beta + \alpha + \beta) && (5.3.17)\\ &= 6\alpha + 8\beta && (5.3.18)\end{aligned}$$

which agrees with Eq. 5.132.

Ex 5.17 For Eq. 5.139

$$\begin{aligned}\langle i \,|\, j\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| + \langle\phi_{2i}|)(|\phi_{2j-1}\rangle + |\phi_{2j}\rangle)\\ &= \frac{1}{2}(\delta_{2i-1,2j-1} + 0 + 0 + \delta_{2i,2j})\\ &= \frac{1}{2}(\delta_{i,j} + \delta_{i,j})\\ &= \delta_{i,j} && (5.3.19)\end{aligned}$$

$\langle i^* \,|\, j^*\rangle$ is similar.

$$\begin{aligned}\langle i \,|\, j^*\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| + \langle\phi_{2i}|)(|\phi_{2j-1}\rangle - |\phi_{2j}\rangle)\\ &= \frac{1}{2}(\delta_{2i-1,2j-1} - 0 + 0 - \delta_{2i,2j})\\ &= \frac{1}{2}(\delta_{i,j} - \delta_{i,j})\\ &= 0 && (5.3.20)\end{aligned}$$

For Eq. 5.140

$$\begin{aligned}\langle i \,|\, h_{\text{eff}} \,|\, i\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| + \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1}\rangle + |\phi_{2i}\rangle)\\ &= \frac{1}{2}(\alpha + \beta + \beta + \alpha)\\ &= \alpha + \beta && (5.3.21)\end{aligned}$$

$$\begin{aligned}\langle i^* \,|\, h_{\text{eff}} \,|\, i^*\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| - \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1}\rangle - |\phi_{2i}\rangle)\\ &= \frac{1}{2}(\alpha - \beta - \beta + \alpha)\\ &= \alpha - \beta && (5.3.22)\end{aligned}$$

$$\begin{aligned}\langle i \,|\, h_{\text{eff}} \,|\, i \pm 1\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| + \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle + |\phi_{2i\pm2}\rangle)\\ &= \begin{cases}\frac{1}{2}(0 + 0 + \beta + 0) & +\\ \frac{1}{2}(0 + \beta + 0 + 0) & -\end{cases}\\ &= \beta/2 && (5.3.23)\end{aligned}$$

$$\begin{aligned}\langle i^* \,|\, h_{\text{eff}} \,|\, (i \pm 1)^*\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| - \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle)\\ &= \begin{cases}\frac{1}{2}(0 - 0 - \beta + 0) & +\\ \frac{1}{2}(0 - \beta - 0 + 0) & -\end{cases}\\ &= -\beta/2 && (5.3.24)\end{aligned}$$

$$\begin{aligned}\langle i \,|\, h_{\text{eff}} \,|\, (i \pm 1)^* \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|) h_{\text{eff}}(|\phi_{2i-1\pm 2}\rangle - |\phi_{2i\pm 2}\rangle) \\ &= \begin{cases} \frac{1}{2}(0 - 0 + \beta - 0) & + \\ \frac{1}{2}(0 - \beta + 0 - 0) & - \end{cases} \\ &= \pm\beta/2 \end{aligned} \tag{5.3.25}$$

Ex 5.18

$$\begin{aligned}\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle &= 2^{-1/2} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle \\ &= 2^{-1/2}[\beta/2 - (-\beta/2)] \\ &= 2^{-1/2}\beta \end{aligned} \tag{5.3.26}$$

$$\begin{aligned}\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \overset{*}{1} \right\rangle &= \frac{1}{2} \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle \\ &= \frac{1}{2}\left[\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle\right] \\ &= \frac{1}{2}[2(\alpha - \beta) - 2(-\beta/2) - 2E_0] \\ &= \alpha - \beta/2 - E_0 \\ &= -\frac{3}{2}\beta \end{aligned} \tag{5.3.27}$$

thus

$$2^{-1/2}\beta c = e_1 \tag{5.3.28}$$

$$2^{-1/2}\beta - \frac{3}{2}\beta c = e_1 c \tag{5.3.29}$$

the solutions are

$$c = \frac{-3 \pm \sqrt{17}}{2\sqrt{2}} \qquad e_1 = \frac{-3 \pm \sqrt{17}}{4}\beta \tag{5.3.30}$$

and we take

$$e_1 = \frac{-3 + \sqrt{17}}{4}\beta \tag{5.3.31}$$

Ex 5.19

a)

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 |\Psi_1^{1*}\rangle + c_2 |\Psi_1^{2*}\rangle + \cdots + c_n |\Psi_1^{n*}\rangle \tag{5.3.32}$$

Since

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{1*} \right\rangle = 0 \tag{5.3.33}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} \right\rangle = \beta/2 \tag{5.3.34}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{j*} \right\rangle = 0 \qquad (1 < j < n) \tag{5.3.35}$$

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_1^{n*} \rangle = -\beta/2 \tag{5.3.36}$$

thus,

$$|\Psi_1\rangle = |\Psi_0\rangle + c \left| \overset{*}{1} \right\rangle \tag{5.3.37}$$

$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\big(\left|\Psi_1^{2*}\right\rangle - \left|\Psi_1^{n*}\right\rangle\big) \tag{5.3.38}$$

As before, we get

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.39}$$

but

$$\begin{aligned}
\left\langle \overset{*}{1} \middle| \mathscr{H} - E_0 \middle| \overset{*}{1} \right\rangle &= \frac{1}{2}\big[\left\langle \Psi_1^{2*} - \Psi_1^{3*} \middle| \mathscr{H} \middle| \Psi_1^{2*} - \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{2*} - \Psi_1^{3*} \middle| E_0 \middle| \Psi_1^{2*} - \Psi_1^{3*} \right\rangle\big] \\
&= \frac{1}{2}[2(\alpha - \beta) - 2 \times 0 - 2E_0] \\
&= \alpha - \beta - E_0 \\
&= -2\beta
\end{aligned} \tag{5.3.40}$$

thus

$$e_1 = \left(-1 + \frac{\sqrt{6}}{2}\right)\beta \tag{5.3.41}$$

$$\begin{aligned}
E_R(\text{IEPA}) &= Ne_1 \\
&= \left(-1 + \frac{\sqrt{6}}{2}\right)N\beta \\
&= 0.2247N\beta
\end{aligned} \tag{5.3.42}$$

b) As $N = 10$,

$$\left|\Psi_1\right\rangle = \left|\Psi_0\right\rangle + c_1\left|\Psi_1^{1*}\right\rangle + c_2\left|\Psi_1^{2*}\right\rangle + c_3\left|\Psi_1^{3*}\right\rangle + +c_4\left|\Psi_1^{4*}\right\rangle + c_5\left|\Psi_1^{5*}\right\rangle \tag{5.3.43}$$

As before, let

$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\big(\left|\Psi_1^{1*}\right\rangle - \left|\Psi_1^{5*}\right\rangle\big) \tag{5.3.44}$$

$$\left|\Psi_1\right\rangle = \left|\Psi_0\right\rangle + c_1\left|\overset{*}{1}\right\rangle + c_3\left|\Psi_1^{3*}\right\rangle + +c_4\left|\Psi_1^{4*}\right\rangle \tag{5.3.45}$$

then the "particle" equations will be

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle c_3 + \left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle c_4 = e_1 \tag{5.3.46}$$

$$\left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle c_3 + \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle c_4 + \left\langle \overset{*}{1} \middle| \mathscr{H} - E_0 \middle| \overset{*}{1} \right\rangle c_1 = e_1c_1 \tag{5.3.47}$$

$$\left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle c_4 + \left\langle \Psi_1^{3*} \middle| \mathscr{H} - E_0 \middle| \Psi_1^{3*} \right\rangle c_3 = e_1c_3 \tag{5.3.48}$$

$$\left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle c_3 + \left\langle \Psi_1^{4*} \middle| \mathscr{H} - E_0 \middle| \Psi_1^{4*} \right\rangle c_4 = e_1c_4 \tag{5.3.49}$$

where

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.50}$$

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle = 0 \tag{5.3.51}$$

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle = 0 \tag{5.3.52}$$

$$\left\langle \overset{*}{1} \middle| \mathscr{H} - E_0 \middle| \overset{*}{1} \right\rangle = -2\beta \tag{5.3.53}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{3*} \right\rangle = \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{4*} \right\rangle = \alpha - \beta - E_0 = -2\beta \tag{5.3.54}$$

$$\begin{aligned}\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle &= 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle\right] \\ &= 2^{-1/2}(-\beta/2)\end{aligned} \tag{5.3.55}$$

$$\begin{aligned}\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle &= 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle\right] \\ &= 2^{-1/2}(\beta/2)\end{aligned} \tag{5.3.56}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle = -\beta/2 \tag{5.3.57}$$

thus

$$2^{-1/2}\beta c_1 = e_1 \tag{5.3.58}$$
$$2^{-1/2}\beta + 2^{-1/2}(-\beta/2)c_3 + 2^{-1/2}(\beta/2)c_4 + (-2\beta)c_1 = e_1c_1 \tag{5.3.59}$$
$$2^{-1/2}(-\beta/2)c_1 + (-\beta/2)c_4 + (-2\beta)c_3 = e_1c_3 \tag{5.3.60}$$
$$2^{-1/2}(\beta/2)c_1 + (-\beta/2)c_3 + (-2\beta)c_4 = e_1c_4 \tag{5.3.61}$$

or

$$\begin{pmatrix} 0 & 2^{-1/2}\beta & 0 & 0 \\ 2^{-1/2}\beta & -2\beta & 2^{-1/2}(-\beta/2) & 2^{-1/2}(\beta/2) \\ 0 & 2^{-1/2}(-\beta/2) & -2\beta & -\beta/2 \\ 0 & 2^{-1/2}(\beta/2) & -\beta/2 & -2\beta \end{pmatrix}\begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} = e_1\begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} \tag{5.3.62}$$

the eigenvalues are

$$-\frac{5}{2}\beta \;\text{ or roots of }\; (2e_1/\beta)^3 + 7(2e_1/\beta)^2 + 9(2e_1/\beta) - 6 = 0 \tag{5.3.63}$$

rearrange the cubic equation, we get

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0 \tag{5.3.64}$$

$$e_1 = -2.4627\beta, -1.2760\beta, 0.2387\beta \tag{5.3.65}$$

so we take

$$e_1 = 0.2387\beta \tag{5.3.66}$$

Ex 5.20

$$\begin{aligned}\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{2} \right\rangle &= \frac{1}{2}\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} - \Psi_2^{1*} \right\rangle \\ &= -\frac{1}{2}\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} \right\rangle \\ &= -\frac{1}{2}(-1)\left\langle 2 \,\middle|\, h_{\text{eff}} \,\middle|\, 1 \right\rangle \\ &= -\frac{1}{2}(-1)\beta/2 \\ &= \beta/4\end{aligned} \tag{5.3.67}$$

$$\begin{aligned}\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{3} \right\rangle &= \frac{1}{2}\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} - \Psi_3^{2*} \right\rangle \\ &= -\frac{1}{2}\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{2*} \right\rangle \\ &= -\frac{1}{2}(-1)\beta/2 \\ &= \beta/4\end{aligned} \tag{5.3.68}$$

$$
\begin{aligned}
\left\langle \overset{*}{2} \middle| \mathscr{H} \middle| \overset{*}{3} \right\rangle &= \frac{1}{2} \left\langle \Psi_2^{3*} - \Psi_2^{1*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} - \Psi_3^{2*} \right\rangle \\
&= -\frac{1}{2} \left\langle \Psi_2^{1*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} \right\rangle \\
&= -\frac{1}{2}(-1)\beta/2 \\
&= \beta/4
\end{aligned}
\tag{5.3.69}
$$

For SCI,

$$
\sum_{bs} v_{bs} c_b^s = E_R(\text{SCI}) \tag{5.3.70}
$$

$$
v_{ra} + (\varepsilon_r^{(0)} + v_{rr}) c_a^r + \sum_s v_{rs} c_a^s - (\varepsilon_a^{(0)} + v_{aa}) c_a^r - \sum_b v_{ba} c_b^r = E_R(\text{SCI}) c_a^r \tag{5.3.71}
$$

thus

$$
6c \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle = E_R(\text{SCI}) \tag{5.3.72}
$$

$$
\left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + c \left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{i} \right\rangle + \sum_{j \neq i} c \left\langle \overset{*}{j} \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = E_R(\text{SCI}) c \tag{5.3.73}
$$

i.e.

$$
6c \times 2^{-1/2} \beta = E_R(\text{SCI}) \tag{5.3.74}
$$

$$
2^{-1/2} \beta + c \left(-\frac{3}{2} \beta + 2 \times \beta/4 \right) = E_R(\text{SCI}) c \tag{5.3.75}
$$

$\therefore$

$$
6c \times 2^{-1/2} \beta = E_R(\text{SCI}) \tag{5.3.76}
$$

$$
2^{-1/2} \beta - c\beta = E_R(\text{SCI}) c \tag{5.3.77}
$$

the solutions are

$$
E_R(\text{SCI}) = \frac{-1 \pm \sqrt{13}}{2} \beta \tag{5.3.78}
$$

we take

$$
E_R(\text{SCI}) = \frac{-1 + \sqrt{13}}{2} \beta \tag{5.3.79}
$$

Ex 5.21 It's clear that

$$
\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = 2^{-1/2} \beta \tag{5.3.80}
$$

while

$$
\begin{aligned}
\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \overset{*}{j} \right\rangle - E_0 \delta_{ij} \\
&= \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle - E_0 \delta_{ij}
\end{aligned}
\tag{5.3.81}
$$

If $i = j$,

$$
\begin{aligned}
\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \frac{1}{2} \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \right\rangle - E_0 \\
&= \frac{1}{2} \times 2(\alpha - \beta) - E_0 \\
&= -2\beta
\end{aligned}
\tag{5.3.82}
$$

else,

$$
\begin{aligned}
\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \frac{1}{2} \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle \\
&= -\frac{1}{2} \left\langle \Psi_i^{(i+1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j-1)*} \right\rangle - \frac{1}{2} \left\langle \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} \right\rangle \\
&= 0
\end{aligned} \tag{5.3.83}
$$

thus

$$
\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle = -2\beta\delta_{ij} \tag{5.3.84}
$$

Similar to Ex. 5.20, the SCI equations are

$$
Nc \times 2^{-1/2}\beta = E_R(\mathrm{SCI}) \tag{5.3.85}
$$

$$
2^{-1/2}\beta + c(-2\beta + 0) = E_R(\mathrm{SCI})c \tag{5.3.86}
$$

$\therefore$

$$
E_R(\mathrm{SCI}) = \frac{-2 + \sqrt{2N+4}}{2}\beta = \left[\sqrt{1 + N/2} - 1\right]\beta \tag{5.3.87}
$$

Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

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Contents

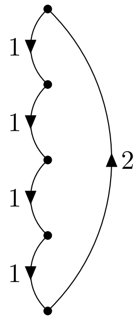
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

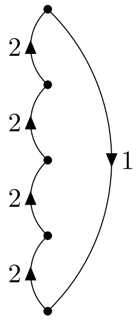
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

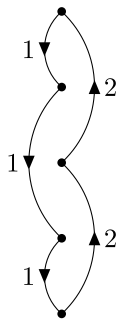
Ex 6.1



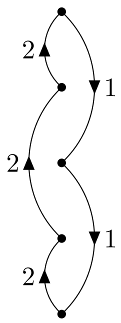
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



$$= (-1)^2 \frac{V_{12}V_{21}V_{22}^3}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{22}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$

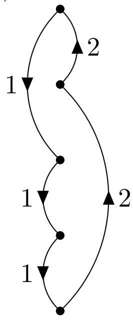


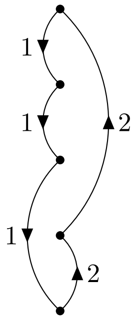
$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$



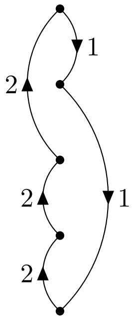
$$= (-1)^3 \frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

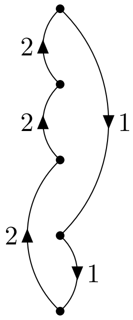
Similarly,



, 

$$= \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$



, 

$$= -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

thus, the sum of above terms is

$$\frac{V_{12}V_{21}(V_{22}^3 - V_{11}^3)}{(E_1^{(0)} - E_2^{(0)})^4} + 3 \times \frac{V_{12}V_{21}(V_{11}^2V_{22} - V_{11}V_{22}^2)}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}(V_{22} - V_{11})^3}{(E_1^{(0)} - E_2^{(0)})^4} \tag{6.2.1}$$

6.2.2 Diagrammatic Perturbation Theory for N States

Ex 6.2 The 4th-order perturbation energy of state i can be expressed as

$$\begin{aligned}
&\sum_{k,n,m\neq i} \frac{V_{ki}V_{nk}V_{mn}V_{im}}{(E_i^{(0)} - E_k^{(0)})(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} + \sum_{n\neq i} \frac{V_{ii}^2V_{ni}V_{in}}{(E_i^{(0)} - E_n^{(0)})^3} - \sum_{m,n\neq i} \frac{V_{ii}V_{mi}V_{in}V_{nm}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} \\
&- \sum_{m,n\neq i} \frac{V_{ii}V_{ni}V_{im}V_{mn}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} - \sum_{m,n\neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})} \\
&- \sum_{m,n\neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})} \\
=& \sum_{k,n,m\neq i} \frac{V_{ki}V_{nk}V_{mn}V_{im}}{(E_i^{(0)} - E_k^{(0)})(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} + \sum_{n\neq i} \frac{V_{ii}^2V_{ni}V_{in}}{(E_i^{(0)} - E_n^{(0)})^3} - 2\sum_{m,n\neq i} \frac{V_{ii}V_{mi}V_{in}V_{nm}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} \\
&- \sum_{m,n\neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})^2}
\end{aligned} \tag{6.2.2}$$

while

$$\left\langle n \middle| \mathscr{H} \middle| \Psi_i^{(3)} \right\rangle + \left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(2)} \right\rangle = E_i^{(0)} \left\langle n \middle| \Psi_i^{(3)} \right\rangle + E_i^{(1)} \left\langle n \middle| \Psi_i^{(2)} \right\rangle + E_i^{(2)} \left\langle n \middle| \Psi_i^{(1)} \right\rangle \tag{6.2.3}$$

$$\begin{aligned}
(E_i^{(0)} - E_n^{(0)}) \left\langle n \middle| \Psi_i^{(3)} \right\rangle &= \left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \left\langle n \middle| \Psi_i^{(2)} \right\rangle - E_i^{(2)} \left\langle n \middle| \Psi_i^{(1)} \right\rangle \\
&= \left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(1)} \right\rangle - E_i^{(1)} \left\langle n \middle| \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} - E_i^{(2)} \left\langle n \middle| \Psi_i^{(1)} \right\rangle \\
&= \left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \middle| \mathscr{V} \middle| \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} + \left[E_i^{(1)}\right]^2 \frac{\langle n \,|\, \mathscr{V} \,|\, i \rangle}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} - E_i^{(2)} \frac{\langle n \,|\, \mathscr{V} \,|\, i \rangle}{E_i^{(0)} - E_n^{(0)}}
\end{aligned} \tag{6.2.4}$$

$$
\begin{aligned}
E_i^{(4)} &= \left\langle i \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(3)} \right\rangle \\
&= \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)} - E_n^{(0)}} \left\{ \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} + \left[E_i^{(1)}\right]^2 \frac{\langle n \,|\, \mathscr{V} \,|\, i\rangle}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} - E_i^{(2)} \frac{\langle n \,|\, \mathscr{V} \,|\, i\rangle}{E_i^{(0)} - E_n^{(0)}} \right\} \\
&= \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)} - E_n^{(0)}} \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\rangle \\
&\quad + \left[E_i^{(1)}\right]^2 \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^3} - E_i^{(2)} \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \\
&= \sum_{n,m\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)} - E_n^{(0)}} \langle n \,|\, \mathscr{V} \,|\, m\rangle \left\langle m \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n,m\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle \langle n \,|\, \mathscr{V} \,|\, m\rangle \langle m \,|\, \mathscr{V} \,|\, i\rangle}{\left[E_i^{(0)} - E_n^{(0)}\right]^2 \left[E_i^{(0)} - E_m^{(0)}\right]} \\
&\quad + \left[E_i^{(1)}\right]^2 \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^3} - E_i^{(2)} \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \\
&= \sum_{n,m\neq i} \frac{V_{in}V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\left\langle m \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\rangle - E_i^{(1)} \left\langle m \,\middle|\, \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_m^{(0)}} - E_i^{(1)} \sum_{n,m\neq i} \frac{V_{in}V_{nm}V_{mi}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2 \left[E_i^{(0)} - E_m^{(0)}\right]} \\
&\quad + \left[E_i^{(1)}\right]^2 \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^3} - E_i^{(2)} \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \\
&= \sum_{n,m,k\neq i} \frac{V_{in}V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m \,|\, \mathscr{V} \,|\, k\rangle \langle k \,|\, \mathscr{V} \,|\, i\rangle}{\left[E_i^{(0)} - E_m^{(0)}\right]\left[E_i^{(0)} - E_k^{(0)}\right]} - E_i^{(1)} \sum_{n,m\neq i} \frac{V_{in}V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m \,|\, \mathscr{V} \,|\, i\rangle}{\left[E_i^{(0)} - E_m^{(0)}\right]^2} \\
&\quad - E_i^{(1)} \sum_{n,m\neq i} \frac{V_{in}V_{nm}V_{mi}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2 \left[E_i^{(0)} - E_m^{(0)}\right]} + \left[E_i^{(1)}\right]^2 \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^3} - E_i^{(2)} \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \\
&= \sum_{n,m,k\neq i} \frac{V_{in}V_{nm}V_{mk}V_{ki}}{\left[E_i^{(0)} - E_n^{(0)}\right]\left[E_i^{(0)} - E_m^{(0)}\right]\left[E_i^{(0)} - E_k^{(0)}\right]} - 2V_{ii} \sum_{n,m\neq i} \frac{V_{in}V_{nm}V_{mi}}{\left[E_i^{(0)} - E_n^{(0)}\right]\left[E_i^{(0)} - E_m^{(0)}\right]^2} \\
&\quad + V_{ii}^2 \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^3} - \sum_{m\neq i} \frac{V_{mi}V_{im}}{\left[E_i^{(0)} - E_m^{(0)}\right]} \sum_{n\neq i} \frac{V_{in}V_{ni}}{\left[E_i^{(0)} - E_n^{(0)}\right]^2} \qquad (6.2.5)
\end{aligned}
$$

which agrees with diagrammatic results above.

6.2.3 Summation of Diagrams

6.3 Orbital Perturbation Theory: One-Particle Perturbations

Ex 6.3 Since $n \neq 0$ and $v(i)$ is one-particle operator, n must be single-excited, i.e. $|\Psi_a^r\rangle$. Thus,

$$\begin{aligned} E_0^{(2)} &= \sum_{a,r} \frac{|\langle \Psi_0 \,|\, \sum_i v(i) \,|\, \Psi_a^r \rangle|^2}{\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_0 \rangle - \langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_a^r \rangle} \\ &= \sum_{a,r} \frac{v_{ar} v_{ra}}{\sum_b \varepsilon_b^{(0)} - \left(\sum_{b \neq a} \varepsilon_b^{(0)} + \varepsilon_r^{(0)} \right)} \\ &= \sum_{a,r} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} \end{aligned} \tag{6.3.1}$$

Ex 6.4 Eq 6.15 in textbook gives

$$\begin{aligned} E_i^{(3)} &= \sum_{n,m \neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n \rangle \langle n \,|\, \mathscr{V} \,|\, m \rangle \langle m \,|\, \mathscr{V} \,|\, i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - E_i^{(1)} \sum_{n \neq i} \frac{|\langle i \,|\, \mathscr{V} \,|\, n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})^2} \\ &= A_i^{(3)} + B_i^{(3)} \end{aligned} \tag{6.3.2}$$

a.

$$\begin{aligned} B_0^{(3)} &= -E_0^{(1)} \sum_{n \neq 0} \frac{|\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2} \\ &= -\sum_b v_{bb} \sum_{a,r} \frac{v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\ &= -\sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} \end{aligned} \tag{6.3.3}$$

b.

$$\begin{aligned} A_0^{(3)} &= \sum_{n,m \neq 0} \frac{\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle \langle n \,|\, \mathscr{V} \,|\, m \rangle \langle m \,|\, \mathscr{V} \,|\, \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} \\ &= \sum_{a,r,b,s} \frac{\langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_a^r \rangle \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle \langle \Psi_b^s \,|\, \mathscr{V} \,|\, \Psi_0 \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} \\ &= \sum_{a,r,b,s} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} \end{aligned} \tag{6.3.4}$$

c. Clearly, if $a \neq b, r \neq s$

$$\langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle = 0 \tag{6.3.5}$$

If $a = b, r \neq s$,

$$\begin{aligned} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle &= \langle r \,|\, v \,|\, s \rangle \\ &= v_{rs} \end{aligned} \tag{6.3.6}$$

If $a \neq b, r = s$,

$$\begin{aligned} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle &= \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^r \rangle \\ &= \langle \Psi_a^r \,|\, \mathscr{V} \,|\, -\Psi_{ab}^{ra} \rangle \\ &= -\langle b \,|\, v \,|\, a \rangle \\ &= -v_{ba} \end{aligned} \tag{6.3.7}$$

If $a = b, r = s$,

$$\begin{aligned} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle &= \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_a^r \rangle \\ &= \sum_c v_{cc} - v_{aa} + v_{rr} \end{aligned} \tag{6.3.8}$$

d.

$$
\begin{aligned}
E_0^{(3)} &= A_0^{(3)} + B_0^{(3)} \\
&= \sum_{a,r,b,s} \frac{v_{ar}v_{sb}\langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b - \varepsilon_r)^2} \\
&= \sum_{a,r\neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a\neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar}v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,b,r} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r\neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a\neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar}v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,r} \frac{\sum_c v_{cc}v_{ar}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r\neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a\neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} + \sum_{a,r} \frac{v_{ar}v_{ra}(-v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r,s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}
\end{aligned} \tag{6.3.9}
$$

e. That's obvious.

Ex 6.5 Since a, b run over all n occupied orbitals i, j and r runs over all n unoccupied orbitals k^*, we have

$$
\begin{aligned}
-2\sum_{a,b,r}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} &= -\frac{2}{(2\beta)^2} \sum_i^n \sum_j^n \sum_k^n \langle i \,|\, v \,|\, j \rangle \langle j \,|\, v \,|\, k^* \rangle \langle k^* \,|\, v \,|\, i \rangle \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 \begin{bmatrix} \langle i \,|\, v \,|\, i+1 \rangle \langle i+1 \,|\, v \,|\, (i+2)^* \rangle \langle (i+2)^* \,|\, v \,|\, i \rangle \\ + \langle i \,|\, v \,|\, i+2 \rangle \langle i+2 \,|\, v \,|\, (i+1)^* \rangle \langle (i+1)^* \,|\, v \,|\, i \rangle \end{bmatrix} \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 [(\beta/2)(\beta/2)(-\beta/2) + (\beta/2)(-\beta/2)(\beta/2)] \\
&= -\frac{2}{(2\beta)^2} \times 3 \times (-\beta^3/4) \\
&= 3\beta/8
\end{aligned} \tag{6.3.10}
$$

Ex 6.6

a. Using the general expression, we get

$$
\begin{aligned}
\mathscr{E}_0 &= 6\alpha - 2\sum_{j=-1}^{1} (\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\frac{2j\pi}{3})^{1/2} \\
&= 6\alpha - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\frac{-2\pi}{3})^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 0)^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\frac{2\pi}{3})^{1/2} \\
&= 6\alpha - 2(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2)^{1/2} - 2(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} \\
&= 6\alpha - 2|\beta_1 + \beta_2| - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} \\
&= 6\alpha + 2(\beta_1 + \beta_2) - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2}
\end{aligned} \tag{6.3.11}
$$

Using Hückel matrix:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta_1 & 0 & 0 & 0 & \beta_2 \\ \beta_1 & \alpha & \beta_2 & 0 & 0 & 0 \\ 0 & \beta_2 & \alpha & \beta_1 & 0 & 0 \\ 0 & 0 & \beta_1 & \alpha & \beta_2 & 0 \\ 0 & 0 & 0 & \beta_2 & \alpha & \beta_1 \\ \beta_2 & 0 & 0 & 0 & \beta_1 & \alpha \end{pmatrix} \tag{6.3.12}$$

Eigenvalues of $\mathbf{H}$ are

$$\begin{aligned} &\alpha + (\beta_1 + \beta_2), \\ &\alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \;\; \text{(2-fold)}, \\ &\alpha + \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \;\; \text{(2-fold)}, \\ &\alpha - (\beta_1 + \beta_2), \end{aligned} \tag{6.3.13}$$

thus

$$\begin{aligned} \mathscr{E}_0 &= 2[\alpha + (\beta_1 + \beta_2)] + 4\left[\alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2}\right] \\ &= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \end{aligned} \tag{6.3.14}$$

b.

$$\begin{aligned} E_R &= \mathscr{E}_0 - (N\alpha + N\beta) \\ &= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} - (6\alpha + 6\beta) \\ &= -4\beta_1 + 2\beta_2 - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \\ &= 4\beta\left(-1 + \frac{1}{2}x + \sqrt{1 + x^2 - x}\right) \end{aligned} \tag{6.3.15}$$

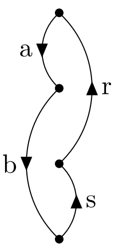
c.

$$\begin{aligned} E_R &= 4\beta\left(-1 + \frac{1}{2}x + \sqrt{1 + x^2 - x}\right) \\ &= 4\beta\left[-1 + \frac{1}{2}x + 1 + \frac{1}{2}(x^2 - x) - \frac{1}{8}(x^2 - x)^2 + \frac{1}{16}(x^2 - x)^3 - \frac{5}{128}(x^2 - x)^4\right] \\ &= 4\beta\left[\frac{1}{2}x^2 - \frac{1}{8}(x^4 + x^2 - 2x^3) + \frac{1}{16}(-x^3 + 3x^4) - \frac{5}{128}x^4 + \cdots\right] \\ &= 4\beta\left[\frac{3}{8}x^2 + \frac{3}{16}x^3 + \frac{3}{128}x^4 + \cdots\right] \\ &= \beta\left[\frac{3}{2}x^2 + \frac{3}{4}x^3 + \frac{3}{32}x^4 + \cdots\right] \end{aligned} \tag{6.3.16}$$

6.4 Diagrammatic Representation of Orbital Perturbation Theory

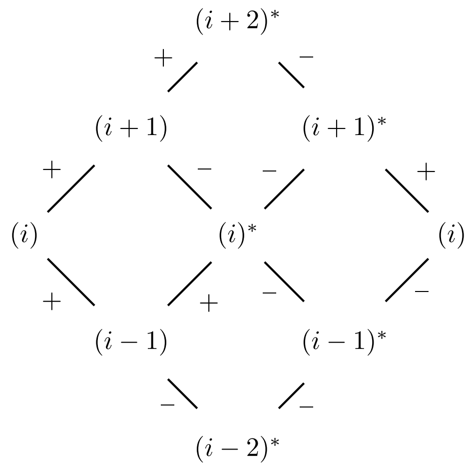
Ex 6.7

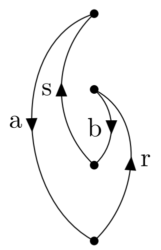
a.



$$
\begin{aligned}
&= -\sum_{a,b,r,s} \frac{v_{ab}v_{bs}v_{sr}v_{ra}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_b^{(0)})} \\
&= -\frac{1}{(2\beta)^3}\sum_{i,j,k,l} \langle i\,|\,v\,|\,j\rangle\,\langle j\,|\,v\,|\,k^*\rangle\,\langle k^*\,|\,v\,|\,l^*\rangle\,\langle l^*\,|\,v\,|\,i\rangle \\
&= -\frac{2}{(2\beta)^3}\sum_{i}^{N/2}[-1+1-1-1+1-1]\times(\beta/2)^4 \\
&= \frac{N\beta}{64}
\end{aligned}
\tag{6.4.1}
$$

The pictorial representation of the summation are as follows





$$
\begin{aligned}
&= -\sum_{a,r,b,s} \frac{v_{ar}v_{rb}v_{bs}v_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})(\varepsilon_a^{(0)}+\varepsilon_b^{(0)}-\varepsilon_r^{(0)}-\varepsilon_s^{(0)})} \\
&= -\frac{1}{(2\beta)^2\times 4\beta}\sum_{i,j,k,l} \langle i\,|\,v\,|\,j^*\rangle\,\langle j^*\,|\,v\,|\,k\rangle\,\langle k\,|\,v\,|\,l^*\rangle\,\langle l^*\,|\,v\,|\,i\rangle \\
&= -\frac{2}{(2\beta)^2\times 4\beta}\sum_{i}^{N/2} 6\times(\beta/2)^4 \\
&= -\frac{3N\beta}{128}
\end{aligned}
\tag{6.4.2}
$$

The pictorial representation of the summation are as follows

$$
\begin{tikzcd}
& & (i+2) & & \\
& (i+1)^* \arrow[ur, dash, "-"] & & (i+1)^* \arrow[ul, dash, "-"'] & \\
(i) \arrow[ur, dash, "+"] \arrow[dr, dash, "-"'] & & (i) \arrow[ul, dash, "+"'] \arrow[ur, dash, "+"] \arrow[dl, dash, "-"] \arrow[dr, dash, "-"'] & & (i) \arrow[ul, dash, "+"'] \arrow[dl, dash, "-"] \\
& (i-1)^* \arrow[dr, dash, "+"'] & & (i-1)^* \arrow[dl, dash, "+"] & \\
& & (i-2) & &
\end{tikzcd}
$$

thus

$$E_0^{(4)} = 4 \times \frac{N\beta}{64} + 3 \times \left(-\frac{3N\beta}{128}\right) = \frac{N\beta}{64} \tag{6.4.3}$$

b. Let $N = 6$, we get

$$E_0^{(4)} = \frac{3\beta}{32} \tag{6.4.4}$$

which agrees with the result in Ex 6.6.

6.5 Perturbation Expansion of the Correlation Energy

Ex 6.8

$$
\begin{aligned}
E_0^{(2)} &= \frac{1}{4} \sum_{a,b,r,s} \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a,b,r,s} \frac{(\langle ab \,|\, rs\rangle - \langle ab \,|\, sr\rangle)(\langle rs \,|\, ab\rangle - \langle sr \,|\, ab\rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ab\rangle - \langle ab \,|\, sr\rangle \langle rs \,|\, ab\rangle - \langle ab \,|\, rs\rangle \langle sr \,|\, ab\rangle + \langle ab \,|\, sr\rangle \langle sr \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \left[\sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s} \frac{\langle ab \,|\, sr\rangle \langle rs \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle sr \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} + \sum_{a,b,r,s} \frac{\langle ab \,|\, sr\rangle \langle sr \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right] \\
&= \frac{1}{4} \left[2 \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - 2 \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle sr \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right] \\
&= \frac{1}{2} \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2} \sum_{a,b,r,s} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{6.5.1}
$$

For a closed-shell system, the possible spin part of a, b, r, s of the non-zero terms are
first term: $\alpha, \alpha, \alpha, \alpha$; $\alpha, \beta, \alpha, \beta$; $\beta, \alpha, \beta, \alpha$; $\beta, \beta, \beta, \beta$
second term: $\alpha, \alpha, \alpha, \alpha$; $\beta, \beta, \beta, \beta$
thus

$$E_0^{(2)} = 2 \sum_{a,b,r,s}^{N/2} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s}^{N/2} \frac{\langle ab \,|\, rs\rangle \langle rs \,|\, ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{6.5.2}$$

Ex 6.9

$$
\begin{aligned}
E_{\text{corr}} &= \Delta - (\Delta^2 + K_{12}^2)^{1/2} \\
&= \Delta - \left[\Delta + \frac{K_{12}^2}{2\Delta}\right] \\
&= -\frac{K_{12}^2}{2\Delta} \\
&= -\frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}} \\
&= -K_{12}^2\left(\frac{1}{2(\varepsilon_2 - \varepsilon_1)} - \frac{J_{11} + J_{22} - 4J_{12} + 2K_{12}}{4(\varepsilon_2 - \varepsilon_1)^2}\right) \\
&= \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}) \qquad (6.5.3)
\end{aligned}
$$

6.6 The N-dependence of the RS Perturbation Expansion

Ex 6.10 From Eq 6.68, we get

$$
\begin{aligned}
E_0^{(1)} = \langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_0 \rangle &= -\frac{1}{2}\sum_{ab} \langle ab \,\|\, ab \rangle \\
&= -\frac{1}{2}\sum_{i=1}^{N} [\langle 1_i \bar{1}_i \,\|\, 1_i \bar{1}_i \rangle + \langle \bar{1}_i 1_i \,\|\, \bar{1}_i 1_i \rangle] \\
&= -\frac{1}{2}\sum_{i=1}^{N} [\langle 1_i \bar{1}_i \,|\, 1_i \bar{1}_i \rangle - \langle 1_i \bar{1}_i \,|\, \bar{1}_i 1_i \rangle + \langle \bar{1}_i 1_i \,|\, \bar{1}_i 1_i \rangle - \langle \bar{1}_i 1_i \,|\, 1_i \bar{1}_i \rangle] \\
&= -\frac{1}{2} \times 2N[1_i 1_i | 1_i 1_i] \\
&= -NJ_{11} \qquad (6.6.1)
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{V} \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle &= \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H} \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle - \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \middle| \mathscr{H}_0 \middle| \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle \\
&= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)\varepsilon_1 - 2\varepsilon_2 \\
&= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)(h_{11} + J_{11}) - 2(h_{22} + 2J_{12} - K_{12}) \\
&= -(N-1)J_{11} + J_{22} - 4J_{12} + 2K_{12} \qquad (6.6.2)
\end{aligned}
$$

6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

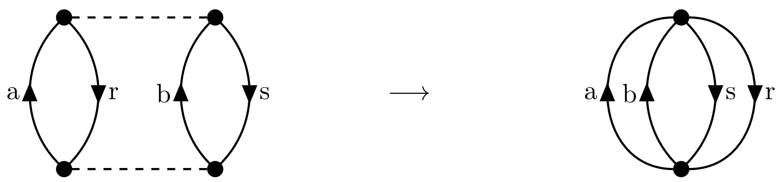
6.7.1 Hugenholtz Diagrams

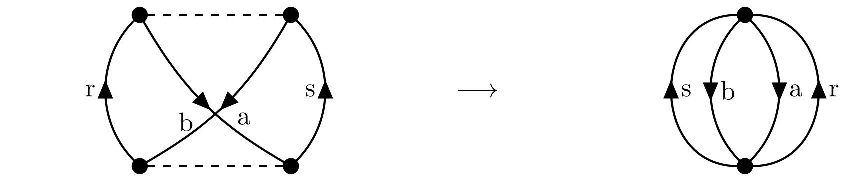
Ex 6.11 The numerator and denominator are obvious.
$h = 5$, and $l = 2$ since closed loops are $r \to a \to d \to t \to e \to r$; $s \to c \to b \to s$. The number of quivalent line pairs is one (r, s). Thus the pre-factor is $-\dfrac{1}{2}$.

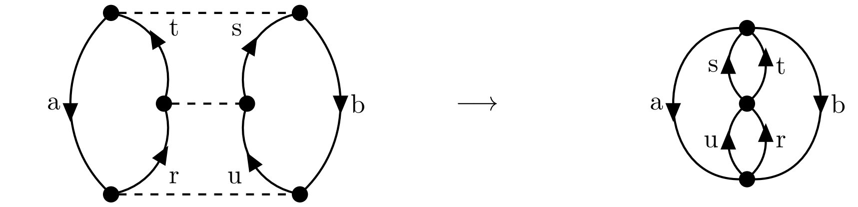
6.7.2 Goldstone Diagrams

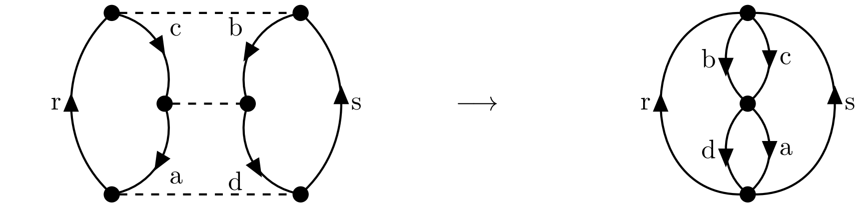
Ex 6.12

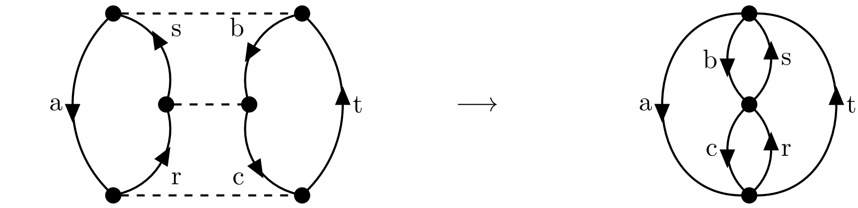
1

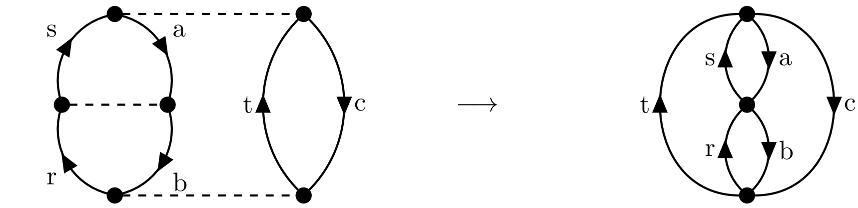


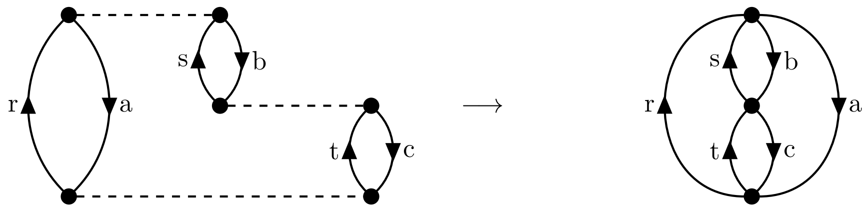
2 
r b a s
⟶
s b a r

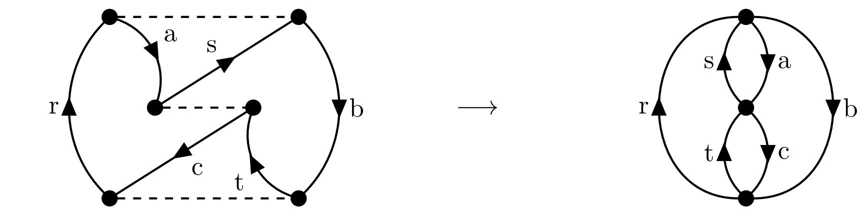
1 
t s a b r u
⟶
a s t b u r

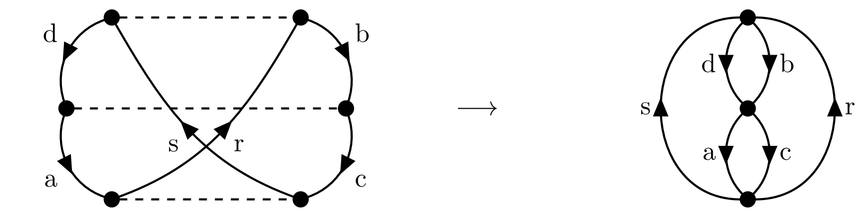
2 
c b r s a d
⟶
b c r s d a

3 
s b a t r c
⟶
b s a t c r

4 
s a t c r b
⟶
s a t c r b

5 
s b r a t c
⟶
s b r a t c

6 
a s r b c t
⟶
s a r b t c

7 
d b s r a c
⟶
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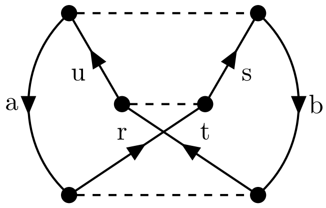
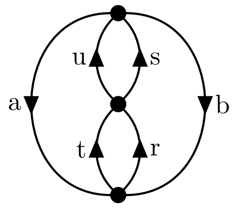
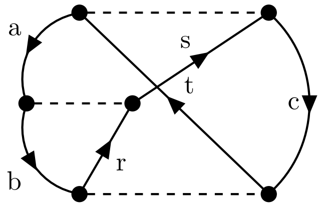
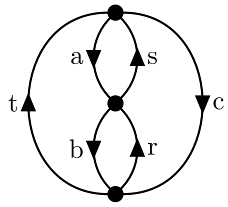
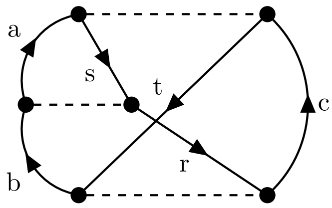
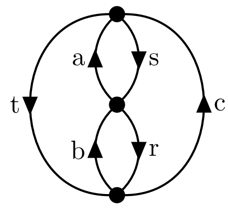
8 

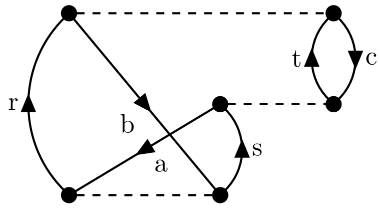
$\longrightarrow$ 

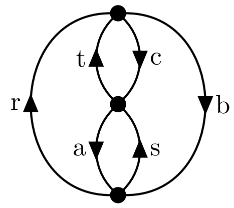
9 

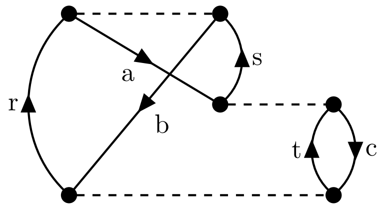
$\longrightarrow$ 

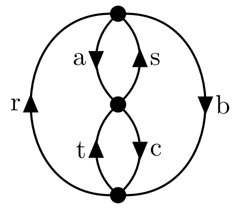
10 

$\longrightarrow$ 

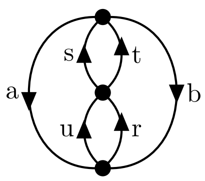
11 

$\longrightarrow$ 

12 

$\longrightarrow$ 

For the Hugenholtz diagram provided, its value is

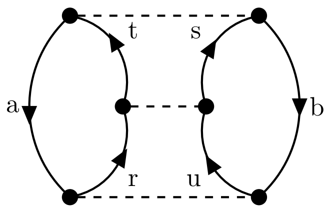


$$
\begin{aligned}
&= \left(\frac{1}{2}\right)^3 (-1)^{2+2} \sum_{a,b,r,s,u,t} \frac{\langle ab \,\|\, ru\rangle \langle ru \,\|\, ts\rangle \langle ts \,\|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} \\
&= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,\|\, ru\rangle \langle ru \,\|\, ts\rangle \langle ts \,\|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{(\langle ab \,|\, ru\rangle - \langle ab \,|\, ur\rangle)(\langle ru \,|\, ts\rangle - \langle ru \,|\, st\rangle)(\langle ts \,|\, ab\rangle - \langle ts \,|\, ba\rangle)}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} \\
&= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ru\rangle \langle ru \,|\, ts\rangle \langle ts \,|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ur\rangle \langle ru \,|\, ts\rangle \langle ts \,|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} \\
&\quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ru\rangle \langle ru \,|\, st\rangle \langle ts \,|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ur\rangle \langle ru \,|\, st\rangle \langle ts \,|\, ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} \\
&\quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ru\rangle \langle ru \,|\, ts\rangle \langle ts \,|\, ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} + \frac{\langle ab \,|\, ur\rangle \langle ru \,|\, ts\rangle \langle ts \,|\, ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} \\
&\quad + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ru\rangle \langle ru \,|\, st\rangle \langle ts \,|\, ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,|\, ur\rangle \langle ru \,|\, st\rangle \langle ts \,|\, ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&\quad - \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ur\,|\,st\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ur\,|\,st\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&\quad - \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{8}\sum_{a,b,r,s,u,t} + \frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&\quad + \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ur\,|\,st\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{8}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ur\,|\,st\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&= \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&\quad - \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{4}\sum_{a,b,r,s,u,t} + \frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ba\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&= \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&\quad - \frac{1}{4}\sum_{a,b,r,s,u,t}\frac{\langle ba\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} + \frac{1}{4}\sum_{a,b,r,s,u,t} + \frac{\langle ba\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}\\
&= \frac{1}{2}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)} - \frac{1}{2}\sum_{a,b,r,s,u,t}\frac{\langle ab\,|\,ur\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_t)}
\end{aligned}
\tag{6.7.1}
$$

=



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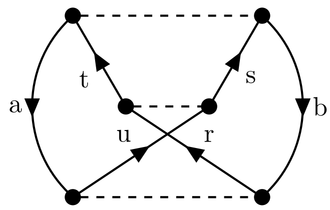

6.7.3 Summation of Diagrams

6.7.4 What Is the Linked-Cluster Theorem?

Ex 6.13 For the 3rd-order Goldstone diagrams in Table 6.2,

$$
\text{diagram1} = (-1)^4\left(\frac{1}{2}\right)\sum_{ab}\sum_{rsut}\frac{\langle ab\,|\,ru\rangle\,\langle ru\,|\,ts\rangle\,\langle ts\,|\,ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_t)} \tag{6.7.2}
$$

a, b, r, s, u, t must come from 1 or 2 molecules. If they come from 2 molecules, $\langle ru\,|\,ts\rangle$ must be zero. Thus they only come from 1 molecule, i.e. the value of each Goldstone diagram is N times the result for a single molecule.

6.8 Some Illustrative Calculations

Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

November 9, 2022

Contents

7 The 1-Particle Many-body Green's Function

7.1 Green's Function in Single-Particle Systems

Ex 7.1

$$\mathbf{V} = \mathbf{G}_0(E)^{-1} - \mathbf{G}(E)^{-1} \tag{7.1.1}$$

thus

$$\begin{aligned}\mathbf{G}_0(E)\mathbf{V}\mathbf{G}(E) &= \mathbf{G}_0(E)[\mathbf{G}_0(E)^{-1} - \mathbf{G}(E)^{-1}]\mathbf{G}(E) \\ &= \mathbf{G}(E) - \mathbf{G}_0(E)\end{aligned} \tag{7.1.2}$$

i.e.

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\mathbf{V}\mathbf{G}(E) \tag{7.1.3}$$

Ex 7.2

a. When $x = 0$,

$$\begin{aligned}\left.\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\right|_{x=0} &= \lim_{\epsilon\to 0}\frac{\left.\frac{\mathrm{d}|x|}{\mathrm{d}x}\right|_{x=\epsilon} - \left.\frac{\mathrm{d}|x|}{\mathrm{d}x}\right|_{x=-\epsilon}}{2\epsilon} \qquad (\epsilon > 0) \\ &= \lim_{\epsilon\to 0}\frac{1-(-1)}{2\epsilon} \\ &= \infty\end{aligned} \tag{7.1.4}$$

otherwise,

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x| &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}[x\ \mathrm{sgn}(x)] \\ &= \frac{\mathrm{d}}{\mathrm{d}x}[1\times\mathrm{sgn}(x) + x\times 0] \\ &= 0\end{aligned} \tag{7.1.5}$$

b.

$$\begin{aligned}\int_{-\infty}^{\infty}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\mathrm{d}x &= \int_{-\infty}^{\infty}\mathrm{d}\left(\frac{\mathrm{d}}{\mathrm{d}x}|x|\right) \\ &= \left.\frac{\mathrm{d}}{\mathrm{d}x}|x|\right|_{-\infty}^{\infty} \\ &= 1-(-1) \\ &= 2\end{aligned} \tag{7.1.6}$$

thus

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x| = 2\delta(x) \tag{7.1.7}$$

c.

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}a(x) &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_\alpha^\beta \mathrm{d}x'|x-x'|b(x') \\ &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_\alpha^x \mathrm{d}x'(x-x')b(x') + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_x^\beta \mathrm{d}x'[-(x-x')]b(x') \\ &= \frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{2}\int_\alpha^x \mathrm{d}x' b(x') - \frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{2}\int_x^\beta \mathrm{d}x' b(x') \\ &= \frac{1}{2}b(x) - \frac{1}{2}[-b(x)] \\ &= b(x)\end{aligned} \tag{7.1.8}$$

Ex 7.3

$$\begin{aligned}\left(E+\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)G_0(x,x',E) &= \left(E+\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\frac{1}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}+\frac{1}{2}\frac{1}{\mathrm{i}(2E)^{1/2}}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}+\frac{1}{2}\frac{1}{\mathrm{i}(2E)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\mathrm{i}(2E)^{1/2}\frac{\mathrm{d}}{\mathrm{d}x}|x-x'|\right]\\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}+\frac{1}{2}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\mathrm{i}(2E)^{1/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}|x-x'|\right)^2+\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x-x'|\right]\\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}+\frac{1}{2}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\left[\mathrm{i}(2E)^{1/2}\times 1+2\delta(x-x')\right]\\
&= \mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\left[\frac{E}{\mathrm{i}(2E)^{1/2}}+\frac{-E}{\mathrm{i}(2E)^{1/2}}+\delta(x-x')\right]\\
&= \mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\delta(x-x')\\
&= \delta(x-x')
\end{aligned}\tag{7.1.9}$$

Ex 7.4

$$\begin{aligned}\phi_n(x)\phi_n^*(x') &= \lim_{E\to E_n}(E-E_n)\frac{1}{\mathrm{i}(2E)^{1/2}}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}-\frac{\mathrm{e}^{\mathrm{i}(2E)^{1/2}(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}}\right]\\
&= \lim_{E\to -1/2}(E+1/2)\frac{1}{-1}\left[\mathrm{e}^{-|x-x'|}-\frac{\mathrm{e}^{-(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}}\right]\\
&= -\lim_{E\to -1/2}(E+1/2)\,\mathrm{e}^{-|x-x'|}+\lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}}\\
&= 0+\lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}(1-\mathrm{i}(2E)^{1/2})}{(1+\mathrm{i}(2E)^{1/2})(1-\mathrm{i}(2E)^{1/2})}\\
&= \lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}(1-\mathrm{i}(2E)^{1/2})}{1+2E}\\
&= \frac{1}{2}\,\mathrm{e}^{-(|x|+|x'|)}(1-(-1))\\
&= \mathrm{e}^{-(|x|+|x'|)}
\end{aligned}\tag{7.1.10}$$

Let $x=x'$,

$$\phi_n^2(x)=\mathrm{e}^{-2|x|}\tag{7.1.11}$$

thus

$$\phi_n(x)=\mathrm{e}^{-|x|}\tag{7.1.12}$$

Ex 7.5

$$\begin{aligned}\mathscr{H}\,\phi &= \left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\delta(x)\right]\mathrm{e}^{-|x|}\\
&= -\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x}\left[\mathrm{e}^{-|x|}\left(-\frac{\mathrm{d}}{\mathrm{d}x}|x|\right)\right]-\delta(x)\,\mathrm{e}^{-|x|}\\
&= \frac{1}{2}\left[-\mathrm{e}^{-|x|}\left(\frac{\mathrm{d}}{\mathrm{d}x}|x|\right)^2+\mathrm{e}^{-|x|}\,\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\right]-\delta(x)\,\mathrm{e}^{-|x|}\\
&= \frac{1}{2}\left[-\mathrm{e}^{-|x|}+\mathrm{e}^{-|x|}\times 2\delta(x)\right]-\delta(x)\,\mathrm{e}^{-|x|}\\
&= -\frac{1}{2}\,\mathrm{e}^{-|x|}
\end{aligned}\tag{7.1.13}$$

thus the eigenvalue is $-\dfrac{1}{2}$.

Ex 7.6

a.

$$\begin{aligned}\mathrm{i}\,\frac{\partial}{\partial t}\phi(x,t) &= \mathrm{i}\int \mathrm{d}x'\,\frac{\partial G(x,x',t)}{\partial t}\psi(x') \\ &= \int \mathrm{d}x'\,\mathscr{H}\,G(x,x',t)\psi(x') \\ &= \mathscr{H}\,\phi(x,t)\end{aligned} \tag{7.1.14}$$

b. From

$$\mathrm{i}\,\frac{\partial G(x,x',t)}{\partial t} = \mathscr{H}\,G(x,x',t) \tag{7.1.15}$$

we get

$$\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{i}\,\frac{\partial G(x,x',t)}{\partial t}[-\,\mathrm{i}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}] = \lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathscr{H}\,G(x,x',t)[-\,\mathrm{i}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}] \tag{7.1.16}$$

$$\begin{aligned}\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\frac{\partial G(x,x',t)}{\partial t}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t} &= \int_0^\infty \mathrm{d}t\,\mathscr{H}\,G(x,x',t)[-\,\mathrm{i}\,\mathrm{e}^{\mathrm{i}\,Et}] \\ &= \mathscr{H}\,G(x,x',E)\end{aligned} \tag{7.1.17}$$

thus

$$\lim_{\varepsilon\to 0}\left[G(x,x',t)\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\Big|_{t=0}^{\infty} - \int_0^\infty \mathrm{d}tG(x,x',t)\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}(\mathrm{i}\,E-\varepsilon)\right] = \mathscr{H}\,G(x,x',E) \tag{7.1.18}$$

$$\begin{aligned}\mathscr{H}\,G(x,x',E) &= -G(x,x',0) - \mathrm{i}\,E\int_0^\infty \mathrm{d}tG(x,x',t)\,\mathrm{e}^{\mathrm{i}\,Et} \\ &= -G(x,x',0) - \mathrm{i}\,EG(x,x',E)/(-\,\mathrm{i}) \\ &= -\delta(x-x') + EG(x,x',E)\end{aligned} \tag{7.1.19}$$

∴

$$(E-\mathscr{H})G(x,x',E) = \delta(x-x') \tag{7.1.20}$$

c.

$$\begin{aligned}\mathrm{i}\,\frac{\partial}{\partial t}\mathscr{G}(t) &= \mathrm{i}\,\frac{\partial}{\partial t}\,\mathrm{e}^{-\,\mathrm{i}\,\mathscr{H}\,t} \\ &= \mathrm{i}\,\mathrm{e}^{-\,\mathrm{i}\,\mathscr{H}\,t}(-\,\mathrm{i}\,\mathscr{H}) \\ &= \mathscr{H}\,\mathscr{G}(t)\end{aligned} \tag{7.1.21}$$

$$\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathrm{i}\,\frac{\partial}{\partial t}\mathscr{G}(t) = \lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{H}\,\mathscr{G}(t) \tag{7.1.22}$$

$$\lim_{\varepsilon\to 0}\left[\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\Big|_0^\infty - (\mathrm{i}\,E-\varepsilon)\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\right] = \mathscr{H}\,\mathscr{G}(E) \tag{7.1.23}$$

∴

$$\begin{aligned}\mathscr{H}\,\mathscr{G}(E) &= \lim_{\varepsilon\to 0}\left[-\mathscr{G}(0) - (\mathrm{i}\,E-\varepsilon)\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\right] \\ &= -\mathscr{G}(0) + E\mathscr{G}(E) \\ &= -1 + E\mathscr{G}(E)\end{aligned} \tag{7.1.24}$$

thus

$$\mathscr{G}(E) = \frac{1}{E-\mathscr{H}} \tag{7.1.25}$$

7.2 The 1-Particle Many-body Green's Function

7.2.1 The Self-Energy

Ex 7.7

$$\begin{aligned}\Sigma_{ij}^{(2)}(E) &= \frac{1}{2}\sum_{ars}\frac{\langle rs\,\|\,ia\rangle\,\langle ja\,\|\,rs\rangle}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\frac{1}{2}\sum_{abr}\frac{\langle ab\,\|\,ir\rangle\,\langle jr\,\|\,ab\rangle}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b}\\ &= \frac{1}{2}\sum_{ars}\frac{(\langle rs\,|\,ia\rangle-\langle rs\,|\,ai\rangle)(\langle ja\,|\,rs\rangle-\langle ja\,|\,sr\rangle)}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\frac{1}{2}\sum_{abr}\frac{(\langle ab\,|\,ir\rangle-\langle ab\,|\,ri\rangle)(\langle jr\,|\,ab\rangle-\langle jr\,|\,ba\rangle)}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b}\end{aligned} \tag{7.2.1}$$

In the 1st summation:
To make the terms non-zero, the spin of r is fixed in the first and last term, and r, s, a are all fixed in the second and third term, thus

$$\begin{aligned}\text{the 1st term} &= \frac{1}{2}\sum_{ars}^{N/2}\frac{1}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}[2\,\langle rs\,|\,ia\rangle\,\langle ja\,|\,rs\rangle-\langle rs\,|\,ai\rangle\,\langle ja\,|\,rs\rangle-\langle rs\,|\,ia\rangle\,\langle ja\,|\,sr\rangle+2\,\langle rs\,|\,ai\rangle\,\langle ja\,|\,sr\rangle]\\ &= \sum_{ars}^{N/2}\frac{1}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}[2\,\langle rs\,|\,ia\rangle\,\langle ja\,|\,rs\rangle-\langle rs\,|\,ia\rangle\,\langle ja\,|\,sr\rangle]\\ &= \sum_{ars}^{N/2}\frac{\langle rs\,|\,ia\rangle\,[2\,\langle ja\,|\,rs\rangle-\langle aj\,|\,rs\rangle]}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}\end{aligned} \tag{7.2.2}$$

Similarly,

$$\Sigma_{ij}^{(2)}(E)=\sum_{ars}^{N/2}\frac{\langle rs\,|\,ia\rangle\,[2\,\langle ja\,|\,rs\rangle-\langle aj\,|\,rs\rangle]}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\sum_{abr}^{N/2}\frac{\langle ab\,|\,ir\rangle\,[2\,\langle jr\,|\,ab\rangle-\langle rj\,|\,ab\rangle]}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b} \tag{7.2.3}$$

Ex 7.8

$$\begin{aligned}[\mathbf{G}_0(E)]_{ij} &= \sum_m\frac{\left\langle {}^N\Psi_0\,\middle|\,a_i^\dagger a_m\,\middle|\,{}^N\Psi_0\right\rangle\,\langle a_m{}^N\Psi_0\,|\,a_j\,|\,{}^N\Psi_0\rangle}{E-(\langle {}^N\Psi_0\,|\,\mathscr{H}\,|\,{}^N\Psi_0\rangle-\langle a_m{}^N\Psi_0\,|\,\mathscr{H}\,|\,a_m{}^N\Psi_0\rangle)}+\sum_p\frac{\langle {}^N\Psi_0\,|\,a_ja_p^\dagger\,|\,{}^N\Psi_0\rangle\,\left\langle a_p^\dagger{}^N\Psi_0\,\middle|\,a_i^\dagger\,\middle|\,{}^N\Psi_0\right\rangle}{E+\left(\langle {}^N\Psi_0\,|\,\mathscr{H}\,|\,{}^N\Psi_0\rangle-\left\langle a_p^\dagger{}^N\Psi_0\,\middle|\,\mathscr{H}\,\middle|\,a_p^\dagger{}^N\Psi_0\right\rangle\right)}\\ &= \sum_m\frac{\delta_{im}\delta_{mj}}{E-\varepsilon_m}+0\\ &= \sum_m\frac{\delta_{ij}}{E-\varepsilon_m}\end{aligned} \tag{7.2.4}$$

7.2.2 The Solution of the Dyson Equation

7.3 Application of the Formalism to H_2 and HeH^+

Ex 7.9

a.

$${}^{N+1}\mathscr{E}_0={}^{N+1}E_0+{}^{N+1}E_{\text{corr}} \tag{7.3.1}$$

Since the ground state ($|1\bar{1}2\rangle$) of ${H_2}^-$ is of ungerade symmetry while the excited state ($|12\bar{2}\rangle$) is of gerade symmetry,

$${}^{N+1}E_{\text{corr}}=0 \tag{7.3.2}$$

thus

$$\begin{aligned}{}^{N+1}\mathscr{E}_0-{}^{N}\mathscr{E}_0 &= {}^{N+1}E_0-{}^{N}E_0-{}^{N}E_{\text{corr}}\\ &= (2\varepsilon_1+\varepsilon_2-J_{11})-(2\varepsilon_1-J_{11})-{}^{N}E_{\text{corr}}\\ &= \varepsilon_2-{}^{N}E_{\text{corr}}\end{aligned} \tag{7.3.3}$$

$$\begin{aligned}{}^{N+1}\mathscr{E}_1 - {}^{N}\mathscr{E}_0 &= {}^{N+1}E_1 - {}^{N}E_0 - {}^{N}E_{\text{corr}} \\ &= (h_{11}h + 2h_{22} + 2J_{12} + J_{22} - K_{12}) - (2\varepsilon_1 - J_{11}) - {}^{N}E_{\text{corr}} \\ &= (\varepsilon_1 + 2\varepsilon_2 - 2J_{12} + K_{12} - J_{11} + J_{22}) - (2\varepsilon_1 - J_{11}) - {}^{N}E_{\text{corr}} \\ &= 2\varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{22} - {}^{N}E_{\text{corr}}\end{aligned} \tag{7.3.4}$$

b.

$$\begin{aligned}\varepsilon_{11}^{+} &= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2} \\ &\approx \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \Delta - \Delta + \sqrt{\Delta^2 + K_{12}^2} \\ &= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \Delta - {}^{N}E_{\text{corr}} \\ &= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + (\varepsilon_2 - \varepsilon_1) + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12} - {}^{N}E_{\text{corr}} \\ &\approx 2\varepsilon_2 - \varepsilon_1 + J_{22} - 2J_{12} + K_{12} - {}^{N}E_{\text{corr}}\end{aligned} \tag{7.3.5}$$

thus

$$\varepsilon_{11}^{+} \approx {}^{N+1}\mathscr{E}_1 - {}^{N}\mathscr{E}_0 \tag{7.3.6}$$

c.

$$E - \varepsilon_2 - \Sigma_{22}^{(2)}(E) = 0 \tag{7.3.7}$$

$$E - \varepsilon_2 - \frac{K_{12}^2}{E - \varepsilon_2 - 2(\varepsilon_1 - \varepsilon_2)} = 0 \tag{7.3.8}$$

$\therefore$

$$\begin{aligned}\varepsilon_{22}^{\pm} &= \varepsilon_1 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + K_{12}^2} \\ &= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) \mp \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right]\end{aligned} \tag{7.3.9}$$

d.

$$\begin{aligned}\varepsilon_{22}^{+} &= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) - \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right] \\ &\approx \varepsilon_2 - \left[\Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \\ &= \varepsilon_2 - {}^{N}E_{\text{corr}} \\ &= {}^{N+1}\mathscr{E}_0 - {}^{N}\mathscr{E}_0\end{aligned} \tag{7.3.10}$$

$$\begin{aligned}\varepsilon_{22}^{-} &= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) + \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right] \\ &\approx \varepsilon_2 + \left[-(\varepsilon_2 - \varepsilon_1) - \Delta + \Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \\ &= \varepsilon_2 - (\varepsilon_2 - \varepsilon_1) - \Delta - {}^{N}E_{\text{corr}} \\ &= \varepsilon_2 - (\varepsilon_2 - \varepsilon_1) - \left(\varepsilon_2 - \varepsilon_1 + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}\right) - {}^{N}E_{\text{corr}} \\ &= 2\varepsilon_1 - \varepsilon_2 - \left(\frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}\right) - {}^{N}E_{\text{corr}} \\ &\approx 2\varepsilon_1 - \varepsilon_2 - J_{11} + 2J_{12} - K_{12}) - {}^{N}E_{\text{corr}} \\ &= {}^{N}\mathscr{E}_0 - {}^{N-1}\mathscr{E}_1\end{aligned} \tag{7.3.11}$$

Ex 7.10 Since

$$\begin{aligned}\Sigma_{11}^{(2)}(\varepsilon_1) &= \frac{K_{12}}{\varepsilon_1+\varepsilon_1-2\varepsilon_2} \\ &= \frac{K_{12}}{2(\varepsilon_1-\varepsilon_2)}\end{aligned} \tag{7.3.12}$$

$$\begin{aligned}\Sigma_{11}^{(3)}(\varepsilon_1) &= \frac{K_{12}^2(J_{22}-2J_{12}+K_{12})}{(\varepsilon_1-2\varepsilon_2+\varepsilon_1)^2} + \frac{K_{12}^2(J_{11}-2J_{12}+K_{12})}{(\varepsilon_1-2\varepsilon_2+\varepsilon_1)(\varepsilon_1-\varepsilon_2)} + \frac{K_{12}^2(2J_{12}-K_{12}-J_{11})}{4(\varepsilon_1-\varepsilon_2)^2} \\ &= \frac{K_{12}^2(J_{22}-2J_{12}+K_{12})}{4(\varepsilon_1-\varepsilon_2)^2} + \frac{K_{12}^2(J_{11}-2J_{12}+K_{12})}{2(\varepsilon_1-\varepsilon_2)^2} + \frac{K_{12}^2(2J_{12}-K_{12}-J_{11})}{4(\varepsilon_1-\varepsilon_2)^2} \\ &= \frac{K_{12}^2(J_{22}+J_{11}-4J_{12}+2K_{12})}{4(\varepsilon_1-\varepsilon_2)^2}\end{aligned} \tag{7.3.13}$$

thus

$$\Sigma_{11}^{(2)}(\varepsilon_1) = E_0^{(2)} \tag{7.3.14}$$

$$\Sigma_{11}^{(3)}(\varepsilon_1) = E_0^{(3)} \tag{7.3.15}$$

Similarly,

$$\begin{aligned}\Sigma_{22}^{(2)}(\varepsilon_2) &= \frac{K_{12}}{\varepsilon_2+\varepsilon_2-2\varepsilon_1} \\ &= \frac{K_{12}}{2(\varepsilon_2-\varepsilon_1)}\end{aligned} \tag{7.3.16}$$

$$\begin{aligned}\Sigma_{22}^{(3)}(\varepsilon_2) &= \frac{K_{12}^2(2J_{12}-K_{12}-J_{11})}{(\varepsilon_2-2\varepsilon_1+\varepsilon_2)^2} + \frac{K_{12}^2(J_{22}-2J_{12}+K_{12})}{(\varepsilon_2-2\varepsilon_1+\varepsilon_2)(\varepsilon_1-\varepsilon_2)} + \frac{K_{12}^2(J_{22}+K_{12}-2J_{12})}{4(\varepsilon_1-\varepsilon_2)^2} \\ &= \frac{K_{12}^2(2J_{12}-K_{12}-J_{11})}{4(\varepsilon_1-\varepsilon_2)^2} - \frac{K_{12}^2(J_{22}-2J_{12}+K_{12})}{2(\varepsilon_1-\varepsilon_2)^2} + \frac{K_{12}^2(J_{22}+K_{12}-2J_{12})}{4(\varepsilon_1-\varepsilon_2)^2} \\ &= \frac{K_{12}^2(-J_{11}-J_{22}+4J_{12}-2K_{12})}{4(\varepsilon_1-\varepsilon_2)^2}\end{aligned} \tag{7.3.17}$$

thus

$$\Sigma_{22}^{(2)}(\varepsilon_2) = -E_0^{(2)} \tag{7.3.18}$$

$$\Sigma_{22}^{(3)}(\varepsilon_2) = -E_0^{(3)} \tag{7.3.19}$$

Ex 7.11 From

$$\begin{pmatrix} h_{11} & h_{22} \\ h_{12} & h_{22}\end{pmatrix}\begin{pmatrix}1 \\ c\end{pmatrix} =^{N-1} \mathscr{E}_0 \begin{pmatrix}1 \\ c\end{pmatrix} \tag{7.3.20}$$

we get

$$h_{11} + h_{12}c =^{N-1} \mathscr{E}_0 \tag{7.3.21}$$

$$h_{12} + h_{22}c =^{N-1} \mathscr{E}_0 c \tag{7.3.22}$$

thus

$${}^{N-1}\mathscr{E}_0 = h_{11} + h_{12}\frac{h_{12}}{{}^{N-1}\mathscr{E}_0 - h_{22}} \tag{7.3.23}$$

$$h_{11} +^{N-1} E_R = h_{11} + h_{12}\frac{h_{12}}{h_{11} +^{N-1} E_R - h_{22}} \tag{7.3.24}$$

$$\begin{aligned}{}^{N-1}E_R &= \frac{h_{12}^2}{h_{11} +^{N-1} E_R - h_{22}} \\ &= \frac{|\langle 11 \,|\, 12\rangle|^2}{\varepsilon_1-\varepsilon_2-(J_{11}-2J_{12}+K_{12}) +^{N-1} E_R}\end{aligned} \tag{7.3.25}$$

Ex 7.12

a.

$$|\Phi\rangle = |\Psi_0\rangle + c\,|\Psi_{\bar{1}}^{\bar{2}}\rangle \tag{7.3.26}$$

thus

$$\begin{pmatrix} 0 & \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{1}}^{\bar{2}} \right\rangle \\ \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{1}}^{\bar{2}} \right\rangle & \left\langle \Psi_{\bar{1}}^{\bar{2}} \,\middle|\, \mathscr{H} - {}^{N+1}E_0 \,\middle|\, \Psi_{\bar{1}}^{\bar{2}} \right\rangle \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = \left({}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0\right) \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.27}$$

$\because$

$$\begin{aligned} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{1}}^{\bar{2}} \right\rangle &= h_{12} + \sum_{b=1,2} \langle \bar{1}b \,\|\, \bar{2}b \rangle \\ &= -\langle 11 \,|\, 12 \rangle + \langle 11 \,|\, 12 \rangle + \langle 12 \,|\, 22 \rangle \\ &= \langle 12 \,|\, 22 \rangle \end{aligned} \tag{7.3.28}$$

$\therefore$

$$\begin{pmatrix} 0 & \langle 12 \,|\, 22 \rangle \\ \langle 12 \,|\, 22 \rangle & \varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = \left({}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0\right) \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.29}$$

Let

$${}^{N+1}E_R = {}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0 \tag{7.3.30}$$

thus

$$\begin{aligned} {}^{N+1}\mathscr{E}_0 &= {}^{N+1}E_0 + {}^{N+1}E_R \\ &= {}^{N}E_0 + \varepsilon_2 + {}^{N+1}E_R \end{aligned} \tag{7.3.31}$$

b. Solving (7.3.29), we get

$$\begin{aligned} {}^{N+1}E_R &= \frac{1}{2}\left(D - \sqrt{D^2 + 4\langle 12 \,|\, 22 \rangle^2}\right) \\ &\approx \frac{1}{2}\left(D - D\left(1 + 2\frac{\langle 12 \,|\, 22 \rangle^2}{D^2}\right)\right) \\ &= -\frac{\langle 12 \,|\, 22 \rangle^2}{D} \\ &\approx -\frac{\langle 12 \,|\, 22 \rangle^2}{\varepsilon_2 - \varepsilon_1} \\ &= \frac{\langle 12 \,|\, 22 \rangle^2}{\varepsilon_1 - \varepsilon_2} \end{aligned} \tag{7.3.32}$$

c.

$$\Sigma_{22}^{(2)}(\varepsilon_2) = \frac{\langle 12 \,|\, 22 \rangle^2}{\varepsilon_1 - \varepsilon_2} + \frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)} \tag{7.3.33}$$

$\therefore$

$$\begin{aligned} \varepsilon_2' &= \varepsilon_2 + \Sigma_{22}^{(2)}(\varepsilon_2) \\ &= {}^{N+1}\tilde{E}_R^{(2)} - {}^{N}E_0^{(2)} \end{aligned} \tag{7.3.34}$$

7.4 Perturbation Theory and the Green's Function Method

Ex 7.13

$$
\begin{aligned}
\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle &= \left\langle {}^{N-1}\Psi_c \,\middle|\, \sum_{i<j}^{N-1} r_{ij}^{-1} - \sum_{i}^{N-1} v_N^{\mathrm{HF}}(i) \,\middle|\, {}^{N-1}\Psi_c \right\rangle \\
&= \sum_{i<j}^{N-1} \left\langle {}^{N-1}\Psi_c \,\middle|\, r_{ij}^{-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle - \sum_{i}^{N-1} \left\langle {}^{N-1}\Psi_c \,\middle|\, v_N^{\mathrm{HF}}(i) \,\middle|\, {}^{N-1}\Psi_c \right\rangle \\
&= \frac{1}{2} \sum_{a\neq c} \sum_{b\neq c} \langle ab \,\|\, ab \rangle - \sum_{a\neq c} \sum_{b} \langle ab \,\|\, ab \rangle \\
&= -\frac{1}{2} \sum_{a\neq c} \sum_{b\neq c} \langle ab \,\|\, ab \rangle + \sum_{a\neq c} \langle ac \,\|\, ac \rangle \\
&= -\frac{1}{2} \left(\sum_{a} \sum_{b} \langle ab \,\|\, ab \rangle - \sum_{a} \langle ac \,\|\, ac \rangle - \sum_{b} \langle cb \,\|\, cb \rangle + \langle cc \,\|\, cc \rangle \right) + \sum_{a} \langle ac \,\|\, ac \rangle \\
&= -\frac{1}{2} \left(\sum_{a} \sum_{b} \langle ab \,\|\, ab \rangle - 2 \sum_{a} \langle ac \,\|\, ac \rangle + 0 \right) + \sum_{a} \langle ac \,\|\, ac \rangle \\
&= -\frac{1}{2} \sum_{a} \sum_{b} \langle ab \,\|\, ab \rangle
\end{aligned} \tag{7.4.1}
$$

thus

$$
\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle = {}^{N}E_0^{(1)} \tag{7.4.2}
$$

Ex 7.14

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)} \binom{r}{a} &= -\sum_{ar} \frac{\left|\langle ac \,\|\, cr \rangle\right|^2}{\varepsilon_r - \varepsilon_a} \\
&= -\frac{\left|\langle 1\bar{1} \,\|\, \bar{1}2 \rangle\right|^2}{\varepsilon_2 - \varepsilon_1} - \frac{\left|\langle \bar{1}1 \,\|\, 1\bar{2} \rangle\right|^2}{\varepsilon_2 - \varepsilon_1} \\
&= \frac{\left|\langle 1\bar{1} \,|\, \bar{1}2 \rangle - \langle 1\bar{1} \,|\, 2\bar{1} \rangle\right|^2}{\varepsilon_1 - \varepsilon_2} \\
&= \frac{\left|\langle 1\bar{1} \,|\, 2\bar{1} \rangle\right|^2}{\varepsilon_1 - \varepsilon_2} \\
&= \frac{\left|\langle 11 \,|\, 12 \rangle\right|^2}{\varepsilon_1 - \varepsilon_2}
\end{aligned} \tag{7.4.3}
$$

Ex 7.15

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)} \binom{r}{a} &= \sum_{a\neq c} \sum_{r} \frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{ca}^{r} \right\rangle\right|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c} \sum_{r} \frac{\left|\sum_{b\neq c} \langle ab \,\|\, rb \rangle - \sum_{b} \langle ab \,\|\, rb \rangle\right|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c} \sum_{r} \frac{\left|\langle ac \,\|\, rc \rangle\right|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c} \sum_{r} \frac{\left|\langle ac \,\|\, cr \rangle\right|^2}{\varepsilon_a - \varepsilon_r}
\end{aligned} \tag{7.4.4}
$$

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{rs}{ab} &= \frac{1}{4}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\sum_{s}\frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{cab}^{rs}\right\rangle\right|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} \\
&= \frac{1}{4}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\sum_{s}\frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} \qquad (7.4.5) \\
&= \frac{1}{4}\sum_{a}\sum_{b}\sum_{r}\sum_{s}\frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{1}{4}\sum_{b}\sum_{r}\sum_{s}\frac{|\langle cb \,\|\, rs\rangle|^2}{\varepsilon_c+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{1}{4}\sum_{a}\sum_{r}\sum_{s}\frac{|\langle ac \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s} \\
&= \frac{1}{4}\sum_{a}\sum_{b}\sum_{r}\sum_{s}\frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{1}{2}\sum_{a}\sum_{r}\sum_{s}\frac{|\langle ca \,\|\, rs\rangle|^2}{\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s} \\
&= {}^{N}E_0^{(2)} + \frac{1}{2}\sum_{a,r,s}\frac{|\langle rs \,\|\, ac\rangle|^2}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_c} \qquad (7.4.6)
\end{aligned}
$$

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{cr}{ab} &= \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{cab}^{cr}\right\rangle\right|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_c} \\
&= \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{|\langle ab \,\|\, cr\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_c} \\
&= -\frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{|\langle ab \,\|\, cr\rangle|^2}{\varepsilon_c+\varepsilon_r-\varepsilon_a-\varepsilon_b} \qquad (7.4.7)
\end{aligned}
$$

7.5 Some Illustrative Calculations

Ex 7.16 For 2-electron system, in

$$
\mathrm{PRX} = -\frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{|\langle ab \,\|\, cr\rangle|^2}{\varepsilon_r+\varepsilon_c-\varepsilon_a-\varepsilon_b} \qquad (7.5.1)
$$

a, b must be the same, thus $\langle ab \,\|\, cr\rangle = 0$, thus

$$
\mathrm{PRX} = 0 \qquad (7.5.2)
$$

$$
\begin{aligned}
\mathrm{PRM} &= \frac{1}{2}\sum_{a,r,s}\frac{|\langle rs \,\|\, ca\rangle|^2}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_c} \\
&= \frac{1}{2}\left(\frac{|\langle \bar{2}2 \,\|\, \bar{1}1\rangle|^2}{\varepsilon_2+\varepsilon_2-\varepsilon_1-\varepsilon_1} + \frac{|\langle 2\bar{2} \,\|\, \bar{1}1\rangle|^2}{\varepsilon_2+\varepsilon_2-\varepsilon_1-\varepsilon_1}\right) \\
&= \frac{1}{2}\times 2\frac{|\langle 22 \,\|\, 11\rangle|^2}{2(\varepsilon_2-\varepsilon_1)} \\
&= -\frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)} \\
&= -{}^{N}E_0^{(2)} \qquad (7.5.3)
\end{aligned}
$$

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Ex C.1

(a)

$$\begin{aligned}\mathbf{H} &= \begin{pmatrix} \dfrac{\partial^2 E}{\partial x^2} & \dfrac{\partial^2 E}{\partial x \partial y} \\ \dfrac{\partial^2 E}{\partial y \partial x} & \dfrac{\partial^2 E}{\partial y^2} \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}\end{aligned} \tag{C.5.1}$$

$$\begin{aligned}\mathbf{f}(\mathbf{X}) &= \begin{pmatrix} \dfrac{\partial E}{\partial x} \\ \dfrac{\partial E}{\partial y} \end{pmatrix} \\ &= \begin{pmatrix} K(x-a) + K''y \\ K'(y-b) + K''x \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} - \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}\mathbf{X} - \begin{pmatrix} Ka \\ K'b \end{pmatrix}\end{aligned} \tag{C.5.2}$$

$$\begin{aligned}\mathbf{q} &= -\mathbf{H}^{-1}\mathbf{f} \\ &= -\mathbf{X} + \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}^{-1}\begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2}\begin{pmatrix} K' & -K'' \\ -K'' & K \end{pmatrix}\begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2}\begin{pmatrix} KK'a - K'K''b \\ -KK''a + KK'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2}\begin{pmatrix} KK' & -K'K'' \\ -KK'' & KK' \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix}\end{aligned} \tag{C.5.3}$$

(b) Since $\mathbf{q} = \mathbf{X}_e - \mathbf{X}$,

$$\begin{aligned}\mathbf{X}_e &= \frac{1}{KK' - K''^2}\begin{pmatrix} KK' & -K'K'' \\ -KK'' & KK' \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} \\ &= \frac{1}{0.1 - K''^2}\begin{pmatrix} 0.1 & -0.1K'' \\ -K'' & 0.1 \end{pmatrix}\begin{pmatrix} 3 \\ 2 \end{pmatrix}\end{aligned} \tag{C.5.4}$$

K''	$\mathbf{X}_e = (x_e, y_e)$
0	(3.000, 2.000)
0.010	(2.983, 1.702)
0.030	(2.967, 1.110)

Ex C.2

$$
\begin{aligned}
\mathbf{H} &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \\
&= \begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix}
\end{aligned} \tag{C.5.5}
$$

$$
\begin{aligned}
\mathbf{f} &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \mathbf{X} - \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\
&= \begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix} \begin{pmatrix} 3.3 \\ 1.8 \end{pmatrix} - \begin{pmatrix} 1.000 \times 3.00 \\ 0.100 \times 2.00 \end{pmatrix} \\
&= \begin{pmatrix} 0.354 \\ 0.079 \end{pmatrix}
\end{aligned} \tag{C.5.6}
$$

$$
\begin{aligned}
\mathbf{q} &= -\mathbf{H}^{-1}\mathbf{f} \\
&= -\begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix}^{-1} \begin{pmatrix} 0.354 \\ 0.079 \end{pmatrix} \\
&= \left(-0.333, -0.690\right)
\end{aligned} \tag{C.5.7}
$$

thus

$$
\begin{aligned}
\mathbf{X}_e &= \mathbf{q} + \mathbf{X} \\
&= \left(2.967, 1.110\right)
\end{aligned} \tag{C.5.8}
$$

which agrees with the result in Ex C.1(b).

Ex C.3 A program is written to solve this problem, which is `C-3.py`.
For example, run the program by `python C-3.py 0.03`, and the Nelder-Mead optimization steps will be printed for $K'' = 0.03$.

Ex C.4 A program is written to solve this problem, which is `C-4.py`.
For example, run the program by `python C-4.py`, and the MS optimization steps will be printed.

C.6 Transition States

C.7 Constrained Variation

D Molecular Integrals for H_2 as a Function of Bond Length