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

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

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

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

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

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

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

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,

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

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

Similarly, we get

$$
\left\langle \Psi^{**}_{a\bar{b}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{**}_{\bar{a}b} \right\rangle = \frac{1}{2}J_{11} \tag{5.1.26}
$$

$$
\left\langle \Psi^{**}_{a\bar{a}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{**}_{\bar{a}b} \right\rangle = \left\langle \Psi^{**}_{b\bar{b}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{**}_{a\bar{b}} \right\rangle = \left\langle \Psi^{**}_{b\bar{b}} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi^{**}_{\bar{a}b} \right\rangle = \frac{1}{2}K_{12} - J_{12} \tag{5.1.27}
$$

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_{\mathrm{corr}}(\mathrm{FO}) &= \sum_{A<B}\sum_{R<S}\frac{|\langle AB \parallel RS\rangle|^2}{\varepsilon_A+\varepsilon_B-\varepsilon_R-\varepsilon_S} \\
&= \frac{|\langle a\bar{a}\parallel r\bar{r}\rangle|^2+|\langle a\bar{a}\parallel r\bar{s}\rangle|^2+|\langle a\bar{a}\parallel s\bar{r}\rangle|^2+|\langle a\bar{a}\parallel s\bar{s}\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}+\frac{\left|\langle a\bar{b}\parallel r\bar{r}\rangle\right|^2+\left|\langle a\bar{b}\parallel r\bar{s}\rangle\right|^2+\left|\langle a\bar{b}\parallel s\bar{r}\rangle\right|^2+\left|\langle a\bar{b}\parallel s\bar{s}\rangle\right|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2} \\
&\quad+\frac{|\langle b\bar{a}\parallel r\bar{r}\rangle|^2+|\langle b\bar{a}\parallel r\bar{s}\rangle|^2+|\langle b\bar{a}\parallel s\bar{r}\rangle|^2+|\langle b\bar{a}\parallel s\bar{s}\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}+\frac{\left|\langle b\bar{b}\parallel r\bar{r}\rangle\right|^2+\left|\langle b\bar{b}\parallel r\bar{s}\rangle\right|^2+\left|\langle b\bar{b}\parallel s\bar{r}\rangle\right|^2+\left|\langle b\bar{b}\parallel 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.

$$
\begin{aligned}
{}^2E_{\mathrm{corr}}(\mathrm{EN(L)}) &= -\sum_{a<b}\sum_{r<s}\frac{|\langle\Psi_0\mid\mathscr{H}\mid\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}\mid\mathscr{H}-E_0\mid\Psi_{ab}^{rs}\rangle} \\
&= -
\end{aligned}
\tag{5.1.37}
$$

Ex 5.10

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

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

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 \\
&= \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}\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\right. \\
&\qquad \left. + 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}^{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

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

which matches Eq. 5.15 and 5.16.

b.

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

Ex 5.15

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

Ex 5.16

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \tag{5.3.4}$$

the eigenvalues are

$$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta \tag{5.3.5}$$

while from Eq. 5.131, we get

$$\varepsilon_i = \alpha + 2\beta \cos \frac{\pi i}{3} \quad (i = 0, \pm 1, \pm 2, 3) \tag{5.3.6}$$

i.e.

$$\{\varepsilon_i\} = \{\alpha + 2\beta, \alpha + \beta, \alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta, \} \tag{5.3.7}$$

which is identical to those eigenvalues.
The total energy is

$$\begin{aligned} \mathscr{E}_0 &= 2(\alpha + 2\beta + \alpha + \beta + \alpha + \beta) && (5.3.8) \\ &= 6\alpha + 8\beta && (5.3.9) \end{aligned}$$

which agrees with Eq. 5.132.

Ex 5.17 For Eq. 5.139

$$\begin{aligned} \langle i \,|\, j \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|)(|\phi_{2j-1}\rangle + |\phi_{2j}\rangle) \\ &= \frac{1}{2}(\delta_{2i-1,2j-1} + 0 + 0 + \delta_{2i,2j}) \\ &= \frac{1}{2}(\delta_{i,j} + \delta_{i,j}) \\ &= \delta_{i,j} \end{aligned} \tag{5.3.10}$$

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

$$\begin{aligned} \langle i \,|\, j^* \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|)(|\phi_{2j-1}\rangle - |\phi_{2j}\rangle) \\ &= \frac{1}{2}(\delta_{2i-1,2j-1} - 0 + 0 - \delta_{2i,2j}) \\ &= \frac{1}{2}(\delta_{i,j} - \delta_{i,j}) \\ &= 0 \end{aligned} \tag{5.3.11}$$

For Eq. 5.140

$$\begin{aligned} \langle i \,|\, h_{\text{eff}} \,|\, i \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|) h_{\text{eff}} (|\phi_{2i-1}\rangle + |\phi_{2i}\rangle) \\ &= \frac{1}{2}(\alpha + \beta + \beta + \alpha) \\ &= \alpha + \beta \end{aligned} \tag{5.3.12}$$

$$\begin{aligned} \langle i^* \,|\, h_{\text{eff}} \,|\, i^* \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| - \langle \phi_{2i}|) h_{\text{eff}} (|\phi_{2i-1}\rangle - |\phi_{2i}\rangle) \\ &= \frac{1}{2}(\alpha - \beta - \beta + \alpha) \\ &= \alpha - \beta \end{aligned} \tag{5.3.13}$$

$$
\begin{aligned}
\langle i \,|\, h_{\text{eff}} \,|\, i \pm 1 \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|) h_{\text{eff}} (|\phi_{2i-1\pm2}\rangle + |\phi_{2i\pm2}\rangle) \\
&= \begin{cases} \dfrac{1}{2}(0 + 0 + \beta + 0) & + \\ \\ \dfrac{1}{2}(0 + \beta + 0 + 0) & - \end{cases} \\
&= \beta/2
\end{aligned} \tag{5.3.14}
$$

$$
\begin{aligned}
\langle i^* \,|\, h_{\text{eff}} \,|\, (i \pm 1)^* \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| - \langle \phi_{2i}|) h_{\text{eff}} (|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle) \\
&= \begin{cases} \dfrac{1}{2}(0 - 0 - \beta + 0) & + \\ \\ \dfrac{1}{2}(0 - \beta - 0 + 0) & - \end{cases} \\
&= -\beta/2
\end{aligned} \tag{5.3.15}
$$

$$
\begin{aligned}
\langle i \,|\, h_{\text{eff}} \,|\, (i \pm 1)^* \rangle &= \frac{1}{2}(\langle \phi_{2i-1}| + \langle \phi_{2i}|) h_{\text{eff}} (|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle) \\
&= \begin{cases} \dfrac{1}{2}(0 - 0 + \beta - 0) & + \\ \\ \dfrac{1}{2}(0 - \beta + 0 - 0) & - \end{cases} \\
&= \pm\beta/2
\end{aligned} \tag{5.3.16}
$$

Ex 5.18

$$
\begin{aligned}
\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle &= 2^{-1/2} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle \\
&= 2^{-1/2}[\beta/2 - (-\beta/2)] \\
&= 2^{-1/2}\beta
\end{aligned} \tag{5.3.17}
$$

$$
\begin{aligned}
\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \overset{*}{1} \right\rangle &= \frac{1}{2} \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle \\
&= \frac{1}{2}\left[\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle\right] \\
&= \frac{1}{2}[2(\alpha - \beta) - 2(-\beta/2) - 2E_0] \\
&= \alpha - \beta/2 - E_0 \\
&= -\frac{3}{2}\beta
\end{aligned} \tag{5.3.18}
$$

thus

$$
2^{-1/2}\beta c = e_1 \tag{5.3.19}
$$

$$
2^{-1/2}\beta - \frac{3}{2}\beta c = e_1 c \tag{5.3.20}
$$

the solutions are

$$
c = \frac{-3 \pm \sqrt{17}}{2\sqrt{2}} \qquad e_1 = \frac{-3 \pm \sqrt{17}}{4}\beta \tag{5.3.21}
$$

and we take

$$
e_1 = \frac{-3 + \sqrt{17}}{4}\beta \tag{5.3.22}
$$

Ex 5.19

a)

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1\,|\Psi_1^{1*}\rangle + c_2\,|\Psi_1^{2*}\rangle + \cdots + c_n\,|\Psi_1^{n*}\rangle \tag{5.3.23}$$

Since

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{1*} \right\rangle = 0 \tag{5.3.24}$$
$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} \right\rangle = \beta/2 \tag{5.3.25}$$
$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{j*} \right\rangle = 0 \qquad (1 < j < n) \tag{5.3.26}$$
$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{n*} \right\rangle = -\beta/2 \tag{5.3.27}$$

thus,

$$|\Psi_1\rangle = |\Psi_0\rangle + c\left|\overset{*}{1}\right\rangle \tag{5.3.28}$$

$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\left(|\Psi_1^{2*}\rangle - |\Psi_1^{n*}\rangle\right) \tag{5.3.29}$$

As before, we get

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.30}$$

but

$$\begin{aligned}
\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \overset{*}{1} \right\rangle &= \frac{1}{2}\left[\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle\right] \\
&= \frac{1}{2}[2(\alpha - \beta) - 2 \times 0 - 2E_0] \\
&= \alpha - \beta - E_0 \\
&= -2\beta
\end{aligned} \tag{5.3.31}$$

thus

$$e_1 = \left(-1 + \frac{\sqrt{6}}{2}\right)\beta \tag{5.3.32}$$

$$\begin{aligned}
E_R(\text{IEPA}) &= Ne_1 \\
&= \left(-1 + \frac{\sqrt{6}}{2}\right)N\beta \\
&= 0.2247N\beta
\end{aligned} \tag{5.3.33}$$

b) As $N = 10$,

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1\,|\Psi_1^{1*}\rangle + c_2\,|\Psi_1^{2*}\rangle + c_3\,|\Psi_1^{3*}\rangle + +c_4\,|\Psi_1^{4*}\rangle + c_5\,|\Psi_1^{5*}\rangle \tag{5.3.34}$$

As before, let

$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\left(|\Psi_1^{1*}\rangle - |\Psi_1^{5*}\rangle\right) \tag{5.3.35}$$

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1\left|\overset{*}{1}\right\rangle + c_3\,|\Psi_1^{3*}\rangle + +c_4\,|\Psi_1^{4*}\rangle \tag{5.3.36}$$

then the "particle" equations will be

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle c_3 + \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle c_4 = e_1 \tag{5.3.37}$$

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle c_3 + \left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle c_4 + \left\langle \overset{*}{1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \overset{*}{1} \right\rangle c_1 = e_1 c_1 \tag{5.3.38}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle c_4 + \left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{3*} \right\rangle c_3 = e_1 c_3 \tag{5.3.39}$$

$$\left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle c_3 + \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{4*} \right\rangle c_4 = e_1 c_4 \tag{5.3.40}$$

where

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.41}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle = 0 \tag{5.3.42}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle = 0 \tag{5.3.43}$$

$$\left\langle \overset{*}{1} \middle| \mathscr{H} - E_0 \middle| \overset{*}{1} \right\rangle = -2\beta \tag{5.3.44}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{3*} \right\rangle = \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{4*} \right\rangle = \alpha - \beta - E_0 = -2\beta \tag{5.3.45}$$

$$\begin{aligned} \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle &= 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle\right] \\ &= 2^{-1/2}(-\beta/2) \end{aligned} \tag{5.3.46}$$

$$\begin{aligned} \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle &= 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle\right] \\ &= 2^{-1/2}(\beta/2) \end{aligned} \tag{5.3.47}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle = -\beta/2 \tag{5.3.48}$$

thus

$$2^{-1/2}\beta c_1 = e_1 \tag{5.3.49}$$

$$2^{-1/2}\beta + 2^{-1/2}(-\beta/2)c_3 + 2^{-1/2}(\beta/2)c_4 + (-2\beta)c_1 = e_1 c_1 \tag{5.3.50}$$

$$2^{-1/2}(-\beta/2)c_1 + (-\beta/2)c_4 + (-2\beta)c_3 = e_1 c_3 \tag{5.3.51}$$

$$2^{-1/2}(\beta/2)c_1 + (-\beta/2)c_3 + (-2\beta)c_4 = e_1 c_4 \tag{5.3.52}$$

or

$$\begin{pmatrix} 0 & 2^{-1/2}\beta & 0 & 0 \\ 2^{-1/2}\beta & -2\beta & 2^{-1/2}(-\beta/2) & 2^{-1/2}(\beta/2) \\ 0 & 2^{-1/2}(-\beta/2) & -2\beta & -\beta/2 \\ 0 & 2^{-1/2}(\beta/2) & -\beta/2 & -2\beta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} = e_1 \begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} \tag{5.3.53}$$

the eigenvalues are

$$-\frac{5}{2}\beta \;\text{ or roots of }\; (2e_1/\beta)^3 + 7(2e_1/\beta)^2 + 9(2e_1/\beta) - 6 = 0 \tag{5.3.54}$$

rearrange the cubic equation, we get

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0 \tag{5.3.55}$$

$$e_1 = -2.4627\beta, -1.2760\beta, 0.2387\beta \tag{5.3.56}$$

so we take

$$e_1 = 0.2387\beta \tag{5.3.57}$$

Ex 5.20

$$\left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \overset{*}{2} \right\rangle = \frac{1}{2} \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} - \Psi_2^{1*} \right\rangle$$
$$= -\frac{1}{2} \left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} \right\rangle$$
$$= -\frac{1}{2}(-1) \left\langle 2 \,|\, h_{\text{eff}} \,|\, 1 \right\rangle$$
$$= -\frac{1}{2}(-1)\beta/2$$
$$= \beta/4 \tag{5.3.58}$$

$$\left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \overset{*}{3} \right\rangle = \frac{1}{2} \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} - \Psi_3^{2*} \right\rangle$$
$$= -\frac{1}{2} \left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{2*} \right\rangle$$
$$= -\frac{1}{2}(-1)\beta/2$$
$$= \beta/4 \tag{5.3.59}$$

$$\left\langle \overset{*}{2} \middle| \mathscr{H} \middle| \overset{*}{3} \right\rangle = \frac{1}{2} \left\langle \Psi_2^{3*} - \Psi_2^{1*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} - \Psi_3^{2*} \right\rangle$$
$$= -\frac{1}{2} \left\langle \Psi_2^{1*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} \right\rangle$$
$$= -\frac{1}{2}(-1)\beta/2$$
$$= \beta/4 \tag{5.3.60}$$

For SCI,

$$\sum_{bs} v_{bs} c_b^s = E_R(\text{SCI}) \tag{5.3.61}$$

$$v_{ra} + (\varepsilon_r^{(0)} + v_{rr})c_a^r + \sum_s v_{rs} c_a^s - (\varepsilon_a^{(0)} + v_{aa})c_a^r - \sum_b v_{ba} c_b^r = E_R(\text{SCI})c_a^r \tag{5.3.62}$$

thus

$$6c \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle = E_R(\text{SCI}) \tag{5.3.63}$$

$$\left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + c \left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{i} \right\rangle + \sum_{j \neq i} c \left\langle \overset{*}{j} \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = E_R(\text{SCI})c \tag{5.3.64}$$

i.e.

$$6c \times 2^{-1/2}\beta = E_R(\text{SCI}) \tag{5.3.65}$$

$$2^{-1/2}\beta + c\left(-\frac{3}{2}\beta + 2 \times \beta/4\right) = E_R(\text{SCI})c \tag{5.3.66}$$

$\therefore$

$$6c \times 2^{-1/2}\beta = E_R(\text{SCI}) \tag{5.3.67}$$

$$2^{-1/2}\beta - c\beta = E_R(\text{SCI})c \tag{5.3.68}$$

the solutions are

$$E_R(\text{SCI}) = \frac{-1 \pm \sqrt{13}}{2}\beta \tag{5.3.69}$$

we take

$$E_R(\text{SCI}) = \frac{-1 + \sqrt{13}}{2}\beta \tag{5.3.70}$$

Ex 5.21 It's clear that

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = 2^{-1/2}\beta \tag{5.3.71}$$

while

$$\begin{aligned}\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \overset{*}{j} \right\rangle - E_0\delta_{ij} \\ &= \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle - E_0\delta_{ij}\end{aligned} \tag{5.3.72}$$

If $i = j$,

$$\begin{aligned}\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \frac{1}{2}\left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \right\rangle - E_0 \\ &= \frac{1}{2} \times 2(\alpha - \beta) - E_0 \\ &= -2\beta\end{aligned} \tag{5.3.73}$$

else,

$$\begin{aligned}\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle &= \frac{1}{2}\left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle \\ &= -\frac{1}{2}\left\langle \Psi_i^{(i+1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j-1)*} \right\rangle - \frac{1}{2}\left\langle \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} \right\rangle \\ &= 0\end{aligned} \tag{5.3.74}$$

thus

$$\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle = -2\beta\delta_{ij} \tag{5.3.75}$$

Similar to Ex. 5.20, the SCI equations are

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

$$2^{-1/2}\beta + c(-2\beta + 0) = E_R(\text{SCI})c \tag{5.3.77}$$

$\therefore$

$$E_R(\text{SCI}) = \frac{-2 + \sqrt{2N+4}}{2}\beta = \left[\sqrt{1 + N/2} - 1\right]\beta \tag{5.3.78}$$