Modern Quantum Chemistry, Szabo & Ostlund HW

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Contents

5 Pair and Coupled-pair Theories . . . **2**
5.1 The Independent Electron Pair Approximation . . . 2
Ex 5.1 . . . 2
Ex 5.2 . . . 2
Ex 5.3 . . . 3
5.1.1 Invariance under Unitary Transformations: An Example . . . 3
Ex 5.4 . . . 3
Ex 5.5 . . . 3
Ex 5.6 . . . 4
Ex 5.7 . . . 4
Ex 5.8 . . . 6
Ex 5.9 . . . 6
Ex 5.10 . . . 7
5.1.2 Some Illustrative Calculations . . . 7
5.2 Coupled-pair Theories . . . 7
5.2.1 The Coupled-cluster Approximation . . . 7
5.2.2 The Cluster Expansion of the Wave Function . . . 7
Ex 5.11 . . . 7
5.2.3 Linear CCA and the Coupled-Electron Pair Approximation . . . 8
Ex 5.12 . . . 8
5.2.4 Some Illustrative Calculations . . . 9
5.3 Many-electron Theories with Single Particle Hamiltonians . . . 9
Ex 5.13 . . . 9
5.3.1 The Relaxation Energy via CI, IEPA, CEPA and CCA . . . 9
Ex 5.14 . . . 9
Ex 5.15 . . . 9
5.3.2 The Resonance Energy of Polyenes in Hückel Theory . . . 10
Ex 5.16 . . . 10
Ex 5.17 . . . 11
Ex 5.18 . . . 12
Ex 5.19 . . . 12
Ex 5.20 . . . 14
Ex 5.21 . . . 15

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

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

5.1.1 Invariance under Unitary Transformations: An Example

Ex 5.4

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

Ex 5.5

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

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

Since

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

we have

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

Ex 5.6 Since

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

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

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

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,

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

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

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

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

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

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

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

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

$\therefore$

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

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

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)} \qquad (5.1.36)
\end{aligned}
$$

Ex 5.9

a.

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

b.

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

c.

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

d.

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

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,

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

and

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

similarly,

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

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

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

while

$$
\begin{aligned}
&\exp\Big(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\Big)\,|1_1\bar{1}_11_2\bar{1}_2\rangle \\
&= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)^2 + \cdots\right]|1_1\bar{1}_11_2\bar{1}_2\rangle
\end{aligned} \tag{5.2.2}
$$

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}_11_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}_11_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 \\
&\qquad + 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}_11_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}_11_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}_11_2\bar{1}_2}^{2_1\bar{2}_12_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}_11_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

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

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

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

For Eq. 5.140

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

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

$$\begin{aligned}\langle i\,|\,h_{\text{eff}}\,|\,i\pm1\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| + \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle + |\phi_{2i\pm2}\rangle)\\ &= \begin{cases}\frac{1}{2}(0+0+\beta+0) & +\\ \\ \frac{1}{2}(0+\beta+0+0) & -\end{cases}\\ &= \beta/2\end{aligned} \tag{5.3.23}$$

$$\begin{aligned}\langle i^*\,|\,h_{\text{eff}}\,|\,(i\pm1)^*\rangle &= \frac{1}{2}(\langle\phi_{2i-1}| - \langle\phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle)\\ &= \begin{cases}\frac{1}{2}(0-0-\beta+0) & +\\ \\ \frac{1}{2}(0-\beta-0+0) & -\end{cases}\\ &= -\beta/2\end{aligned} \tag{5.3.24}$$

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

Ex 5.18

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

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

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

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

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 $N = 10$,

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

As before, let

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

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

then the "particle" equations will be

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

$$\left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle c_3 + \left\langle \overset{*}{1} \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle c_4 + \left\langle \overset{*}{1} \middle| \mathscr{H} - E_0 \middle| \overset{*}{1} \right\rangle c_1 = e_1 c_1 \tag{5.3.47}$$

$$\left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{3*} \middle| \mathscr{H} \middle| \Psi_1^{4*} \right\rangle c_4 + \left\langle \Psi_1^{3*} \middle| \mathscr{H} - E_0 \middle| \Psi_1^{3*} \right\rangle c_3 = e_1 c_3 \tag{5.3.48}$$

$$\left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + \left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \overset{*}{1} \right\rangle c_1 + \left\langle \Psi_1^{4*} \middle| \mathscr{H} \middle| \Psi_1^{3*} \right\rangle c_3 + \left\langle \Psi_1^{4*} \middle| \mathscr{H} - E_0 \middle| \Psi_1^{4*} \right\rangle c_4 = e_1 c_4 \tag{5.3.49}$$

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

$$2^{-1/2}\beta c_1 = e_1 \tag{5.3.58}$$

$$2^{-1/2}\beta + 2^{-1/2}(-\beta/2)c_3 + 2^{-1/2}(\beta/2)c_4 + (-2\beta)c_1 = e_1 c_1 \tag{5.3.59}$$

$$2^{-1/2}(-\beta/2)c_1 + (-\beta/2)c_4 + (-2\beta)c_3 = e_1 c_3 \tag{5.3.60}$$

$$2^{-1/2}(\beta/2)c_1 + (-\beta/2)c_3 + (-2\beta)c_4 = e_1 c_4 \tag{5.3.61}$$

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

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

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

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

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

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

If $i = j$,

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

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

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

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

$\therefore$

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