

Modern Quantum Chemistry, Szabo & Ostlund

HW

WSR

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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	8
5.3	Many-electron Theories with Single Particle Hamiltonians	8
	Ex 5.13	8
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	10
	Ex 5.18	11
	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.

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

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

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

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

\therefore

$$c_{1_i \bar{1}_i}^{2_i \bar{2}_i} \langle \Psi_0 | \mathcal{H} | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle = e_{1_i \bar{1}_i} \tag{5.1.5}$$

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

(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

$$K_{12} + \sum_{j \neq k} \langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathcal{H} - E_0 | \Psi_{1_i \bar{1}_i}^{2_j \bar{2}_k} \rangle c_{1_i \bar{1}_i}^{2_j \bar{2}_k} = e_{1_i \bar{1}_i} c_{1_i \bar{1}_i}^{2_i \bar{2}_i} \tag{5.1.8}$$

Since

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

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

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

Ex 5.5

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

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

Since

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

we have

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

Ex 5.6 Since

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

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

$$\begin{aligned} \langle \Psi_{ab}^{**} | \mathcal{H} - E_0 | \Psi_{ab}^{**} \rangle &= 2^{-1} (\langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} - E_0 | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} - E_0 | \Psi_{ab}^{s\bar{r}} \rangle \\ &\quad + \langle \Psi_{ab}^{s\bar{r}} | \mathcal{H} - E_0 | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{ab}^{s\bar{r}} | \mathcal{H} - E_0 | \Psi_{ab}^{s\bar{r}} \rangle) \\ &= 2^{-1} \left[\left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12} \right) - (4h_{11} + 2J_{11}) \right. \\ &\quad \left. + \frac{1}{2}J_{22} + \frac{1}{2}J_{22} \right. \\ &\quad \left. + \left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12} \right) - (4h_{11} + 2J_{11}) \right] \\ &= \dots \\ &= 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \equiv 2\Delta' \end{aligned} \quad (5.1.19)$$

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

$$\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle = \langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle = \langle \Psi_0 | \mathcal{H} | \Psi_{\bar{a}b}^{**} \rangle = 2^{-1/2} K_{12} \quad (5.1.20)$$

$$\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle = \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle = \langle \Psi_{\bar{a}b}^{**} | \mathcal{H} - E_0 | \Psi_{\bar{a}b}^{**} \rangle = 2\Delta' \quad (5.1.21)$$

Similarly, we get

$$\langle \Psi_0 | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle = 2^{-1/2} K_{12} \quad (5.1.22)$$

$$\langle \Psi_{b\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{b\bar{b}}^{**} \rangle = 2\Delta' \quad (5.1.23)$$

For the rest,

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

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

Similarly, we get

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

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

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{|\langle a\bar{b} \| r\bar{r} \rangle|^2 + |\langle a\bar{b} \| r\bar{s} \rangle|^2 + |\langle a\bar{b} \| s\bar{r} \rangle|^2 + |\langle a\bar{b} \| s\bar{s} \rangle|^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{|\langle b\bar{b} \| r\bar{r} \rangle|^2 + |\langle b\bar{b} \| r\bar{s} \rangle|^2 + |\langle b\bar{b} \| s\bar{r} \rangle|^2 + |\langle b\bar{b} \| s\bar{s} \rangle|^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{|\frac{1}{2}K_{12}|^2 + 0 + 0 + |\frac{1}{2}K_{12}|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{0 + |\frac{1}{2}K_{12}|^2 + |\frac{1}{2}K_{12}|^2 + 0}{2(\varepsilon_1 - \varepsilon_2)} \\
&\quad + \frac{0 + 0 + |\frac{1}{2}K_{12}|^2 + |\frac{1}{2}K_{12}|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{|\frac{1}{2}K_{12}|^2 + 0 + 0 + |\frac{1}{2}K_{12}|^2}{2(\varepsilon_1 - \varepsilon_2)} \\
&= \frac{2K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \tag{5.1.36}
\end{aligned}$$

Ex 5.9

a.

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

b.

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

c.

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

d.

$${}^2E_{\text{corr}}(\text{EN(L)}) = -0.04168 \quad (5.1.40)$$

$${}^2E_{\text{corr}}(\text{EN(D)}) = -0.02755 \quad (5.1.41)$$

$${}^2E_{\text{corr}}^{\text{singlet}}(\text{EN(D)}) = -0.02585 \quad (5.1.42)$$

thus EN pairs is not invariant to unitary transformations.

Ex 5.10 From Ex 5.7,

$$\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle = \langle \Psi_0 | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle = 2^{-1/2} K_{12} \quad (5.1.43)$$

$$\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle = \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{b\bar{b}}^{**} \rangle = 2\Delta' \quad (5.1.44)$$

$$\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{b\bar{b}}^{**} \rangle = \frac{1}{2} J_{11} \quad (5.1.45)$$

From Eq 5.42 in the textbook,

$$\langle \Psi_0 | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle = K_{12} \quad (5.1.46)$$

$$\langle {}^B\Psi_{ab}^{rs} | \mathcal{H} - E_0 | {}^B\Psi_{ab}^{rs} \rangle = 2\Delta'' \quad (5.1.47)$$

and

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

similarly,

$$\langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle = 2^{-1/2} (\times K_{12} - 2J_{12}) \quad (5.1.49)$$

thus the DCI equation is

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

by solving the DCI equation,

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

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

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

while

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

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

$$\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\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. \\ &\quad \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} \quad (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

$$\mathbf{D}_{rabb, rabs} = \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle \quad (5.2.4)$$

thus

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

which matches Eq. 5.15 and 5.16.

b. From Ex 4.12, we get

$$\mathbf{B} = \begin{pmatrix} K_{12} \\ K_{12} \end{pmatrix} \quad (5.2.6)$$

$$\mathbf{D} = \begin{pmatrix} 2\Delta & 0 \\ 0 & 2\Delta \end{pmatrix} \quad (5.2.7)$$

thus

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

5.2.4 Some Illustrative Calculations

5.3 Many-electron Theories with Single Particle Hamiltonians

Ex 5.13

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

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

while the eigenvalues of the matrix is

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

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

Ex 5.14

a.

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

b. Similarly

$$\langle \Psi_a^r | \mathcal{H} | \Psi_0 \rangle = v_{ra} \quad (5.3.5)$$

c.

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

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

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

Ex 5.15

a.

$$\begin{aligned}
|\Phi_0\rangle &= a_1 b_1 \cdot 0 + a_1 b_2 |\chi_1^{(0)} \chi_2^{(0)}\rangle + a_1 b_3 |\chi_1^{(0)} \chi_3^{(0)}\rangle + a_1 b_4 |\chi_1^{(0)} \chi_4^{(0)}\rangle \\
&\quad + a_2 b_1 |\chi_2^{(0)} \chi_1^{(0)}\rangle + a_2 b_2 \cdot 0 + a_2 b_3 |\chi_2^{(0)} \chi_3^{(0)}\rangle + a_2 b_4 |\chi_2^{(0)} \chi_4^{(0)}\rangle \\
&\quad + a_3 b_1 |\chi_3^{(0)} \chi_1^{(0)}\rangle + a_3 b_2 |\chi_3^{(0)} \chi_2^{(0)}\rangle + a_3 b_3 \cdot 0 + a_3 b_4 |\chi_3^{(0)} \chi_4^{(0)}\rangle \\
&\quad + a_4 b_1 |\chi_4^{(0)} \chi_1^{(0)}\rangle + a_4 b_2 |\chi_4^{(0)} \chi_2^{(0)}\rangle + a_4 b_3 |\chi_4^{(0)} \chi_3^{(0)}\rangle + a_4 b_4 \cdot 0 \\
&= (a_1 b_2 - a_2 b_1) |\chi_1^{(0)} \chi_2^{(0)}\rangle + (a_1 b_3 - a_3 b_1) |\chi_1^{(0)} \chi_3^{(0)}\rangle + (a_1 b_4 - a_4 b_1) |\chi_1^{(0)} \chi_4^{(0)}\rangle \\
&\quad - (a_2 b_3 - a_3 b_2) |\chi_3^{(0)} \chi_2^{(0)}\rangle - (a_2 b_4 - a_4 b_2) |\chi_4^{(0)} \chi_2^{(0)}\rangle + (a_3 b_4 - a_4 b_3) |\chi_3^{(0)} \chi_4^{(0)}\rangle
\end{aligned} \tag{5.3.8}$$

thus, with intermediate normalization

$$\begin{aligned}
|\Phi_0\rangle &= |\Psi_0\rangle + \frac{a_1 b_3 - a_3 b_1}{a_1 b_2 - a_2 b_1} |\Psi_2^3\rangle + \frac{a_1 b_4 - a_4 b_1}{a_1 b_2 - a_2 b_1} |\Psi_2^4\rangle \\
&\quad - \frac{a_2 b_3 - a_3 b_2}{a_1 b_2 - a_2 b_1} |\Psi_1^3\rangle - \frac{a_2 b_4 - a_4 b_2}{a_1 b_2 - a_2 b_1} |\Psi_1^4\rangle + \frac{a_3 b_4 - a_4 b_3}{a_1 b_2 - a_2 b_1} |\Psi_{12}^{34}\rangle
\end{aligned} \tag{5.3.9}$$

$$\begin{aligned}
c_1^3 c_2^4 - c_1^4 c_2^3 &= -\frac{a_2 b_3 - a_3 b_2}{a_1 b_2 - a_2 b_1} \frac{a_1 b_4 - a_4 b_1}{a_1 b_2 - a_2 b_1} + \frac{a_2 b_4 - a_4 b_2}{a_1 b_2 - a_2 b_1} \frac{a_1 b_3 - a_3 b_1}{a_1 b_2 - a_2 b_1} \\
&= \frac{a_2 a_4 b_1 b_3 + a_1 a_3 b_2 b_4 - a_2 a_3 b_1 b_4 - a_1 a_4 b_2 b_3}{(a_1 b_2 - a_2 b_1)^2} \\
&= \frac{(a_1 b_2 - a_2 b_1)(a_3 b_4 - a_4 b_3)}{(a_1 b_2 - a_2 b_1)^2} \\
&= \frac{a_3 b_4 - a_4 b_3}{a_1 b_2 - a_2 b_1} \\
&= c_{12}^{34}
\end{aligned} \tag{5.3.10}$$

b.

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

$$\begin{aligned}
(\mathbf{U}_{BA} \mathbf{U}_{AA}^{-1})_{11} &= \frac{1}{\det(\mathbf{U}_{AA})} (a_3 b_2 - b_3 a_2) \\
&= -\frac{a_2 b_3 - a_3 b_2}{a_1 b_2 - a_2 b_1} \\
&= c_1^3
\end{aligned} \tag{5.3.12}$$

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.

$$\{\varepsilon_i\} = \{\alpha + 2\beta, \alpha + \beta, \alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta, \} \quad (5.3.16)$$

which is identical to those eigenvalues.

The total energy is

$$\mathcal{E}_0 = 2(\alpha + 2\beta + \alpha + \beta + \alpha + \beta) \quad (5.3.17)$$

$$= 6\alpha + 8\beta \quad (5.3.18)$$

which agrees with Eq. 5.132.

Ex 5.17 For Eq. 5.139

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

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

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

For Eq. 5.140

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

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

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

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

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

Ex 5.18

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

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

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

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

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

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{1*} \rangle = 0 \tag{5.3.33}$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{2*} \rangle = \beta/2 \tag{5.3.34}$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{j*} \rangle = 0 \quad (1 < j < n) \tag{5.3.35}$$

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

thus,

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

$$\left| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle = 2^{-1/2}(|\Psi_1^{2*}\rangle - |\Psi_1^{n*}\rangle) \quad (5.3.38)$$

As before, we get

$$\left\langle \Psi_0 \left| \mathcal{H} \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle = 2^{-1/2}\beta \quad (5.3.39)$$

but

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

thus

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

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

b) As $N = 10$,

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 |\Psi_1^{1*}\rangle + c_2 |\Psi_1^{2*}\rangle + c_3 |\Psi_1^{3*}\rangle + c_4 |\Psi_1^{4*}\rangle + c_5 |\Psi_1^{5*}\rangle \quad (5.3.43)$$

As before, let

$$\left| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle = 2^{-1/2}(|\Psi_1^{1*}\rangle - |\Psi_1^{5*}\rangle) \quad (5.3.44)$$

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 \left| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle + c_3 |\Psi_1^{3*}\rangle + c_4 |\Psi_1^{4*}\rangle \quad (5.3.45)$$

then the "particle" equations will be

$$\left\langle \Psi_0 \left| \mathcal{H} \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle c_1 + \langle \Psi_0 | \mathcal{H} | \Psi_1^{3*} \rangle c_3 + \langle \Psi_0 | \mathcal{H} | \Psi_1^{4*} \rangle c_4 = e_1 \quad (5.3.46)$$

$$\left\langle \begin{smallmatrix} * \\ 1 \end{smallmatrix} \left| \mathcal{H} \right| \Psi_0 \right\rangle + \left\langle \begin{smallmatrix} * \\ 1 \end{smallmatrix} \left| \mathcal{H} \right| \Psi_1^{3*} \right\rangle c_3 + \left\langle \begin{smallmatrix} * \\ 1 \end{smallmatrix} \left| \mathcal{H} \right| \Psi_1^{4*} \right\rangle c_4 + \left\langle \begin{smallmatrix} * \\ 1 \end{smallmatrix} \left| \mathcal{H} - E_0 \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle c_1 = e_1 c_1 \quad (5.3.47)$$

$$\langle \Psi_1^{3*} | \mathcal{H} | \Psi_0 \rangle + \left\langle \Psi_1^{3*} \left| \mathcal{H} \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle c_1 + \langle \Psi_1^{3*} | \mathcal{H} | \Psi_1^{4*} \rangle c_4 + \langle \Psi_1^{3*} | \mathcal{H} - E_0 | \Psi_1^{3*} \rangle c_3 = e_1 c_3 \quad (5.3.48)$$

$$\langle \Psi_1^{4*} | \mathcal{H} | \Psi_0 \rangle + \left\langle \Psi_1^{4*} \left| \mathcal{H} \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle c_1 + \langle \Psi_1^{4*} | \mathcal{H} | \Psi_1^{3*} \rangle c_3 + \langle \Psi_1^{4*} | \mathcal{H} - E_0 | \Psi_1^{4*} \rangle c_4 = e_1 c_4 \quad (5.3.49)$$

where

$$\left\langle \Psi_0 \left| \mathcal{H} \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle = 2^{-1/2}\beta \quad (5.3.50)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{3*} \rangle = 0 \quad (5.3.51)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{4*} \rangle = 0 \quad (5.3.52)$$

$$\left\langle \begin{smallmatrix} * \\ 1 \end{smallmatrix} \left| \mathcal{H} - E_0 \right| \begin{smallmatrix} * \\ 1 \end{smallmatrix} \right\rangle = -2\beta \quad (5.3.53)$$

$$\langle \Psi_1^{3*} | \mathcal{H} - E_0 | \Psi_1^{3*} \rangle = \langle \Psi_1^{4*} | \mathcal{H} - E_0 | \Psi_1^{4*} \rangle = \alpha - \beta - E_0 = -2\beta \quad (5.3.54)$$

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

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

$$\langle \Psi_1^{3*} | \mathcal{H} | \Psi_1^{4*} \rangle = -\beta/2 \quad (5.3.57)$$

thus

$$2^{-1/2}\beta c_1 = e_1 \quad (5.3.58)$$

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

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

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

or

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

the eigenvalues are

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

rearrange the cubic equation, we get

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0 \quad (5.3.64)$$

$$e_1 = -2.4627\beta, -1.2760\beta, 0.2387\beta \quad (5.3.65)$$

so we take

$$e_1 = 0.2387\beta \quad (5.3.66)$$

Ex 5.20

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

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

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

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

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

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

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

$$\left\langle \Psi_0 \middle| \mathcal{H} \middle| \begin{smallmatrix} * \\ i \end{smallmatrix} \right\rangle = 2^{-1/2}\beta \tag{5.3.80}$$

while

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

If $i = j$,

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

else,

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

thus

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

Similar to Ex. 5.20, the SCI equations are

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

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

\therefore

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