

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

WSF

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## 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.**

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

**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

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

while

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

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}_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 \\
&= \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}_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 \quad (5.2.3)
\end{aligned}$$

### 5.2.3 Linear CCA and the Coupled-Electron Pair Approximation

#### Ex 5.12

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

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

thus

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

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

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

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

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

#### Ex 5.15

### 5.3.2 The Resonance Energy of Polyenes in Hückel Theory

**Ex 5.16**

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \quad (5.3.4)$$

the eigenvalues are

$$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta \quad (5.3.5)$$

while from Eq. 5.131, we get

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

i.e.

$$\{\varepsilon_i\} = \{\alpha + 2\beta, \alpha + \beta, \alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta, \} \quad (5.3.7)$$

which is identical to those eigenvalues.

The total energy is

$$\mathcal{E}_0 = 2(\alpha + 2\beta + \alpha + \beta + \alpha + \beta) \quad (5.3.8)$$

$$= 6\alpha + 8\beta \quad (5.3.9)$$

which agrees with Eq. 5.132.

**Ex 5.17** For Eq. 5.139

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

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

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

For Eq. 5.140

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

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



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

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

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

**Ex 5.18**

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

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

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

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

and we take

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

**Ex 5.19**

a)

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

Since

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{1*} \rangle = 0 \quad (5.3.24)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{2*} \rangle = \beta/2 \quad (5.3.25)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{j*} \rangle = 0 \quad (1 < j < n) \quad (5.3.26)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_1^{n*} \rangle = -\beta/2 \quad (5.3.27)$$

thus,

$$|\Psi_1\rangle = |\Psi_0\rangle + c \begin{vmatrix} * \\ 1 \end{vmatrix} \quad (5.3.28)$$

$$\begin{vmatrix} * \\ 1 \end{vmatrix} = 2^{-1/2} (|\Psi_1^{2*}\rangle - |\Psi_1^{n*}\rangle) \quad (5.3.29)$$

As before, we get

$$\left\langle \Psi_0 \left| \mathcal{H} \right| \begin{vmatrix} * \\ 1 \end{vmatrix} \right\rangle = 2^{-1/2} \beta \quad (5.3.30)$$

but

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

thus

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

$$\begin{aligned} E_R(\text{IEPA}) &= N e_1 \\ &= \left( -1 + \frac{\sqrt{6}}{2} \right) N \beta \\ &= 0.2247 N \beta \end{aligned} \quad (5.3.33)$$

b)

**Ex 5.20**

**Ex 5.21**