Modern Quantum Chemistry, Szabo & Ostlund HW

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Contents

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

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

b.

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

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

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

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

$\therefore$

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

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

(5.1.5) gives

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

(5.1.6) gives

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

Since

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

we have

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

Ex 5.3

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

5.1.1 Invariance under Unitary Transformations: An Example

Ex 5.4

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

Ex 5.5

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

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

Since

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

we have

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

Ex 5.6 Since

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

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

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

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.
$\therefore e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$.