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

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

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

Since

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

we have

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

Ex 5.6 Since

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

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

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

Thus the equations determining $e_{a\bar{b}}$ are identical to that of $e_{a\bar{a}}$. Similarly, $e_{\bar{a}b}$ shares the same equations with them.
$\therefore\ e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$.

Ex 5.7

a. As shown in Ex 5.5, 5.6

$$\langle \Psi_0 | \mathscr{H} | \Psi^{**}_{a\bar{a}} \rangle = \left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi^{**}_{a\bar{b}} \right\rangle = \langle \Psi_0 | \mathscr{H} | \Psi^{**}_{\bar{a}b} \rangle = 2^{-1/2}K_{12} \tag{5.1.20}$$

$$\langle \Psi^{**}_{a\bar{a}} | \mathscr{H} - E_0 | \Psi^{**}_{a\bar{a}} \rangle = \left\langle \Psi^{**}_{a\bar{b}} \middle| \mathscr{H} - E_0 \middle| \Psi^{**}_{a\bar{b}} \right\rangle = \langle \Psi^{**}_{\bar{a}b} | \mathscr{H} - E_0 | \Psi^{**}_{\bar{a}b} \rangle = 2\Delta' \tag{5.1.21}$$

Similarly, we get

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \Psi^{**}_{b\bar{b}} \right\rangle = 2^{-1/2}K_{12} \tag{5.1.22}$$

$$\left\langle \Psi^{**}_{b\bar{b}} \middle| \mathscr{H} - E_0 \middle| \Psi^{**}_{b\bar{b}} \right\rangle = 2\Delta' \tag{5.1.23}$$

For the rest,

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

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

Similarly, we get

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

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

thus the DCI equation is

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

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

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

and

$$
c_1 = c_2 = c_3 = c_4 = \frac{2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12}) + \sqrt{16(2^{-1/2}K_{12})^2 + [2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12})]^2}}{8 \times 2^{-1/2}K_{12}} \tag{5.1.30}
$$

Since

$$
2\Delta' = 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \tag{5.1.31}
$$

$$
2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \tag{5.1.32}
$$

we have

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

$\therefore$

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

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