Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

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Contents

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

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

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

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

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

$\therefore$

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

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

(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

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

Since

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

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

$$^2E_{\text{corr}}(\text{FO}) = \sum_i \frac{|\langle 1_i\bar{1}_i \,\|\, 2_i\bar{2}_i \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$= 2 \times \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{K_{12}^2}{(\varepsilon_1 - \varepsilon_2)} \tag{5.1.11}$$

5.1.1 Invariance under Unitary Transformations: An Example

Ex 5.4

$$|a\bar{a}b\bar{b}\rangle = 2^{-1/2}\big(|1_1\bar{a}b\bar{b}\rangle + |1_2\bar{a}b\bar{b}\rangle\big)$$

$$= 2^{-1}\big(|1_1\bar{1}_1b\bar{b}\rangle + |1_1\bar{1}_2b\bar{b}\rangle + |1_2\bar{1}_1b\bar{b}\rangle + |1_2\bar{1}_2b\bar{b}\rangle\big)$$

$$= 2^{-2}(|1_1\bar{1}_11_1\bar{1}_1\rangle - |1_1\bar{1}_11_1\bar{1}_2\rangle - |1_1\bar{1}_11_2\bar{1}_1\rangle + |1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$+ |1_1\bar{1}_21_1\bar{1}_1\rangle - |1_1\bar{1}_21_1\bar{1}_2\rangle - |1_1\bar{1}_21_2\bar{1}_1\rangle + |1_1\bar{1}_21_2\bar{1}_2\rangle$$

$$+ |1_2\bar{1}_11_1\bar{1}_1\rangle - |1_2\bar{1}_11_1\bar{1}_2\rangle - |1_2\bar{1}_11_2\bar{1}_1\rangle + |1_2\bar{1}_11_2\bar{1}_2\rangle$$

$$+ |1_2\bar{1}_21_1\bar{1}_1\rangle - |1_2\bar{1}_21_1\bar{1}_2\rangle - |1_2\bar{1}_21_2\bar{1}_1\rangle + |1_2\bar{1}_21_2\bar{1}_2\rangle)$$

$$= 2^{-2}(2|1_1\bar{1}_11_1\bar{1}_1\rangle + 2|1_1\bar{1}_11_2\bar{1}_2\rangle - 2|1_1\bar{1}_21_1\bar{1}_2\rangle - 2|1_1\bar{1}_21_2\bar{1}_1\rangle)$$

$$= 2^{-2}(2|1_1\bar{1}_11_2\bar{1}_2\rangle - 2|1_1\bar{1}_11_2\bar{1}_2\rangle)$$

$$= |1_1\bar{1}_11_2\bar{1}_2\rangle \tag{5.1.12}$$

Ex 5.5

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2^{-1/2}\big(\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle\big)$$

$$= 2^{-1/2}\left(2 \times \frac{1}{2}K_{12}\right)$$

$$= 2^{-1/2}K_{12} \tag{5.1.13}$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2^{-1}(\langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle$$

$$+ \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle)$$

$$= 2^{-1}\left[\left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11})\right.$$

$$+ \frac{1}{2}J_{22} + \frac{1}{2}J_{22}$$

$$+ \left.\left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11})\right]$$

$$= 2^{-1}\left(-2h_{11} + 2h_{22} - \frac{3}{2}J_{11} + J_{22} + 2J_{12} - K_{12}\right) \times 2$$

$$= -2h_{11} + 2h_{22} - \frac{3}{2}J_{11} + J_{22} + 2J_{12} - K_{12} \tag{5.1.14}$$

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

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

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

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

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

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{a}}^{**}\rangle = \langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{b}}^{**}\rangle = \langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{\bar{a}b}^{**}\rangle = 2^{-1/2}K_{12} \tag{5.1.20}$$

$$\langle\Psi_{a\bar{a}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{a}}^{**}\rangle = \langle\Psi_{a\bar{b}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{**}\rangle = \langle\Psi_{\bar{a}b}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{\bar{a}b}^{**}\rangle = 2\Delta' \tag{5.1.21}$$

Similarly, we get

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{b\bar{b}}^{**}\rangle = 2^{-1/2}K_{12} \tag{5.1.22}$$

$$\langle\Psi_{b\bar{b}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{**}\rangle = 2\Delta' \tag{5.1.23}$$

For the rest,

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

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

Similarly, we get

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

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

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

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

$\therefore$

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

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

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Ex 5.8

$$E_{\text{corr}}(\text{FO}) = \sum_{A<B} \sum_{R<S} \frac{|\langle AB \| RS \rangle|^2}{\varepsilon_A + \varepsilon_B - \varepsilon_R - \varepsilon_S}$$

$$= \frac{|\langle a\bar{a} \| r\bar{r} \rangle|^2 + |\langle a\bar{a} \| r\bar{s} \rangle|^2 + |\langle a\bar{a} \| s\bar{r} \rangle|^2 + |\langle a\bar{a} \| s\bar{s} \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} + \frac{|\langle a\bar{b} \| r\bar{r} \rangle|^2 + |\langle a\bar{b} \| r\bar{s} \rangle|^2 + |\langle a\bar{b} \| s\bar{r} \rangle|^2 + |\langle a\bar{b} \| s\bar{s} \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$+ \frac{|\langle b\bar{a} \| r\bar{r} \rangle|^2 + |\langle b\bar{a} \| r\bar{s} \rangle|^2 + |\langle b\bar{a} \| s\bar{r} \rangle|^2 + |\langle b\bar{a} \| s\bar{s} \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} + \frac{|\langle b\bar{b} \| r\bar{r} \rangle|^2 + |\langle b\bar{b} \| r\bar{s} \rangle|^2 + |\langle b\bar{b} \| s\bar{r} \rangle|^2 + |\langle b\bar{b} \| s\bar{s} \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$= \frac{|(ar|ar)|^2 + |(ar|as)|^2 + |(as|ar)|^2 + |(as|as)|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{|(ar|br)|^2 + |(ar|bs)|^2 + |(as|br)|^2 + |(as|bs)|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$+ \frac{|(br|ar)|^2 + |(br|as)|^2 + |(bs|ar)|^2 + |(bs|as)|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{|(br|br)|^2 + |(br|bs)|^2 + |(bs|br)|^2 + |(bs|bs)|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{\left|\frac{1}{2}K_{12}\right|^2 + 0 + 0 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{0 + \left|\frac{1}{2}K_{12}\right|^2 + \left|\frac{1}{2}K_{12}\right|^2 + 0}{2(\varepsilon_1 - \varepsilon_2)}$$

$$+ \frac{0 + 0 + \left|\frac{1}{2}K_{12}\right|^2 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{\left|\frac{1}{2}K_{12}\right|^2 + 0 + 0 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{2K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \tag{5.1.36}$$

Ex 5.9

a.

$$^2E_{\text{corr}}(\text{EN(L)}) = -\sum_{a<b} \sum_{r<s} \frac{|\langle \Psi_0 | \mathscr{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \mathscr{H} - E_0 | \Psi_{ab}^{rs} \rangle}$$

$$= - \tag{5.1.37}$$

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

$$|\Phi_0\rangle = |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} |2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} |1_1\bar{1}_1 2_2\bar{2}_2\rangle + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} |2_1\bar{2}_1 2_2\bar{2}_2\rangle$$

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

while

$$\exp\left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} \right) |1_1\bar{1}_1 1_2\bar{1}_2\rangle$$

$$= \tag{5.2.2}$$

5.2.3   Linear CCA and the Coupled-Electron Pair Approximation

Ex 5.12

5.2.4   Some Illustrative Calculations

5.3   Many-electron Theories with Single Particle Hamiltonians

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

Ex 5.17

Ex 5.18

Ex 5.19

Ex 5.20

Ex 5.21