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.

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

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

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

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

$\therefore$

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

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

(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

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

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

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

5.1.1   Invariance under Unitary Transformations: An Example

Ex 5.4

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

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

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

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

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

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

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

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

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

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

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

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

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

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,

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

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

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

$$= 2^{-1}\left[\left\langle \bar{r}\bar{b} \,\middle\|\, \bar{a}\bar{s} \right\rangle - \left\langle r\bar{b} \,\middle\|\, s\bar{a} \right\rangle + \left\langle s\bar{b} \,\middle\|\, r\bar{a} \right\rangle - \left\langle \bar{s}\bar{b} \,\middle\|\, \bar{a}\bar{r} \right\rangle\right]$$

$$= 2^{-1}[(ra|bs) - (rs|ba) - (rs|ba) - (sr|ba) + (sa|br) - (sr|ba)]$$

$$= 2^{-1}[(ra|bs) + (sa|br) - 4(ab|sr)]$$

$$= 2^{-1}\left[2 \times \frac{1}{2}K_{12} - 4 \times \frac{1}{2}J_{12}\right]$$

$$= \frac{1}{2}K_{12} - J_{12} \tag{5.1.25}$$

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

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

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

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

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

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

$\therefore$

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

$$= \Delta - \sqrt{2K_{12}^2 + \Delta^2} \tag{5.1.34}$$

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

$$= \frac{\Delta + \sqrt{2K_{12}^2 + \Delta^2}}{2\sqrt{2}K_{12}} \tag{5.1.35}$$

5

Ex 5.8

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

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

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

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

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

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

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

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