

# CHAPTER 5

## Pair and Coupled-Pair Theories

### 5.1 The Independent Electron Pair Approximation (IEPA)

#### Exercise 5.1

The application of pair theory to minimal basis  $H_2$  is trivial since we are dealing with a two-electron system for which the IEPA is exact, i.e., it gives the full CI result obtained in the last chapter, viz.

$${}^1E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

where (see Eq.(4.20))

$$\Delta = (\varepsilon_2 - \varepsilon_1) + \frac{1}{2}(J_{11} + J_{22} - 4J_{12} + 2K_{12}).$$

- a. Calculate the correlation energy using first-order pairs. Remember that the summations in Eq.(5.19) go over spin orbitals (i.e.,  $a = 1, \bar{1}$ , and  $r = 2, \bar{2}$ ). Show that

$${}^1E_{\text{corr}}(\text{FO}) = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}.$$

- b. Approximate  $\Delta$  in the exact correlation energy by  $\varepsilon_2 - \varepsilon_1$  and recover the first-order pair correlation energy by expanding the exact answer to first order using the relation  $(1 + x)^{1/2} \approx 1 + x/2$ .

#### Solution 5.1

- a. At this time, there is only one pair of electrons and one pair of virtual spin orbitals. Thus,

$$E_{\text{corr}}(\text{FO}) = \sum_{\substack{a < b \\ r < s}} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \frac{|\langle 1\bar{1} | 2\bar{2} \rangle|^2}{\varepsilon_1 + \varepsilon_{\bar{1}} - \varepsilon_2 - \varepsilon_{\bar{2}}} = -\frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)}. \quad (5.1-1)$$

- b. As  $K_{12} \ll \Delta$ , we find that

$${}^1E_{\text{corr}} = \Delta \left[ 1 - \sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \right] = \Delta \left[ 1 - \left( 1 + \frac{K_{12}^2}{2\Delta^2} + \dots \right) \right] = -\frac{K_{12}^2}{2\Delta} + \dots$$

Here, the truth that when  $|x| \ll 1$ ,

$$(1 + x)^{\frac{1}{2}} \approx 1 + \frac{x}{2},$$

has been used.

After substitute  $\Delta = \varepsilon_2 - \varepsilon_1$ , we obtain

$${}^1E_{\text{corr}}(\text{FO}) = -\frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}. \quad (5.1)$$

#### Exercise 5.2

Derive Eqs.(5.22a) and (5.22b).

**Solution 5.2**

From (5.9a), with  $\langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathcal{H} | \Psi_0 \rangle = \langle \Psi_0 | \mathcal{H} | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle = \langle 1_i \bar{1}_i | 2_i \bar{2}_i \rangle = K_{12}$ , we obtain

$$K_{12} c_{1_i \bar{1}_i}^{2_i \bar{2}_i} = e_{1_i \bar{1}_i}, \quad (5.2-1)$$

which is (5.22a). Similarly, with (4.20), we obtain

$$K_{12} + \langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathcal{H} - E_0 | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle = e_{1_i \bar{1}_i} c_{1_i \bar{1}_i}^{2_i \bar{2}_i} \quad (5.2-2)$$

which is (5.22b).

**Exercise 5.3**

Calculate the total first-order pair correlation energy for the dinner using Eq.(5.19) and show that it is twice the result obtained in Exercise 5.1.

**Solution 5.3**

Note that only  $|2_1 \bar{2}_1 1_2 \bar{1}_2\rangle$  and  $|1_1 \bar{1}_1 2_2 \bar{2}_2\rangle$  can interact with  $\langle \Phi_0 |$  via the Hamiltonian  $\mathcal{H}$ , thus

$$E_{\text{corr}}(\text{FO}, 2\text{H}_2) = \frac{\langle \Psi_0 | \mathcal{H} | 2_1 \bar{2}_1 1_2 \bar{1}_2 \rangle}{\varepsilon_1 + \varepsilon_{\bar{1}} - \varepsilon_2 - \varepsilon_{\bar{2}}} + \frac{\langle \Psi_0 | \mathcal{H} | 1_1 \bar{1}_1 2_2 \bar{2}_2 \rangle}{\varepsilon_1 + \varepsilon_{\bar{1}} - \varepsilon_2 - \varepsilon_{\bar{2}}} = -\frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} - \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} = 2E_{\text{corr}}(\text{FO}, \text{H}_2). \quad (5.3-1)$$

It is twice the result obtained in Exercise 5.1.

**5.1.1 Invariance under Unitary Transformations: An Example****Exercise 5.4**

Show that  $|a\bar{a}b\bar{b}\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle$ . *Hint:* use Eq.(1.40) repeatedly. Eq.(1.40) for Slater determinants is

$$|\chi_1 \chi_2 \cdots \left( \sum_k c_k \chi'_k \right) \cdots \chi_N\rangle = \sum_k c_k |\chi_1 \chi_2 \cdots \chi'_k \cdots \chi_N\rangle.$$

**Solution 5.4**

Note that if any two rows (or columns) of a determinant are equal, the value of the determinant is zero. Therefore, we find that

$$\begin{aligned} |a\bar{a}b\bar{b}\rangle &= \frac{1}{\sqrt{2}} (|1_1 \bar{a} b \bar{b}\rangle + |1_2 \bar{a} b \bar{b}\rangle) \\ &= \frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2}} |1_1 \bar{a} 1_1 \bar{b}\rangle - \frac{1}{\sqrt{2}} |1_1 \bar{a} 1_2 \bar{b}\rangle \right) + \frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2}} |1_2 \bar{a} 1_1 \bar{b}\rangle - \frac{1}{\sqrt{2}} |1_2 \bar{a} 1_2 \bar{b}\rangle \right) \\ &= -\frac{1}{2} |1_1 \bar{a} 1_2 \bar{b}\rangle + \frac{1}{2} |1_2 \bar{a} 1_1 \bar{b}\rangle = -|1_1 \bar{a} 1_2 \bar{b}\rangle \\ &= -\frac{1}{\sqrt{2}} (|1_1 \bar{1}_1 1_2 \bar{b}\rangle + |1_1 \bar{1}_2 1_2 \bar{b}\rangle) \\ &= -\frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2}} |1_1 \bar{1}_1 1_2 \bar{1}_1\rangle - \frac{1}{\sqrt{2}} |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle \right) - \frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2}} |1_1 \bar{1}_2 1_2 \bar{1}_1\rangle - \frac{1}{\sqrt{2}} |1_1 \bar{1}_2 1_2 \bar{1}_2\rangle \right) \\ &= \frac{1}{2} |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle - \frac{1}{2} |1_1 \bar{1}_2 1_2 \bar{1}_1\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle. \end{aligned}$$

Concisely,

$$|a\bar{a}b\bar{b}\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle. \quad (5.4-1)$$

**Exercise 5.5**

Derive Eqs.(5.31a) and (5.31b).

**Solution 5.5**

With (5.28a), (5.28b), and (5.29), we find that

$$\begin{aligned}\langle \Psi_0 | \mathcal{H} | \Psi_{aa}^{**} \rangle &= \langle \Psi_0 | \mathcal{H} | \left( \frac{1}{\sqrt{2}} |\Psi_{aa}^{r\bar{r}}\rangle + \frac{1}{\sqrt{2}} |\Psi_{aa}^{s\bar{s}}\rangle \right) \rangle = \frac{1}{\sqrt{2}} \langle \Psi_0 | \mathcal{H} | \Psi_{aa}^{r\bar{r}} \rangle + \frac{1}{\sqrt{2}} \langle \Psi_0 | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle \\ &= \frac{1}{\sqrt{2}} \frac{K_{12}}{2} + \frac{1}{\sqrt{2}} \frac{K_{12}}{2} = \frac{K_{12}}{\sqrt{2}}.\end{aligned}$$

This is (5.31a). From (4.17a) and (4.17d), we know that

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = 2(2h_{11} + J_{11}) = 4\varepsilon_1 - 2J_{11}.$$

And it is evident that

$$\begin{aligned}\langle \Psi_{aa}^{**} | \mathcal{H} | \Psi_{aa}^{**} \rangle &= \left( \frac{1}{\sqrt{2}} \langle \Psi_{aa}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{aa}^{s\bar{s}} | \right) \mathcal{H} \left( \frac{1}{\sqrt{2}} |\Psi_{aa}^{r\bar{r}}\rangle + \frac{1}{\sqrt{2}} |\Psi_{aa}^{s\bar{s}}\rangle \right) \\ &= \frac{1}{2} \langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{r\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{aa}^{r\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle.\end{aligned}$$

We have to calculate  $\langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{r\bar{r}} \rangle$ ,  $\langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle$  and  $\langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle$ . Before their formal derivation, note that

$$h_{rr} = h_{ss} = h_{22}, \quad h_{aa} = h_{bb} = h_{11}.$$

With (5.26a)-(5.26d), we obtain

$$\begin{aligned}\langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{r\bar{r}} \rangle &= \langle \Psi_{aa}^{r\bar{r}} | \mathcal{O}_1 | \Psi_{aa}^{r\bar{r}} \rangle + \langle \Psi_{aa}^{r\bar{r}} | \mathcal{O}_2 | \Psi_{aa}^{r\bar{r}} \rangle \\ &= \langle r|h|r \rangle + \langle \bar{r}|h|\bar{r} \rangle + \langle b|h|b \rangle + \langle \bar{b}|h|\bar{b} \rangle \\ &\quad + \langle r\bar{r}||r\bar{r} \rangle + \langle r\bar{b}||r\bar{b} \rangle + \langle r\bar{b}||r\bar{b} \rangle + \langle \bar{r}b||\bar{r}b \rangle + \langle \bar{r}\bar{b}||\bar{r}\bar{b} \rangle + \langle b\bar{b}||b\bar{b} \rangle \\ &= 2h_{rr} + 2h_{bb} + J_{rr} + (J_{rb} - K_{rb}) + J_{rb} + J_{rb} + (J_{rb} - K_{rb}) + J_{bb} \\ &= 2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12} \\ &= 2\varepsilon_1 + 2\varepsilon_2 - \frac{3}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12}.\end{aligned}$$

Similarly, we obtain that

$$\langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle = \langle r\bar{r}||s\bar{s} \rangle = J_{rs} = \frac{1}{2}J_{22},$$

and

$$\begin{aligned}\langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{aa}^{s\bar{s}} \rangle &= 2h_{ss} + 2h_{aa} + J_{ss} + J_{sb} - K_{sb} + J_{sb} + J_{sb} + J_{sb} - K_{sb} + J_{bb} \\ &= 2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}, \\ &= 2\varepsilon_1 + 2\varepsilon_2 - \frac{3}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12}.\end{aligned}$$

Hence,

$$\begin{aligned}\langle \Psi_{aa}^{**} | \mathcal{H} | \Psi_{aa}^{**} \rangle &= 2\varepsilon_1 + 2\varepsilon_2 - \frac{3}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12} + \frac{1}{2}J_{22} \\ &= 2\varepsilon_1 + 2\varepsilon_2 - \frac{3}{2}J_{11} + J_{22} - 2J_{12} + K_{12}, \\ \langle \Psi_{aa}^{**} | \mathcal{H} - E_0 | \Psi_{aa}^{**} \rangle &= 2\varepsilon_1 + 2\varepsilon_2 - \frac{3}{2}J_{11} + J_{22} - 2J_{12} + K_{12} - (4\varepsilon_1 - 2J_{11}) \\ &= 2(\varepsilon_2 - \varepsilon_1) + \frac{1}{2}J_{11} + J_{22} - 2J_{12} + K_{12}.\end{aligned}$$

In conclusion, we obtain

$$\langle \Psi_{aa}^{**} | \mathcal{H} | \Psi_{aa}^{**} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{22} + \frac{1}{2}(J_{11} - 4J_{12} + 2K_{12}) \equiv 2\Delta'. \quad (5.5-1)$$

This is (5.31b).

**Exercise 5.6**

Show that  $e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$ .

**Solution 5.6**

The key point is to prove that the equations which determine  $e_{a\bar{b}}$  are identical to that of  $e_{a\bar{a}}$ . Note that similar to Exercise 5.5, we can obtain

$$\begin{aligned}\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{**} \rangle &= \frac{K_{12}}{\sqrt{2}}, \\ \langle \Psi_{ab}^{**} | \mathcal{H} | \Psi_{ab}^{**} \rangle &= 2\Delta'.\end{aligned}$$

Thus the equations of  $e_{a\bar{b}}$  are

$$\begin{aligned}\frac{K_{12}}{\sqrt{2}}c &= e_{a\bar{b}}, \\ \frac{K_{12}}{\sqrt{2}} + 2\Delta'c &= e_{a\bar{b}}c.\end{aligned}$$

They are identical to that of  $e_{a\bar{a}}$ , thus  $e_{a\bar{b}} = e_{a\bar{a}}$  and so does  $e_{\bar{a}b}$ .

**Exercise 5.7**

Show that DCI is invariant to unitary transformations for the above model.

a. The DCI wave function is

$$|\Psi_{\text{DCI}}\rangle = |\Psi_0\rangle + c_1|\Psi_{a\bar{a}}^{**}\rangle + c_2|\Psi_{b\bar{b}}^{**}\rangle + c_3|\Psi_{a\bar{b}}^{**}\rangle + c_4|\Psi_{\bar{a}b}^{**}\rangle.$$

Show that the corresponding eigenvalue problem which determines the DCI correlation energy of the dimer ( ${}^2E_{\text{corr}}(\text{DCI})$ ) is

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

b. Show that  $c_1 = c_2 = c_3 = c_4 = c$  and then solve the equations to show

$${}^2E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + 2K_{12}^2)^{1/2},$$

which is the same result as found in the last chapter (see Eq.(4.60)).

**Solution 5.7**

a. Some matrix elements have been solved in Exercise 5.5 and Exercise 5.6, and they are listed as follows.

$$\begin{aligned}\langle \Psi_0 | \mathcal{H} - E_0 | \Psi_0 \rangle &= 0, \\ \langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle &= \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_0 | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle &= \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle &= \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_0 | \mathcal{H} | \Psi_{\bar{a}b}^{**} \rangle &= \langle \Psi_{\bar{a}b}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle &= 2\Delta', \\ \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{b\bar{b}}^{**} \rangle &= 2\Delta',\end{aligned}$$



$$= \frac{1}{2} (\langle \bar{a}b | \bar{b}a \rangle + 0 + 0 + \langle \bar{a}b | \bar{b}a \rangle) = \frac{1}{2} (K_{ab} + K_{ab}) = \frac{1}{2} J_{11}.$$

Thus, the corresponding DCI eigenvalue problem is

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}}K_{12} & \frac{1}{\sqrt{2}}K_{12} & \frac{1}{\sqrt{2}}K_{12} & \frac{1}{\sqrt{2}}K_{12} \\ \frac{1}{\sqrt{2}}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{\sqrt{2}}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{\sqrt{2}}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{\sqrt{2}}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = {}^2E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}. \quad (5.7-1)$$

b. From (5.7-1), we know that

$$\begin{aligned} \frac{K_{12}}{\sqrt{2}} + 2\Delta'c_1 + \frac{J_{11}}{2}c_2 + \frac{K_{12} - J_{12}}{2}c_3 + \frac{K_{12} - J_{12}}{2}c_4 &= {}^2E_{\text{corr}}(\text{DCI})c_1, \\ \frac{K_{12}}{\sqrt{2}} + \frac{J_{11}}{2}c_1 + 2\Delta'c_2 + \frac{K_{12} - J_{12}}{2}c_3 + \frac{K_{12} - J_{12}}{2}c_4 &= {}^2E_{\text{corr}}(\text{DCI})c_2. \end{aligned}$$

The first equation can be subtracted by the second one, viz.,

$$(2\Delta' - \frac{J_{11}}{2} - {}^2E_{\text{corr}}(\text{DCI}))(c_1 - c_2) = 0.$$

Assume that  ${}^2E_{\text{corr}}(\text{DCI}) \neq 2\Delta' - \frac{J_{11}}{2}$  (in fact, this holds true), we find that

$$c_1 = c_2.$$

In this way, we can prove  $c_1 = c_2 = c_3 = c_4$ . In fact, we can permute 1 and 2 of the second equation of (5.7-1), then we will find that the third equation of (5.7-1) is obtained, and vice versa. Thus  $c_1 = c_2$ . This method is suitable for not only  $c_1$  and  $c_2$ , but also  $c_1$  and  $c_3$ ,  $c_1$  and  $c_4$ . Hence we can also conclude that  $c_1 = c_2 = c_3 = c_4$ .

Thus, we set  $c_1 = c$ , thus

$$\begin{aligned} {}^2E_{\text{corr}}(\text{DCI}) &= 2\sqrt{2}K_{12}c, \\ {}^2E_{\text{corr}}(\text{DCI})c &= \frac{K_{12}}{\sqrt{2}} + (2\Delta' + \frac{1}{2}J_{11} + \frac{1}{2}K_{12} - J_{12} + \frac{1}{2}K_{12} - J_{12})c = \frac{K_{12}}{\sqrt{2}} + 2\Delta c. \end{aligned}$$

In fact, they can be converted to a quadratic equation,

$$({}^2E_{\text{corr}}(\text{DCI}))^2 - 2\Delta({}^2E_{\text{corr}}(\text{DCI})) - 2K_{12}^2 = 0,$$

The discriminant  $\Delta_E$  of this quadratic equation is

$$\Delta_E = (-2\Delta)^2 - 4 \times 1 \times (-2K_{12}^2) = 4(\Delta^2 + 2K_{12}^2) > 0,$$

and the root are

$$E_1 = \Delta + \sqrt{\Delta^2 + 2K_{12}^2}, \quad E_2 = \Delta - \sqrt{\Delta^2 + 2K_{12}^2}.$$

Therefore, the lowest root is the correlation energy, viz.,

$${}^2E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + 2K_{12}^2}. \quad (5.7-2)$$

which is the same result as found in the last chapter (see Eq.(4.60)).

### Exercise 5.8

Show directly from Eq.(5.19) using delocalized orbitals and the two-electron integrals in Eq.(5.26) that the total first-order pair correlation energy (which is the same as the many-body second-order perturbation energy) of the dimer is given by Eq.(5.46).

**Solution 5.8**

In fact, from Eq.(5.18) using delocalized orbitals and the two-electron integrals in Eq.(5.26), it is also easy to derive the the total first-order pair correlation energy. However, I think this method is much better because it shows the absence of  $e_{aa}^{\text{FO}}$  and  $e_{bb}^{\text{FO}}$  as their corresponding configurations are *ungerade* while  $\Psi_0$  is *gerade*. Thus I will firstly show  $e_{ab}^{\text{FO}}$ ,  $e_{ab}^{\text{FO}}$ ,  $e_{ba}^{\text{FO}}$ ,  $e_{bb}^{\text{FO}}$  and then calculate  ${}^2E_{\text{corr}}(\text{FO}(D))$ . Note that the integrals, which have three *gerade* orbitals and one *ungerade* orbital, or three *ungerade* orbitals and one *gerade* orbital, vanish. Thus,

$$\begin{aligned} e_{aa}^{\text{FO}} &= \frac{|\langle a\bar{a}||r\bar{r}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{a}} - \varepsilon_r - \varepsilon_{\bar{r}}} + \frac{|\langle a\bar{a}||s\bar{s}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{a}} - \varepsilon_s - \varepsilon_{\bar{s}}} + \frac{|\langle a\bar{a}||r\bar{s}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{a}} - \varepsilon_r - \varepsilon_{\bar{s}}} + \frac{|\langle a\bar{a}||s\bar{r}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{a}} - \varepsilon_s - \varepsilon_{\bar{r}}} \\ &= \frac{1}{2(\varepsilon_1 - \varepsilon_2)} \left( \frac{1}{4}K_{12}^2 + \frac{1}{4}K_{12}^2 + 0 + 0 \right) = \frac{K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)}. \end{aligned}$$

Similarly, we obtain

$$\begin{aligned} e_{ab}^{\text{FO}} &= \frac{|\langle a\bar{b}||r\bar{r}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_r - \varepsilon_{\bar{r}}} + \frac{|\langle a\bar{b}||s\bar{s}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_s - \varepsilon_{\bar{s}}} + \frac{|\langle a\bar{b}||r\bar{s}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_r - \varepsilon_{\bar{s}}} + \frac{|\langle a\bar{b}||s\bar{r}\rangle|^2}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_s - \varepsilon_{\bar{r}}} = \frac{K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)}, \\ e_{ba}^{\text{FO}} &= \frac{|\langle b\bar{a}||r\bar{r}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{a}} - \varepsilon_r - \varepsilon_{\bar{r}}} + \frac{|\langle b\bar{a}||s\bar{s}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{a}} - \varepsilon_s - \varepsilon_{\bar{s}}} + \frac{|\langle b\bar{a}||r\bar{s}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{a}} - \varepsilon_r - \varepsilon_{\bar{s}}} + \frac{|\langle b\bar{a}||s\bar{r}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{a}} - \varepsilon_s - \varepsilon_{\bar{r}}} = \frac{K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)}, \\ e_{bb}^{\text{FO}} &= \frac{|\langle b\bar{b}||r\bar{r}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{b}} - \varepsilon_r - \varepsilon_{\bar{r}}} + \frac{|\langle b\bar{b}||s\bar{s}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{b}} - \varepsilon_s - \varepsilon_{\bar{s}}} + \frac{|\langle b\bar{b}||r\bar{s}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{b}} - \varepsilon_r - \varepsilon_{\bar{s}}} + \frac{|\langle b\bar{b}||s\bar{r}\rangle|^2}{\varepsilon_b + \varepsilon_{\bar{b}} - \varepsilon_s - \varepsilon_{\bar{r}}} = \frac{K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)}. \end{aligned}$$

Thus

$${}^2E_{\text{corr}}(\text{FO}(D)) = e_{aa}^{\text{FO}} + e_{ab}^{\text{FO}} + e_{ba}^{\text{FO}} + e_{bb}^{\text{FO}} = \frac{K_{12}^2}{\varepsilon_1 - \varepsilon_2} = 2 \left( \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \right). \quad (5.8-1)$$

**Exercise 5.9**

Show that the total correlation energy obtained using Epstein-Nesbet pairs is not invariant to unitary transformations.

- a. Show, using localized orbitals, that

$${}^2E_{\text{corr}}(\text{EN}(L)) = -\frac{K_{12}^2}{\Delta}.$$

- b. Show, using delocalized spin-orbital pairs, that

$${}^2E_{\text{corr}}(\text{EN}(D)) = -\frac{K_{12}^2}{\Delta'}.$$

- c. Show, using delocalized spin-adapted pairs, that

$${}^2E_{\text{corr}}^{\text{singlet}}(\text{EN}(D)) = -\frac{K_{12}^2}{2\Delta'} - \frac{K_{12}^2}{2\Delta''}.$$

- d. Using the STO-3G integrals for  $\text{H}_2$  in Appendix D compare the numerical values of the above expressions at  $R = 1.4$  a.u.

**Solution 5.9**

5-9 so