

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 Δ 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

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

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

$$\langle \Psi_{aa}^{**} | \mathcal{H} - E_0 | \Psi_{aa}^{**} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{22} + \frac{1}{2}(J_{11} - 4J_{12} + 2K_{12}) \equiv 2\Delta'. \quad (5.5-1)$$

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

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

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.

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

$$\begin{aligned}\langle \Psi_{a\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle &= 2\Delta', \\ \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle &= 2\Delta'.\end{aligned}$$

Now we pay attention to calculate other matrix elements.

$$\begin{aligned}\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{b\bar{b}}^{s\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{b\bar{b}}^{s\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{b\bar{b}}^{s\bar{s}} \rangle \\ &= \frac{1}{2} (\langle b\bar{b} | a\bar{a} \rangle + 0 + 0 + \langle b\bar{b} | a\bar{a} \rangle) = \frac{1}{2} (K_{ab} + K_{ab}) = K_{ab} = \frac{1}{2} J_{11}, \\ \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle &= (\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle)^* = \frac{1}{2} J_{11}, \\ \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle \\ &= \frac{1}{2} (\langle \bar{r}\bar{b} | \bar{a}\bar{s} \rangle - \langle \bar{r}\bar{b} | s\bar{a} \rangle - \langle \bar{s}\bar{b} | r\bar{a} \rangle + \langle \bar{s}\bar{b} | \bar{a}\bar{r} \rangle) \\ &= \frac{1}{2} ((ra|bs) - (rs|ba) - (rs|ba) - (sr|ba) + (sa|br) - (sr|ba)) \\ &= \frac{1}{2} \left(\frac{K_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} \right) = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle &= (\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle)^* = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle \\ &= \frac{1}{2} (-\langle \bar{r}\bar{b} | \bar{s}\bar{a} \rangle + \langle \bar{r}\bar{b} | as \rangle + \langle \bar{s}\bar{b} | ar \rangle - \langle \bar{s}\bar{b} | \bar{r}\bar{a} \rangle) \\ &= \frac{1}{2} (-(rs|ba) + (ra|bs) - (rs|ba) + (sa|br) - (sr|ba) - (sr|ba)) \\ &= \frac{1}{2} \left(-\frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} \right) = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle &= (\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle)^* = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{b\bar{b}}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle \\ &= \frac{1}{2} (-\langle a\bar{r} | b\bar{s} \rangle + \langle ar | sb \rangle + \langle as | rb \rangle - \langle a\bar{s} | b\bar{r} \rangle) \\ &= \frac{1}{2} (-(ab|rs) + (as|rb) - (ab|rs) + (ar|sb) - (ab|sr) - (ab|sr)) \\ &= \frac{1}{2} \left(-\frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} \right) = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle &= (\langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle)^* = \frac{1}{2} K_{12} - J_{12}, \\ \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{b\bar{b}}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{a\bar{b}}^{r\bar{s}} \rangle \\ &= \frac{1}{2} (\langle \bar{a}\bar{r} | \bar{s}\bar{b} \rangle - \langle \bar{a}\bar{r} | \bar{b}\bar{s} \rangle - \langle \bar{a}\bar{s} | \bar{b}\bar{r} \rangle + \langle \bar{a}\bar{s} | \bar{r}\bar{b} \rangle) \\ &= \frac{1}{2} ((as|rb) - (ab|rs) - (ab|rs) - (ab|sr) + (ar|sb) - (ab|sr))\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \left(\frac{K_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} - \frac{J_{12}}{2} + \frac{K_{12}}{2} - \frac{J_{12}}{2} \right) = \frac{1}{2} K_{12} - J_{12}, \\
\langle \Psi_{ab}^{**} | \mathcal{H} | \Psi_{bb}^{**} \rangle &= (\langle \Psi_{bb}^{**} | \mathcal{H} | \Psi_{ab}^{**} \rangle)^* = \frac{1}{2} K_{12} - J_{12}, \\
\langle \Psi_{ab}^{**} | \mathcal{H} | \Psi_{ab}^{**} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{ab}^{r\bar{s}} | + \frac{1}{\sqrt{2}} \langle \Psi_{ab}^{s\bar{r}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{ab}^{s\bar{r}} \rangle \right) \\
&= \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{ab}^{s\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{ab}^{s\bar{r}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle \\
&= \frac{1}{2} (\langle \bar{a}b | \bar{b}a \rangle + 0 + 0 + \langle \bar{a}b | \bar{b}a \rangle) = \frac{1}{2} (K_{ab} + K_{ab}) = \frac{1}{2} J_{11}, \\
\langle \Psi_{ab}^{**} | \mathcal{H} | \Psi_{ab}^{**} \rangle &= (\langle \Psi_{ab}^{**} | \mathcal{H} | \Psi_{ab}^{**} \rangle)^* = \frac{1}{2} J_{11}.
\end{aligned}$$

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 Δ_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}^{FO} and e_{bb}^{FO} as their corresponding configurations are *ungerade* while Ψ_0 is *gerade*. Thus I will firstly show e_{ab}^{FO} , $e_{a\bar{b}}^{\text{FO}}$, $e_{b\bar{a}}^{\text{FO}}$, $e_{b\bar{b}}^{\text{FO}}$ 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,

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

Similarly, we obtain

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

Thus

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

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 H_2 in Appendix D compare the numerical values of the above expressions at $R = 1.4$ a.u..

Solution 5.9

a. From Exercise 5.2, we know

$$\begin{aligned} \langle \Psi_0 | \mathcal{H} | \Psi_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} \rangle &= \langle \Psi_0 | \mathcal{H} | \Psi_{1_2 \bar{1}_2}^{2_2 \bar{2}_2} \rangle = K_{12}, \\ \langle \Psi_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} | \mathcal{H} - E_0 | \Psi_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} \rangle &= \langle \Psi_{1_2 \bar{1}_2}^{2_2 \bar{2}_2} | \mathcal{H} - E_0 | \Psi_{1_2 \bar{1}_2}^{2_2 \bar{2}_2} \rangle = 2\Delta, \end{aligned}$$

thus we obtain that

$$e_{1_1\bar{1}_1}^{\text{EN}} = -\frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \rangle|^2}{\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} | \mathcal{H} - E_0 | \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \rangle} = -\frac{K_{12}^2}{2\Delta},$$

$$e_{1_2\bar{1}_2}^{\text{EN}} = -\frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} \rangle|^2}{\langle \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} | \mathcal{H} - E_0 | \Psi_{1_2\bar{1}_2}^{2_2\bar{2}_2} \rangle} = -\frac{K_{12}^2}{2\Delta}.$$

Therefore, with (5.16), we find that

$${}^2E_{\text{corr}}(\text{EN}(L)) = e_{1_1\bar{1}_1}^{\text{EN}} + e_{1_2\bar{1}_2}^{\text{EN}} = -\frac{K_{12}^2}{\Delta}. \quad (5.9-1)$$

b. From Exercise 5.5, we know

$$\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle = \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{K_{12}}{\sqrt{2}},$$

$$\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{22} + \frac{1}{2}(J_{11} - 4J_{12} + 2K_{12}) \equiv 2\Delta',$$

thus we obtain that

$$e_{a\bar{a}}^{\text{EN}} = -\frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle|^2}{\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle} = -\frac{K_{12}^2}{4\Delta'}.$$

As described in the textbook, $e_{b\bar{b}}^{\text{EN}}$ equals $e_{a\bar{a}}^{\text{EN}}$ due to the high symmetry of this problem. Besides, in Exercise 5.6, we know that

$$\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle = \langle \Psi_{a\bar{b}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{K_{12}}{\sqrt{2}},$$

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

and thus

$$e_{a\bar{b}}^{\text{EN}} = -\frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{b}}^{**} \rangle|^2}{\langle \Psi_{a\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{b}}^{**} \rangle} = -\frac{K_{12}^2}{4\Delta'}.$$

Similarly, we know $e_{a\bar{b}}^{\text{EN}} = e_{a\bar{b}}^{\text{EN}}$. Hence, we find that

$${}^2E_{\text{corr}}(\text{EN}(D)) = e_{a\bar{a}}^{\text{EN}} + e_{a\bar{b}}^{\text{EN}} + e_{a\bar{b}}^{\text{EN}} + e_{b\bar{b}}^{\text{EN}} = -\frac{K_{12}^2}{\Delta'}. \quad (5.9-2)$$

c. From (5.42a) and (5.42b), we know that

$$\langle \Psi_0 | \mathcal{H} | {}^B\Psi_{a\bar{b}}^{rs} \rangle = \langle {}^B\Psi_{a\bar{b}}^{rs} | \mathcal{H} | \Psi_0 \rangle = K_{12},$$

$$\langle {}^B\Psi_{a\bar{b}}^{rs} | \mathcal{H} - E_0 | {}^B\Psi_{a\bar{b}}^{rs} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 2J_{12} + K_{12} \equiv 2\Delta'',$$

and thus,

$$e_{a\bar{b}}^{\text{singlet,EN}} = -\frac{|\langle \Psi_0 | \mathcal{H} | {}^B\Psi_{a\bar{b}}^{rs} \rangle|^2}{\langle {}^B\Psi_{a\bar{b}}^{rs} | \mathcal{H} - E_0 | {}^B\Psi_{a\bar{b}}^{rs} \rangle} = -\frac{K_{12}^2}{2\Delta''}.$$

Therefore, we obtain that

$${}^2E_{\text{corr}}^{\text{singlet}}(\text{EN}(D)) = e_{a\bar{a}}^{\text{EN}} + e_{b\bar{b}}^{\text{EN}} + e_{a\bar{b}}^{\text{singlet,EN}} = -\frac{K_{12}^2}{2\Delta'} - \frac{K_{12}^2}{2\Delta''}. \quad (5.9-3)$$

d. As $R = 1.4$ a.u., we know that

$$\begin{aligned} \varepsilon_1 &= -0.5782 \text{ a.u.}, & \varepsilon_2 &= 0.6703 \text{ a.u.}, & J_{11} &= 0.6746 \text{ a.u.}, \\ J_{12} &= 0.6636 \text{ a.u.}, & J_{22} &= 0.6975 \text{ a.u.}, & K_{12} &= 0.1813 \text{ a.u.} \end{aligned}$$

Thus, we obtain that

$$\begin{aligned}\Delta &= \varepsilon_2 - \varepsilon_1 + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12} = 0.78865 \text{ a.u.}, \\ \Delta' &= \varepsilon_2 - \varepsilon_1 + \frac{1}{4}J_{11} + \frac{1}{2}J_{22} - J_{12} + \frac{1}{2}K_{12} = 1.19295 \text{ a.u.}, \\ \Delta'' &= \varepsilon_2 - \varepsilon_1 + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} - J_{12} + \frac{1}{2}K_{12} = 1.3616 \text{ a.u.},\end{aligned}$$

Finally, we get that

$$\begin{aligned}{}^2E_{\text{corr}}(\text{EN}(L)) &= -0.04168 \text{ a.u.}, \\ {}^2E_{\text{corr}}(\text{EN}(D)) &= -0.02755 \text{ a.u.}, \\ {}^2E_{\text{corr}}^{\text{singlet}}(\text{EN}(D)) &= -0.02585 \text{ a.u.}\end{aligned}$$

Now we conclude that the Epstein-Nesbet pair theory is not only variant to unitary transformations of degenerate HF orbitals, but also gives different answers depending on whether one uses spin-orbital or spin-adapted pair functions.

Exercise 5.10

The DCI wave function for the H_2 dimer using spin-adapted configurations is

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

Show that the corresponding DCI eigenvalue problem is

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

and then solve the resulting equations to show that

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

Solution 5.10

From Exercise 5.7 and Exercise 5.9, we know that

$$\begin{aligned}\langle \Psi_0 | \mathcal{H} - E_0 | \Psi_0 \rangle &= 0, \\ \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} - E_0 | \Psi_{a\bar{a}}^{**} \rangle &= 2\Delta', \\ \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} - E_0 | \Psi_{b\bar{b}}^{**} \rangle &= 2\Delta', \\ \langle {}^B\Psi_{ab}^{rs} | \mathcal{H} - E_0 | {}^B\Psi_{ab}^{rs} \rangle &= 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 2J_{12} + K_{12} = 2\Delta'', \\ \langle \Psi_0 | \mathcal{H} | \Psi_{a\bar{a}}^{**} \rangle &= \langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_0 | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle &= \langle \Psi_{b\bar{b}}^{**} | \mathcal{H} | \Psi_0 \rangle = \frac{1}{\sqrt{2}}K_{12}, \\ \langle \Psi_0 | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle &= \langle {}^B\Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle = K_{12}.\end{aligned}$$

Thus, we pay attention to calculating $\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle$, $\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | {}^B\Psi_{ab}^{rs} \rangle$.

$$\begin{aligned}\langle \Psi_{a\bar{a}}^{**} | \mathcal{H} | \Psi_{b\bar{b}}^{**} \rangle &= \left(\frac{1}{\sqrt{2}}\langle \Psi_{a\bar{a}}^{r\bar{r}} | + \frac{1}{\sqrt{2}}\langle \Psi_{a\bar{a}}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{\sqrt{2}}| \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{\sqrt{2}}| \Psi_{b\bar{b}}^{s\bar{s}} \rangle \right) \\ &= \frac{1}{2}\langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{2}\langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{b\bar{b}}^{s\bar{s}} \rangle + \frac{1}{2}\langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{b\bar{b}}^{r\bar{r}} \rangle + \frac{1}{2}\langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{b\bar{b}}^{s\bar{s}} \rangle \\ &= \frac{1}{2}(\langle b\bar{b} | | a\bar{a} \rangle + 0 + 0 + \langle b\bar{b} | | a\bar{a} \rangle) = \frac{1}{2}(K_{ba} + K_{ba}) = K_{ab} = \frac{1}{2}J_{11},\end{aligned}$$

$$\begin{aligned}
\langle \Psi_{aa}^{**} | \mathcal{H} |^B \Psi_{ab}^{rs} \rangle &= \left(\frac{1}{\sqrt{2}} \langle \Psi_{aa}^{r\bar{r}} | + \frac{1}{\sqrt{2}} \langle \Psi_{aa}^{s\bar{s}} | \right) \mathcal{H} \left(\frac{1}{2} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} | \Psi_{ab}^{s\bar{r}} \rangle \right) \\
&= \frac{1}{2\sqrt{2}} [\langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{aa}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle \\
&\quad + \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \langle \Psi_{aa}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle] \\
&= \frac{1}{2\sqrt{2}} (-\langle \bar{r}b | | \bar{s}a \rangle + \langle rb | | as \rangle + \langle \bar{r}\bar{b} | | \bar{a}\bar{s} \rangle - \langle r\bar{b} | | s\bar{a} \rangle \\
&\quad + \langle sb | | ar \rangle - \langle \bar{s}b | | \bar{r}a \rangle - \langle s\bar{b} | | r\bar{a} \rangle + \langle \bar{s}\bar{b} | | \bar{a}\bar{r} \rangle) \\
&= \frac{1}{2\sqrt{2}} (-\langle rs | ba \rangle + \langle ra | bs \rangle - \langle rs | ba \rangle + \langle ra | bs \rangle - \langle rs | ba \rangle - \langle rs | ba \rangle \\
&\quad + \langle sa | br \rangle - \langle sr | ba \rangle - \langle sr | ba \rangle - \langle sr | ba \rangle + \langle sa | br \rangle - \langle sr | ba \rangle) \\
&= \frac{1}{2\sqrt{2}} \left(-8 \times \frac{J_{12}}{2} + 4 \times \frac{K_{12}}{2} \right) = -\sqrt{2}J_{12} + \frac{1}{\sqrt{2}}K_{12} = \frac{1}{\sqrt{2}}(K_{12} - 2J_{12}).
\end{aligned}$$

Due to the high symmetry of this problem, we find that

$$\langle \Psi_{bb}^{**} | \mathcal{H} |^B \Psi_{ab}^{rs} \rangle = \langle \Psi_{aa}^{**} | \mathcal{H} |^B \Psi_{ab}^{rs} \rangle = \frac{1}{\sqrt{2}}(K_{12} - 2J_{12}).$$

and

$$\begin{aligned}
\langle \Psi_{bb}^{**} | \mathcal{H} | \Psi_{aa}^{**} \rangle &= (\langle \Psi_{aa}^{**} | \mathcal{H} | \Psi_{bb}^{**} \rangle)^* = \frac{1}{2}J_{11}, \\
\langle {}^B \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{aa}^{**} \rangle &= (\langle \Psi_{aa}^{**} | \mathcal{H} |^B \Psi_{ab}^{rs} \rangle)^* = \frac{1}{\sqrt{2}}(K_{12} - 2J_{12}). \\
\langle {}^B \Psi_{ab}^{rs} | \mathcal{H} | \Psi_{bb}^{**} \rangle &= (\langle \Psi_{bb}^{**} | \mathcal{H} |^B \Psi_{ab}^{rs} \rangle)^* = \frac{1}{\sqrt{2}}(K_{12} - 2J_{12}).
\end{aligned}$$

Thus, we obtain the corresponding DCI eigenvalue problem is

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

In the same way, it is evident that $c_1 = c_2$. Let $c_1 = c$ and then, the matrix can be converted into

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

Note that a minor of the coefficient matrix is zero, viz.,

$$\begin{vmatrix} \sqrt{2}K_{12} & K_{12} \\ 2\Delta - {}^2E_{\text{corr}}(\text{DCI}) & \frac{1}{\sqrt{2}}(2\Delta - {}^2E_{\text{corr}}(\text{DCI})) \end{vmatrix} = 0,$$

and we conclude that the first two equations are linearly dependent if c and c_3 exist. Thus,

$$\frac{{}^2E_{\text{corr}}(\text{DCI})}{\sqrt{2}K_{12}} = -\frac{\sqrt{2}K_{12}}{2\Delta - {}^2E_{\text{corr}}(\text{DCI})} \Leftrightarrow ({}^2E_{\text{corr}}(\text{DCI}))^2 - 2\Delta({}^2E_{\text{corr}}(\text{DCI})) - 2K_{12}^2 = 0.$$

The discriminant Δ_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 lowest root is

$${}^2E_{\text{corr}}(\text{DCI}) = \Delta - \sqrt{\Delta^2 + 2K_{12}^2}. \quad (5.10-1)$$

As the textbook mentioned, the DCI gives the same answer regardless of using spin-orbital or spin-adapted pair functions.

5.1.2 Some Illustrative Calculations

5.2 Coupled-Pair Theories

5.2.1 The Coupled Cluster Approximation (CCA)

5.2.2 The Cluster Expansion of the Wave Function

Exercise 5.11

Show that the wave function two independent H₂ molecules in Eqs.(5.49) and (5.50) can be written as

$$|\Phi\rangle = \exp(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}) |1_1\bar{1}_1 1_2\bar{1}_2\rangle.$$

Solution 5.11

It is evident that

$$\begin{aligned} |\Phi\rangle &= \exp(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}) |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\ &= (1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2} + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}) |1_1\bar{1}_1 1_2\bar{1}_2\rangle \\ &= |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} |2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} |1_1\bar{1}_1 2_2\bar{2}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1} c_{1_2\bar{1}_2}^{2_2\bar{2}_2} |2_1\bar{2}_1 2_2\bar{2}_2\rangle, \end{aligned}$$

which equals (5.49) and (5.50).

5.2.3 Linear CCA and the Coupled Electron Pair Approximation (CEPA)

Exercise 5.12

- Show that if the matrix \mathbf{D} is approximated by its diagonal elements, the L-CCA correlation energy is identical to the result obtained using Epstein-Nesbet pairs (i.e., Eqs.(5.15) and (5.16)).
- Show that linear CCA is invariant under unitary transformations for the problem of two independent H₂ molecules. First show that for this model the correlation energy of the dimer using localized orbitals is the same as that obtained in Exercise 5.9a. Then show using delocalized spin orbitals that, in contrast to the results of Exercise 5.9, one gets the same correlation energy. You will find the DCI matrix given in Exercise 5.7 useful.

Solution 5.12

- If the matrix \mathbf{D} is approximated by its diagonal elements, their mathematical expression will be

$$(\mathbf{D})_{rasb,tcud} = \delta_{rs,tu} \delta_{ab,cd} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle.$$

It is evident that the mathematical expression of matrix elements of \mathbf{D}^{-1} is

$$(\mathbf{D}^{-1})_{rasb,tcud} = \frac{\delta_{rs,tu} \delta_{ab,cd}}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle}.$$

Thus, at this time, the L-CCA correlation energy is

$$\begin{aligned} E_{\text{corr}}(\text{L-CCA}(\text{diagonal } \mathbf{D})) &= - \sum_{\substack{a < b \\ r < s}} \sum_{\substack{c < d \\ t < u}} \mathbf{B}_{rasb}^\dagger (\mathbf{D}^{-1})_{rasb,tcud} \mathbf{B}_{tcud} \\ &= - \sum_{\substack{a < b \\ r < s}} \sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle \frac{\delta_{rs,tu} \delta_{ab,cd}}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle} \langle \Psi_{cd}^{tu} | \mathcal{H} | \Psi_0 \rangle \\ &= - \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle}. \end{aligned}$$

However, the (5.15) and (5.16) gives

$$E_{\text{corr}}(\text{EN}) = \sum_{a < b} e_{ab}^{\text{EN}} = \sum_{a < b} \left(- \sum_{r < s} \frac{|\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle|^2}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle} \right) = - \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle}{\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{ab}^{rs} \rangle}.$$

In conclusion, if the matrix \mathbf{D} is approximated by its diagonal elements, the L-CCA correlation energy is identical to the result obtained using Epstein-Nesbet pairs.

b. When localized orbitals are used, based on $|2_1\bar{2}_11_2\bar{1}_2\rangle$ and $|1_1\bar{1}_12_2\bar{2}_2\rangle$, its \mathbf{B} and \mathbf{D} are

$$\mathbf{B} = \begin{pmatrix} K_{12} \\ K_{12} \end{pmatrix}, \quad \mathbf{D} = \begin{pmatrix} 2\Delta & 0 \\ 0 & 2\Delta \end{pmatrix} \Rightarrow \mathbf{D}^{-1} = \begin{pmatrix} \frac{1}{2\Delta} & 0 \\ 0 & \frac{1}{2\Delta} \end{pmatrix}.$$

From (5.65), we obtain that

$$E_{\text{corr}}(\text{L-CCA}(L)) = - (K_{12} \quad K_{12}) \begin{pmatrix} \frac{1}{2\Delta} & 0 \\ 0 & \frac{1}{2\Delta} \end{pmatrix} \begin{pmatrix} K_{12} \\ K_{12} \end{pmatrix} = -\frac{K_{12}^2}{\Delta}. \quad (5.12-1)$$

When delocalized orbitals are used, based on $|\Psi_{a\bar{a}}^{**}\rangle$, $|\Psi_{b\bar{b}}^{**}\rangle$, $|\Psi_{a\bar{b}}^{**}\rangle$, $|\Psi_{\bar{a}b}^{**}\rangle$, its \mathbf{B} and \mathbf{D} are

$$\mathbf{B} = \begin{pmatrix} \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \end{pmatrix}, \quad \mathbf{D} = \begin{pmatrix} 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix}.$$

In fact, it is difficult to calculate the inverse of \mathbf{D} directly. Here I will introduce how to calculate it. Notations are listed as follows.

$$a = 2\Delta' + \frac{1}{2}J_{11}, \quad c = \frac{1}{2}K_{12} - J_{12}, \quad A \equiv \begin{pmatrix} 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix}, \quad \delta \equiv \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Thus, the matrix \mathbf{D} can be expressed as

$$\mathbf{D} = \begin{pmatrix} A & c\delta\delta^T \\ c\delta\delta^T & A \end{pmatrix}.$$

Due to the symmetry of \mathbf{D} , its inverse \mathbf{D}^{-1} can be set in the form of

$$\begin{pmatrix} M & N \\ N & M \end{pmatrix},$$

where M and N are 2×2 matrices and M is symmetric. Then,

$$\mathbf{D}\mathbf{D}^{-1} = \begin{pmatrix} A & c\delta\delta^T \\ c\delta\delta^T & A \end{pmatrix} \begin{pmatrix} M & N \\ N & M \end{pmatrix} = \begin{pmatrix} \mathbf{1}_2 & 0_2 \\ 0_2 & \mathbf{1}_2 \end{pmatrix},$$

where $\mathbf{1}_2$ is a 2-order identity matrix and 0_2 is a 2×2 zero matrix. Thus, two matrix equations are obtained, viz.,

$$AM + c\delta\delta^T N = \mathbf{1}_2, \quad (a)$$

$$AN + c\delta\delta^T M = 0_2. \quad (b)$$

Note that

$$\delta^T A = (1, 1) \begin{pmatrix} 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} = (a, a) = a\delta^T, \quad \delta^T \delta = (1, 1) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 2.$$

The equation (a) can be left-multiplied by δ^T ,

$$\delta^T = \delta^T \mathbf{1}_2 = \delta^T AM + c\delta^T \delta \delta^T N = a\delta^T M + 2c\delta^T N,$$

so does the equation (b),

$$0_2 = \delta^T 0_2 = \delta^T AN + c\delta^T \delta \delta^T M = a\delta^T N + 2c\delta^T M.$$

In other words, we obtain a new equation.

$$\begin{pmatrix} a & 2c \\ 2c & a \end{pmatrix} \begin{pmatrix} \delta^T M \\ \delta^T N \end{pmatrix} = \begin{pmatrix} \delta^T \\ \mathbf{0} \end{pmatrix}$$

The determinant of the coefficient matrix is

$$a^2 - 4c^2 = (a + 2c)(a - 2c) = 2\Delta(a - 2c) = 2\Delta \left[2(\varepsilon_2 - \varepsilon_1) + \frac{1}{2}J_{11} + J_{22} \right] \neq 0,$$

thus the coefficient matrix is reversible. With the truth that for a general 2×2 matrix \mathbf{C} , if its determinant $|\mathbf{C}| \neq 0$, its inverse

$$\mathbf{C}^{-1} = \frac{1}{|\mathbf{C}|} \begin{pmatrix} c_{22} & -c_{12} \\ -c_{21} & c_{11} \end{pmatrix},$$

we find that

$$\begin{pmatrix} \delta^T M \\ \delta^T N \end{pmatrix} = \frac{1}{a^2 - 4c^2} \begin{pmatrix} a & -2c \\ -2c & a \end{pmatrix} \begin{pmatrix} \delta^T \\ \mathbf{0} \end{pmatrix} = \frac{1}{a^2 - 4c^2} \begin{pmatrix} a\delta^T \\ -2c\delta^T \end{pmatrix}.$$

Now we know that

$$\begin{aligned} \delta^T M &= \frac{a}{a^2 - 4c^2} \delta^T, \\ \delta^T N &= -\frac{2c}{a^2 - 4c^2} \delta^T. \end{aligned}$$

Hence, we take it into the equation (a),

$$\begin{aligned} M &= A^{-1}(\mathbf{1}_2 - c\delta\delta^T N) \\ &= \frac{1}{(2\Delta')^2 - (\frac{1}{2}J_{11})^2} \begin{pmatrix} 2\Delta' & -\frac{1}{2}J_{11} \\ -\frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - c \times \frac{-2c}{a^2 - 4c^2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \right] \\ &= \frac{1}{a(a - J_{11})} \begin{pmatrix} 2\Delta' & -\frac{1}{2}J_{11} \\ -\frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \times \frac{1}{2\Delta(a - 2c)} \begin{pmatrix} a^2 - 2c^2 & 2c^2 \\ 2c^2 & a^2 - 2c^2 \end{pmatrix} \\ &= \frac{1}{2\Delta(a - 2c)(a - J_{11})} \begin{pmatrix} 2(\Delta'a - c^2) & 2c^2 - \frac{1}{2}J_{11}a \\ 2c^2 - \frac{1}{2}J_{11}a & 2(\Delta'a - c^2) \end{pmatrix} \end{aligned}$$

and the equation (b),

$$N = -A^{-1}c\delta\delta^T M = -c(A^{-1}\delta)(\delta^T M) = -c \frac{a - J_{11}}{a(a - J_{11})} \delta \times \frac{a}{a^2 - 4c^2} \delta^T = -\frac{c}{a^2 - 4c^2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

In conclusion, the inverse of \mathbf{D} is

$$\mathbf{D}^{-1} = \begin{pmatrix} M & N \\ N & M \end{pmatrix} = \frac{1}{a^2 - 4c^2} \begin{pmatrix} \frac{2(\Delta'a - c^2)}{a - J_{11}} & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & -c & -c \\ \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & \frac{2(\Delta'a - c^2)}{a - J_{11}} & -c & -c \\ -c & -c & \frac{2(\Delta'a - c^2)}{a - J_{11}} & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} \\ -c & -c & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & \frac{2(\Delta'a - c^2)}{a - J_{11}} \end{pmatrix}.$$

Now, it is turn to calculate the correlation energy, note that $a + 2c = \Delta$ and $2\Delta' - \frac{1}{2}J_{11} = a - J_{11}$, we find that

$$\begin{aligned} E_{\text{corr}}(\mathbf{L} - \text{CCA}(D)) &= -\mathbf{B}^\dagger \mathbf{D} \mathbf{B} \\ &= -\frac{1}{a^2 - 4c^2} \begin{pmatrix} \frac{K_{12}}{\sqrt{2}}, \frac{K_{12}}{\sqrt{2}}, \frac{K_{12}}{\sqrt{2}}, \frac{K_{12}}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{2(\Delta'a - c^2)}{a - J_{11}} & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & -c & -c \\ \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & \frac{2(\Delta'a - c^2)}{a - J_{11}} & -c & -c \\ -c & -c & \frac{2(\Delta'a - c^2)}{a - J_{11}} & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} \\ -c & -c & \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} & \frac{2(\Delta'a - c^2)}{a - J_{11}} \end{pmatrix} \begin{pmatrix} \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \\ \frac{K_{12}}{\sqrt{2}} \end{pmatrix} \\ &= -\frac{1}{a^2 - 4c^2} \left(\frac{K_{12}}{\sqrt{2}} \right)^2 \left[-8c + 4 \times \frac{2(\Delta'a - c^2)}{a - J_{11}} + 4 \times \frac{2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} \right] \\ &= -\frac{1}{2\Delta(a - 2c)} \times \frac{K_{12}^2}{2} \left[-8c + 4 \times \frac{2\Delta'a - 2c^2 + 2c^2 - \frac{1}{2}J_{11}a}{a - J_{11}} \right] \\ &= -\frac{K_{12}^2}{4\Delta(a - 2c)} \times 4 \left(-2c + \frac{(2\Delta' - J_{11})a}{a - J_{11}} \right) \\ &= -\frac{K_{12}^2}{\Delta(a - 2c)} \times (a - 2c) = -\frac{K_{12}^2}{\Delta}. \end{aligned}$$

This states that one gets the same correlation energy using delocalized orbitals.

5.2.4 Some Illustrative Calculations

5.3 Many-Electron Theories with Single Particle Hamiltonians