

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,

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

- 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

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

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.

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

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

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_{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 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) \\ &= \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{a}}^{**} | \mathcal{H} | \Psi_{ab}^{**} \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_{ab}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{ab}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{a\bar{a}}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle \\ &= \frac{1}{2} (-\langle \bar{r}\bar{b} | \bar{s}a \rangle + \langle r\bar{b} | as \rangle + \langle s\bar{b} | ar \rangle - \langle \bar{s}\bar{b} | \bar{r}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_{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_{b\bar{b}}^{**} | \mathcal{H} | \Psi_{ab}^{**} \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_{ab}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{ab}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{r\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{b\bar{b}}^{s\bar{s}} | \mathcal{H} | \Psi_{ab}^{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)) \\ &= \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_{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}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{ab}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \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 \Psi_{ab}^{s\bar{r}} | \mathcal{H} | \Psi_{ab}^{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)) \\ &= \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_{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}^{s\bar{r}} \rangle + \frac{1}{\sqrt{2}} | \Psi_{ab}^{r\bar{s}} \rangle \right) \\ &= \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \mathcal{H} | \Psi_{ab}^{s\bar{r}} \rangle + \frac{1}{2} \langle \Psi_{ab}^{r\bar{s}} | \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 \Psi_{ab}^{s\bar{r}} | \mathcal{H} | \Psi_{ab}^{r\bar{s}} \rangle\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 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_{ab}^{FO} , e_{ba}^{FO} , e_{bb}^{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 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

Exercise 5.10

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

$$|\Psi_{\text{DCI}}\rangle = |\Phi_0\rangle + c_1|\Phi_{a\bar{a}}^{**}\rangle + c_2|\Phi_{b\bar{b}}^{**}\rangle + c_3|{}^B\Phi_{ab}^{rs}\rangle.$$

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

5-10 so

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 H_2 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 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 H_2 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

5-12 so

5.2.4 Some Illustrative Calculations

5.3 Many-Electron Theories with Single Particle Hamiltonians

Exercise 5.13

For the 2×2 matrix

$$\begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

where $H_{11} < H_{22}$ and $H_{12} > 0$. Equation (5.96) simplifies to

$$E_R = \varepsilon_1 - H_{11} = H_{12}C$$

and

$$H_{21} + H_{22}C - CH_{11} - C^2H_{12} = 0.$$

Solve this quadratic equation for the lowest C and then show that ε_1 thus obtained is the lowest eigenvalue of the matrix.

Solution 5.13

$$H_{12}c^2 + (H_{11} - H_{22})c - H_{21} = 0$$

$$\Delta_c = (H_{11} - H_{22})^2 - 4 \times H_{12} \times (-H_{21}) = (H_{11} - H_{22})^2 + 4H_{12}H_{21} > 0$$

$$c_{1,2} = \frac{1}{2H_{12}} \left[H_{22} - H_{11} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}H_{21}} \right]$$

5.3.1 The Relaxation Energy via CI, IEPA, CEPA, and CCA

Exercise 5.14

Show that

a.

$$\langle \Psi_0 | \mathcal{H} | \Psi_b^s \rangle = v_{bs}.$$

b.

$$\langle \Psi_a^r | \mathcal{H} | \Psi_0 \rangle = v_{ra}.$$

c.

$$\begin{aligned} \langle \Psi_a^r | \mathcal{H} - E_0 | \Psi_b^s \rangle &= 0, & \text{if } a \neq b, r \neq s, \\ &= v_{rs}, & \text{if } a = b, r \neq s. \\ &= -v_{ba}, & \text{if } a \neq b, r = s. \\ &= \varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa} & \text{if } a = b, r = s. \end{aligned}$$

d.

$$\begin{aligned} \langle \Psi_a^r | \mathcal{H} | \Psi_{ab}^{rs} \rangle &= v_{bs}, & \text{if } a \neq b, r \neq s, \\ &= 0, & \text{otherwise.} \end{aligned}$$

Solution 5.14

5-14 so

Exercise 5.15

Repeat the above analysis using

$$\begin{aligned} |\chi_1\rangle &= a_1|\chi_1^{(0)}\rangle + a_2|\chi_2^{(0)}\rangle + a_3|\chi_3^{(0)}\rangle + a_4|\chi_4^{(0)}\rangle, \\ |\chi_2\rangle &= b_1|\chi_1^{(0)}\rangle + b_2|\chi_2^{(0)}\rangle + b_3|\chi_3^{(0)}\rangle + b_4|\chi_4^{(0)}\rangle \end{aligned}$$

instead of Eqs.(5.121a,b).

a. By repeated use of Eq.(1.40) show that

$$\begin{aligned} |\Phi_0\rangle &= (a_1b_2 - b_1a_2)|\chi_1^{(0)}\chi_2^{(0)}\rangle + (a_1b_3 - b_1a_3)|\chi_1^{(0)}\chi_3^{(0)}\rangle + (a_1b_4 - b_1a_4)|\chi_1^{(0)}\chi_4^{(0)}\rangle \\ &\quad + (a_3b_2 - b_3a_2)|\chi_3^{(0)}\chi_2^{(0)}\rangle + (a_4b_2 - b_4a_2)|\chi_4^{(0)}\chi_2^{(0)}\rangle + (a_3b_4 - b_3a_4)|\chi_3^{(0)}\chi_4^{(0)}\rangle. \end{aligned}$$

Intermediate normalize this wave function by dividing the right-hand side by $a_1b_2 - b_1a_2$ and then explicitly verify that Eq.(5.123) is satisfied.

b. To make contact with the general formalism, note that

$$\mathbf{U}_{AA} = \begin{pmatrix} a_1 & b_2 \\ a_2 & b_2 \end{pmatrix}, \quad \mathbf{U}_{BA} = \begin{pmatrix} a_3 & b_3 \\ a_4 & b_4 \end{pmatrix}.$$

Note that $|\mathbf{U}_{AA}| = a_1b_2 - b_1a_2$ as required to make Eq.(5.120a) consistent with the result obtained in part (a). Use the result of Exercise 1.4(f) to evaluate \mathbf{U}_{AA}^{-1} and then verify the general result given in Eq.(5.120b) by calculating

$$(\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1})_{11} = c_1^3$$

and showing that it is identical to the coefficient of $|\chi_3^{(0)}\chi_2^{(0)}\rangle$ obtained in part (a).

Solution 5.15

$$\begin{aligned} |\Phi_0\rangle &= |(a_1\chi_1^{(0)} + a_2\chi_2^{(0)} + a_3\chi_3^{(0)} + a_4\chi_4^{(0)})(b_1\chi_1^{(0)} + b_2\chi_2^{(0)} + b_3\chi_3^{(0)} + b_4\chi_4^{(0)})\rangle \\ &= a_1b_2|\chi_1^{(0)}\chi_2^{(0)}\rangle + a_1b_3|\chi_1^{(0)}\chi_3^{(0)}\rangle + a_1b_4|\chi_1^{(0)}\chi_4^{(0)}\rangle + a_2b_1|\chi_2^{(0)}\chi_1^{(0)}\rangle \\ &\quad + a_2b_3|\chi_2^{(0)}\chi_3^{(0)}\rangle + a_2b_4|\chi_2^{(0)}\chi_4^{(0)}\rangle + a_3b_1|\chi_3^{(0)}\chi_1^{(0)}\rangle + a_3b_2|\chi_3^{(0)}\chi_2^{(0)}\rangle \\ &\quad + a_3b_4|\chi_3^{(0)}\chi_4^{(0)}\rangle + a_4b_1|\chi_4^{(0)}\chi_1^{(0)}\rangle + a_4b_2|\chi_4^{(0)}\chi_2^{(0)}\rangle + a_4b_3|\chi_4^{(0)}\chi_3^{(0)}\rangle \\ &= (a_1b_2 - a_2b_1)|\chi_1^{(0)}\chi_2^{(0)}\rangle + (a_1b_3 - a_3b_1)|\chi_1^{(0)}\chi_3^{(0)}\rangle + (a_1b_4 - a_4b_1)|\chi_1^{(0)}\chi_4^{(0)}\rangle \\ &\quad + (a_2b_3 - a_3b_2)|\chi_2^{(0)}\chi_3^{(0)}\rangle + (a_2b_4 - a_4b_2)|\chi_2^{(0)}\chi_4^{(0)}\rangle + (a_3b_4 - a_4b_3)|\chi_3^{(0)}\chi_4^{(0)}\rangle \\ &= (a_1b_2 - a_2b_1)|\Psi_0\rangle + (a_1b_3 - a_3b_1)|\Phi_2^3\rangle + (a_1b_4 - a_4b_1)|\Phi_2^4\rangle \\ &\quad - (a_2b_3 - a_3b_2)|\Psi_1^3\rangle - (a_2b_4 - a_4b_2)|\Psi_1^4\rangle + (a_3b_4 - a_4b_3)|\Psi_{12}^{34}\rangle. \end{aligned}$$

$$\begin{aligned} |\Phi'_0\rangle &= |\Psi_0\rangle + \frac{1}{a_1b_2 - a_2b_1} [(a_1b_3 - a_3b_1)|\Phi_2^3\rangle + (a_1b_4 - a_4b_1)|\Phi_2^4\rangle \\ &\quad - (a_2b_3 - a_3b_2)|\Psi_1^3\rangle - (a_2b_4 - a_4b_2)|\Psi_1^4\rangle + (a_3b_4 - a_4b_3)|\Psi_{12}^{34}\rangle]. \end{aligned}$$

$$\begin{aligned} c_2^3 &= \frac{a_1b_3 - a_3b_1}{a_1b_2 - a_2b_1}, \\ c_2^4 &= \frac{a_1b_4 - a_4b_1}{a_1b_2 - a_2b_1}, \\ c_1^3 &= -\frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1}, \\ c_1^4 &= -\frac{a_2b_4 - a_4b_2}{a_1b_2 - a_2b_1}, \end{aligned}$$

$$c_{12}^{34} = \frac{a_3 b_4 - a_4 b_3}{a_1 b_2 - a_2 b_1}.$$

$$\begin{aligned} c_1^3 c_2^4 - c_1^4 c_2^3 &= \left(-\frac{a_2 b_3 - a_3 b_2}{a_1 b_2 - a_2 b_1} \right) \left(\frac{a_1 b_4 - a_4 b_1}{a_1 b_2 - a_2 b_1} \right) - \left(-\frac{a_2 b_4 - a_4 b_2}{a_1 b_2 - a_2 b_1} \right) \left(\frac{a_1 b_3 - a_3 b_1}{a_1 b_2 - a_2 b_1} \right) \\ &= -\frac{a_2 a_3 b_1 b_4 + a_1 a_4 b_2 b_3 - a_2 a_4 b_1 b_3 - a_1 a_3 b_2 b_4}{(a_1 b_2 - a_2 b_1)^2} = -\frac{(a_1 b_2 - a_2 b_1)(a_4 b_3 - a_3 b_4)}{(a_1 b_2 - a_2 b_1)^2} \\ &= -\frac{a_4 b_3 - a_3 b_4}{a_1 b_2 - a_2 b_1} = \frac{a_3 b_4 - a_4 b_3}{a_1 b_2 - a_2 b_1} = c_{12}^{34}. \end{aligned}$$

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

Exercise 5.16

Set up the Hückel matrix for benzene and find its eigenvalues. Remember that if the carbon atoms are labeled clockwise from 1 to 6, then atoms 1 and 6 are nearest neighbors. Show that the six eigenvalues are identical to those given by Eq.(5.131). Find the total energy and compare it with the result given by Eq.(5.132).

Solution 5.16

$$H = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

$$\det(H - \varepsilon I) = (\alpha - \varepsilon - 2\beta)(\alpha - \varepsilon - \beta)^2(\alpha - \varepsilon + \beta)^2(\alpha - \varepsilon + 2\beta) = 0$$

$$\varepsilon_1 = \alpha + 2\beta, \quad \varepsilon_2 = \varepsilon_3 = \alpha + \beta, \quad \varepsilon_4 = \varepsilon_5 = \alpha - \beta, \quad \varepsilon_6 = \alpha - 2\beta.$$

$$E = \sum_{i=1}^3 \varepsilon_i = 6\alpha + 8\beta \quad (5.2)$$

Exercise 5.17

Verify Eqs.(5.139) and (5.140).

Solution 5.17

$$\begin{aligned} \langle i|j \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | \phi_{2j-1} \rangle + \langle \phi_{2i-1} | \phi_{2j} \rangle + \langle \phi_{2i} | \phi_{2j-1} \rangle + \langle \phi_{2i} | \phi_{2j} \rangle] = \delta_{ij}, \\ \langle i^* | j^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | \phi_{2j-1} \rangle - \langle \phi_{2i-1} | \phi_{2j} \rangle - \langle \phi_{2i} | \phi_{2j-1} \rangle + \langle \phi_{2i} | \phi_{2j} \rangle] = \delta_{ij}, \\ \langle i | j^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | \phi_{2j-1} \rangle - \langle \phi_{2i-1} | \phi_{2j} \rangle + \langle \phi_{2i} | \phi_{2j-1} \rangle - \langle \phi_{2i} | \phi_{2j} \rangle] = 0, \\ \langle i^* | j \rangle &= (\langle i | j^* \rangle)^* = 0^* = 0, \\ \langle i | h_{\text{eff}} | i-1 \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-3} \rangle + \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-2} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-3} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-2} \rangle] = \frac{1}{2}\beta, \\ \langle i | h_{\text{eff}} | i \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-1} \rangle + \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i} \rangle] = \alpha + \beta, \\ \langle i | h_{\text{eff}} | i+1 \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+1} \rangle + \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+2} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+2} \rangle] = \frac{1}{2}\beta, \end{aligned}$$

$$\begin{aligned}
\langle i^* | h_{\text{eff}} | (i-1)^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-3} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-2} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-3} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-2} \rangle] = -\frac{1}{2}\beta, \\
\langle i^* | h_{\text{eff}} | i^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-1} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i} \rangle] = \alpha - \beta, \\
\langle i^* | h_{\text{eff}} | (i+1)^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+1} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+2} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+2} \rangle] = -\frac{1}{2}\beta, \\
\langle i | h_{\text{eff}} | (i-1)^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-3} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-2} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-3} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-2} \rangle] = -\frac{1}{2}\beta, \\
\langle i | h_{\text{eff}} | i^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i-1} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i-1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i} \rangle] = \alpha - \beta, \\
\langle i | h_{\text{eff}} | (i+1)^* \rangle &= \frac{1}{2} [\langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+1} \rangle - \langle \phi_{2i-1} | h_{\text{eff}} | \phi_{2i+2} \rangle - \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+1} \rangle + \langle \phi_{2i} | h_{\text{eff}} | \phi_{2i+2} \rangle] = \frac{1}{2}\beta,
\end{aligned}$$

Exercise 5.18

Evaluate the matrix elements given in Eq.(5.149) and fill in the remaining steps leading to Eq.(5.150).

Solution 5.18

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}}\beta \\ \frac{1}{\sqrt{2}}\beta & -\frac{3}{2}\beta \end{pmatrix} \begin{pmatrix} 1 & c \end{pmatrix} = e_1 \begin{pmatrix} 1 & c \end{pmatrix}.$$

Exercise 5.19

- a) Extend the above analysis to calculate the IEPA resonance energy for a cyclic polyene with $N = 2n$ ($N > 6$) carbon atoms. As before, argue that all “particle” energies are the same so that

$$E_R = N e_1.$$

Consider only single excitations that mix with $|\Psi_0\rangle$. Show that the “particle” function $|\Psi_1\rangle$ is

$$|\Psi_1\rangle = |\Psi_0\rangle + c|_1^*\rangle$$

where $|_1^*\rangle$ is obtained from Eq.(5.146),

$$|_1^*\rangle = \frac{1}{\sqrt{2}} (|\Psi_1^{2*}\rangle - |\Psi_1^{n*}\rangle).$$

Now show that

$$\langle \Psi_0 | \mathcal{H} |_1^* \rangle = \frac{1}{\sqrt{2}}\beta$$

as before, but that here

$$\langle _1^* | \mathcal{H} - E_0 |_1^* \rangle = -2\beta,$$

instead of the result in Eq.(5.149b). Why the difference? Finally, solve the resulting “particle” equations to show that

$$E_R(\text{IEPA}) = N \left(\sqrt{\frac{3}{2}} - 1 \right) \beta = 0.2247N\beta.$$

Note that the IEPA is indeed size consistent and that in the limit of large N it gives 82% of the exact resonance energy.

- b) The above result is not really exact within the IEPA. The reason for this is that there exist single excitations involving orbital $|1\rangle$ that do not mix with $|\Psi_0\rangle$ but do mix with $|_1^*\rangle$ and thus have some effect on the “particle” energy e_1 . These excitations are analogous to single excitations in CI for a real many-particle system in the sense that although single excitations do not mix with the HF wave function because of Brillouin’s theorem, they do mix indirectly through the double

excitations. Investigate the effect of such excitations for the case $N = 10$. Show that the exact “particle” function $|\Psi_1\rangle$ is

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1|_1^* + c_3|\Psi_1^{3*}\rangle + c_4|\Psi_1^{4*}\rangle.$$

Now show that

$$\begin{aligned}\langle\Psi_0|\mathcal{H}|\Psi_1^{3*}\rangle &= \langle\Psi_0|\mathcal{H}|\Psi_1^{4*}\rangle = 0, \\ \langle\Psi_1^{3*}|\mathcal{H} - E_0|\Psi_1^{3*}\rangle &= \langle\Psi_1^{4*}|\mathcal{H} - E_0|\Psi_1^{4*}\rangle = -2\beta, \\ \langle\Psi_1^{3*}|\mathcal{H}|\Psi_1^{4*}\rangle &= -\frac{1}{2}\beta, \\ \langle_1^*|\mathcal{H}|\Psi_1^{3*}\rangle &= -\frac{1}{2\sqrt{2}}\beta, \\ \langle_1^*|\mathcal{H}|\Psi_1^{4*}\rangle &= \frac{1}{2\sqrt{2}}\beta.\end{aligned}$$

Finally, show from the resulting “particle” equations that e_1 is the solution of

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0.$$

The cubic equation can be solved to yield $e_1 = 0.2387\beta$ so that the exact IEPA resonance energy for $N = 10$ is 2.387β , which is to be compared with the approximate result of 2.247β obtained in part (a), so that there is a 6% difference. The exact resonance energy found from Eq.(5.135) is 2.944β for this case.

Solution 5.19

a.

b.

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}}\beta & 0 & 0 \\ \frac{1}{\sqrt{2}}\beta & -2\beta & -\frac{1}{2\sqrt{2}}\beta & \frac{1}{2\sqrt{2}}\beta \\ 0 & -\frac{1}{2\sqrt{2}}\beta & -2\beta & -\frac{1}{2}\beta \\ 0 & \frac{1}{2\sqrt{2}}\beta & -\frac{1}{2}\beta & -2\beta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = e_1 \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix}.$$

Exercise 5.20

Verify Eq.(5.152c), derive Eq.(5.153a,b), and solve them to obtain the result shown in Eq.(5.154).

Solution 5.20

$$\begin{aligned}\langle_1^*|\mathcal{H}|_2^*\rangle &= \frac{1}{2} [\langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{3*}\rangle - \langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{1*}\rangle - \langle\Psi_1^{3*}|\mathcal{H}|\Psi_2^{3*}\rangle + \langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{1*}\rangle] \\ &= -\frac{1}{2}\langle\Psi_1^{3*}|\mathcal{H}|\Psi_2^{3*}\rangle = -\frac{1}{2}(-v_{12}) = \frac{1}{2}\frac{\beta}{2} = \frac{\beta}{4}, \\ \langle_1^*|\mathcal{H}|_3^*\rangle &= \frac{1}{2} [\langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{1*}\rangle - \langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{2*}\rangle - \langle\Psi_1^{3*}|\mathcal{H}|\Psi_3^{1*}\rangle + \langle\Psi_1^{3*}|\mathcal{H}|\Psi_3^{2*}\rangle] \\ &= -\frac{1}{2}\langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{2*}\rangle = -\frac{1}{2}(-v_{13}) = \frac{1}{2}\frac{\beta}{2} = \frac{\beta}{4}, \\ \langle_2^*|\mathcal{H}|_3^*\rangle &= \frac{1}{2} [\langle\Psi_2^{3*}|\mathcal{H}|\Psi_3^{1*}\rangle - \langle\Psi_2^{3*}|\mathcal{H}|\Psi_3^{2*}\rangle - \langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{1*}\rangle + \langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{2*}\rangle] \\ &= -\frac{1}{2}\langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{1*}\rangle = -\frac{1}{2}(-v_{23}) = \frac{1}{2}\frac{\beta}{2} = \frac{\beta}{4}.\end{aligned}$$

$$\begin{pmatrix} 0 & 3\sqrt{2}\beta \\ \frac{1}{\sqrt{2}}\beta & -\beta \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_R(\text{SCI}) \begin{pmatrix} 1 \\ c \end{pmatrix}.$$

Exercise 5.21

Extend the above analysis to calculate the SCI resonance energy for a cyclic polyene with $N = 2n$ ($N > 6$) carbon atoms. If we restrict ourselves to only those configurations which interact with $|\Psi_0\rangle$, then the appropriate generalization of Eq.(5.151) is

$$|\Psi_{\text{SCI}}\rangle = |\Psi_0\rangle + \sum_{i=1}^n c_i |i^*\rangle + \sum_{i=1}^n \bar{c}_i |\bar{i}^*\rangle.$$

As discussed in Exercise 5.19b, this is not the complete SCI wave function because there exist additional singly excited configurations which, although they do not mix with $|\Psi_0\rangle$, they do mix with $|i^*\rangle$. The omission of these does not affect our qualitative conclusions. Show that the required matrix elements are

$$\begin{aligned}\langle\Psi_0|\mathcal{H}|i^*\rangle &= \frac{1}{\sqrt{2}}\beta, \\ \langle i^*|\mathcal{H} - E_0|j^*\rangle &= (-2\beta)\delta_{ij}.\end{aligned}$$

Why are Eqs.(5.152b) and Eqs.(5.152c) different? Using these matrix elements, show that the SCI equations are

$$\begin{aligned}E_R(\text{SCI}) &= \frac{1}{\sqrt{2}}Nc\beta, \\ \frac{1}{\sqrt{2}}\beta - 2c\beta &= E_R(\text{SCI})c.\end{aligned}$$

Finally, solve them to obtain

$$E_R(\text{SCI}) = \left(\sqrt{1 + \frac{N}{2}} - 1 \right) \beta$$

which is proportional to $N^{1/2}$ as N becomes large.

Solution 5.21

$$\langle\Psi_0|\mathcal{H}|i^*\rangle = \frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i+1)*}\rangle - \frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i-1)*}\rangle = \frac{1}{\sqrt{2}}\left(\frac{\beta}{2}\right) - \frac{1}{\sqrt{2}}\left(-\frac{\beta}{2}\right) = \frac{\beta}{\sqrt{2}}.$$