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,

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

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

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

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

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

Exercise 5.2

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

Solution 5.2

From (5.9a)

$$K_{12}c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i} \tag{5.2-1}$$

$$K_{12} + \langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathscr{H} - E_0|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle = e_{1_i\bar{1}_i}c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \tag{5.2-2}$$

$$h_{11} = \varepsilon_1 - J_{11}, \quad h_{22} = \varepsilon_2 - 2J_{12} + K_{12}$$

$$\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathscr{H} - E_0|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle = 2\Delta$$