

Modern Quantum Chemistry, Szabo & Ostlund

HW

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5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

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

b.

$$\begin{aligned}
 {}^1E_{\text{corr}} &= \Delta - \Delta \sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \\
 &= \Delta - \Delta \left(1 + \frac{K_{12}^2}{2\Delta^2} \right) \\
 &= -\frac{K_{12}^2}{2\Delta} \\
 &\approx \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
 \end{aligned} \tag{5.1.2}$$

Ex 5.2 From Eq. 5.9a and 5.9b in the textbook, we get

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

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

\therefore

$$c_{1_i \bar{1}_i}^{2_i \bar{2}_i} \langle \Psi_0 | \mathcal{H} | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle = e_{1_i \bar{1}_i} \tag{5.1.5}$$

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

(5.1.5) gives

$$K_{12} c_{1_i \bar{1}_i}^{2_i \bar{2}_i} = e_{1_i \bar{1}_i} \tag{5.1.7}$$

For (5.1.6)

$$\langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathcal{H} | \Psi_0 \rangle + \sum_{jk} \langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathcal{H} - E_0 | \Psi_{1_i \bar{1}_i}^{2_j \bar{2}_k} \rangle c_{1_i \bar{1}_i}^{2_j \bar{2}_k} = e_{1_i \bar{1}_i} c_{1_i \bar{1}_i}^{2_i \bar{2}_i} \tag{5.1.8}$$