Modern Quantum Chemistry, Szabo & Ostlund HW

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Contents

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

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

b.

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