5.1节(独立电子对近似)习题解似.

练习5.1 (a)对于H_2来讲,只有一对电子,讲不上对电子对求和;只有一~~对~~个空轨道,也谈不上对空轨道求和.

故应用式(5.19)有 $E_{corr}(FO)=\sum_{a<b}\sum_{r<s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}=\frac{|\langle 1\bar1||2\bar2\rangle|^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}=-\frac{K_{12}^2}{2(\varepsilon_2-\varepsilon_1)}$

(b) ${}^1E_{corr}=\Delta\left[1-\sqrt{1+\frac{K_{12}^2}{\Delta^2}}\right]\doteq\Delta\left[1-\left(1+\frac{K_{12}^2}{2\Delta^2}+o\left(\frac{K_{12}^2}{\Delta^2}\right)\right)\right]=-\frac{K_{12}^2}{2\Delta}+o\left(\frac{K_{12}^2}{\Delta^2}\right)$.从而记$\Delta=\varepsilon_2-\varepsilon_1$,得到${}^1E_{corr}(FO)=-\frac{K_{12}^2}{2(\varepsilon_2-\varepsilon_1)}$.

练习5.2 同前,在教材式(5.21)左侧进行$\mathcal{H}-E_0$变换后,依次左乘$\langle\Psi_0|$,$\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|$,得

左乘$\langle\Psi_0|$,得 $K_{12}C_{1_1\bar1_1}^{2_1\bar2_1}=e_{1_1\bar1_1}$;左乘$\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|$得, $K_{12}+\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|\mathcal{H}-E_0|\Psi_{1_1\bar1_1}^{2_1\bar2_1}\rangle=e_{1_1\bar1_1}C_{1_1\bar1_1}^{2_1\bar2_1}$.

其中,$\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|\mathcal{H}-E_0|\Psi_{1_1\bar1_1}^{2_1\bar2_1}\rangle=\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|\mathcal{H}|\Psi_{1_1\bar1_1}^{2_1\bar2_1}\rangle-E_0=(2h_{22}+J_{11}+J_{22})-(2h_{11}+2J_{11})=2h_{22}-2h_{11}+J_{22}-J_{11}$.

注意,2H_2间无相互作用!而$h_{11}=\varepsilon_1-J_{11}$,$h_{22}=\varepsilon_2-2J_{12}+K_{12}$.从而代入后得 $\langle\Psi_{1_1\bar1_1}^{2_1\bar2_1}|\mathcal{H}-E_0|\Psi_{1_1\bar1_1}^{2_1\bar2_1}\rangle=2\Delta$.

从而式(5.22a)与式(5.22b)得证.

练习5.3 $E_{corr}(FO,2H_2)$由式(5.19)即得,而$|\langle 1_1\bar1_1||2_1\bar2_1\rangle|^2=K_{12}^2$,$|\langle 1_1\bar1_1||2_2\bar2_2\rangle|^2=0$,$|\langle 1_2\bar1_2||2_2\bar2_2\rangle|^2=K_{12}^2$,$|\langle 1_2\bar1_2||2_1\bar2_1\rangle|^2=0$.

从而$E_{corr}(FO,2H_2)=\frac{K_{12}^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}+\frac{K_{12}^2}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}=-\frac{K_{12}^2}{\varepsilon_2-\varepsilon_1}=2E_{corr}(H_2,FO)$.

5.1.1节(幺正变换下的不变性:一个例子)习题解析.

练习5.4. 要注意,Slater行列式中形如 $|1_2\bar{1}_1 1_1\bar{1}_2\rangle$, $|1_2\bar{2}_1 1_1\bar{1}_2\rangle$ 的行列式为零,因其违反了Pauli不相容原理.

$\therefore |a\bar a b\bar b\rangle = \frac{1}{\sqrt2}|1_1\bar a b\bar b\rangle + \frac{1}{\sqrt2}|1_2\bar a b\bar b\rangle = \frac12(|1_1\bar a 1_1\bar b\rangle - |1_1\bar a 1_2\bar b\rangle) + \frac12(|1_2\bar a 1_1\bar b\rangle - |1_2\bar a 1_2\bar b\rangle)$

$= \frac12|1_2\bar a 1_1\bar b\rangle - \frac12|1_1\bar a 1_2\bar b\rangle = -\frac14|1_2\bar1_1 1_1\bar1_2\rangle + \frac14|1_2\bar2_1 1_1\bar1_1\rangle + \frac14|1_1\bar1_1 1_2\bar1_2\rangle - \frac14|1_1\bar1_2 2_1\bar1_1\rangle = |1_1\bar1_1 1_1\bar1_2\rangle$.

练习5.5 $\langle\Psi_0|\mathcal H|\Psi_{a\bar a}^{**}\rangle = \frac1{\sqrt2}\langle\Psi_0|\mathcal H|\Psi_{a\bar a}^{r\bar r}\rangle + \frac1{\sqrt2}\langle\Psi_0|\mathcal H|\Psi_{a\bar a}^{s\bar s}\rangle = \frac1{\sqrt2}\langle a\bar a||r\bar r\rangle + \frac1{\sqrt2}\langle a\bar a||s\bar s\rangle$

$\cancel{\frac1{\sqrt2}[ar||\bar a\bar r] + \frac1{\sqrt2}[as||\bar a\bar s]} = \frac1{\sqrt2}\langle a\bar a|r\bar r\rangle - \frac1{\sqrt2}\langle a\bar a|\bar r r\rangle + \frac1{\sqrt2}\langle a\bar a|s\bar s\rangle - \frac1{\sqrt2}\langle a\bar a|\bar s s\rangle$

$= \frac1{\sqrt2}[ar|\bar a\bar r] - \frac1{\sqrt2}[a\bar r|\bar a r] + \frac1{\sqrt2}[as|\bar a\bar s] - \frac1{\sqrt2}[a\bar s|\bar a s] = \frac1{\sqrt2}(ar|ar) + \frac1{\sqrt2}(as|as) = \frac1{\sqrt2}K_{12}$.

$E_0 = \langle\Psi_0|\mathcal H|\Psi_0\rangle = \langle\Psi_0|\mathcal O_1|\Psi_0\rangle + \langle\Psi_0|\mathcal O_2|\Psi_0\rangle$

$\langle\Psi_0|\mathcal O_1|\Psi_0\rangle = \langle a|h|a\rangle + \langle\bar a|h|\bar a\rangle + \langle b|h|b\rangle + \langle\bar b|h|\bar b\rangle = 4h_{11}$

$\langle\Psi_0|\mathcal O_2|\Psi_0\rangle = \langle a\bar a||a\bar a\rangle + \langle ab||ab\rangle + \langle a\bar b||a\bar b\rangle + \langle\bar a b||\bar a b\rangle + \langle\bar a\bar b||\bar a\bar b\rangle + \langle b\bar b||b\bar b\rangle$.

$= \langle a\bar a|a\bar a\rangle - \langle a\bar a|\bar a a\rangle + \langle ab|ab\rangle - \langle ab|ba\rangle + \langle a\bar b|a\bar b\rangle - \langle a\bar b|\bar b a\rangle + \langle\bar a b|\bar a b\rangle - \langle\bar a b|b\bar a\rangle$
$+ \langle\bar a\bar b|\bar a\bar b\rangle - \langle\bar a\bar b|\bar b\bar a\rangle + \langle b\bar b|b\bar b\rangle - \langle b\bar b|\bar b b\rangle$

$= (aa|aa) + (aa|bb) - (ab|ba) + (aa|bb) + (aa|bb) + (aa|bb) - (ab|ba) + (bb|bb)$

$= (aa|aa) + 4(aa|bb) - 2(ab|ba) + (bb|bb) = \frac12J_{11} + 2J_{11} - J_{11} + \frac12J_{11} = 2J_{11}$.

$\therefore E_0 = 4h_{11} + 2J_{11}$.

而 $\langle\Psi_{a\bar a}^{**}|\mathcal H|\Psi_{a\bar a}^{**}\rangle = \frac12\langle\Psi_{a\bar a}^{r\bar r}|\mathcal H|\Psi_{a\bar a}^{r\bar r}\rangle + \frac12\langle\Psi_{a\bar a}^{r\bar r}|\mathcal H|\Psi_{a\bar a}^{s\bar s}\rangle + \frac12\langle\Psi_{a\bar a}^{s\bar s}|\mathcal H|\Psi_{a\bar a}^{r\bar r}\rangle + \frac12\langle\Psi_{a\bar a}^{s\bar s}|\mathcal H|\Psi_{a\bar a}^{s\bar s}\rangle$.

$\langle\Psi_{a\bar a}^{r\bar r}|\mathcal H|\Psi_{a\bar a}^{r\bar r}\rangle = \langle\Psi_{a\bar a}^{r\bar r}|\mathcal O_1|\Psi_{a\bar a}^{r\bar r}\rangle + \langle\Psi_{a\bar a}^{r\bar r}|\mathcal O_2|\Psi_{a\bar a}^{r\bar r}\rangle$. 同上,有

$\langle\Psi_{a\bar a}^{r\bar r}|\mathcal O_1|\Psi_{a\bar a}^{r\bar r}\rangle = \langle r|h|r\rangle + \langle\bar r|h|\bar r\rangle + \langle b|h|b\rangle + \langle\bar b|h|\bar b\rangle = 2h_{11} + 2h_{22}$.

$\langle\Psi_{a\bar a}^{r\bar r}|\mathcal O_2|\Psi_{a\bar a}^{r\bar r}\rangle = \langle r\bar r||r\bar r\rangle + \langle rb||rb\rangle + \langle r\bar b||r\bar b\rangle + \langle\bar r b||\bar r b\rangle + \langle\bar r\bar b||\bar r\bar b\rangle + \langle b\bar b||b\bar b\rangle$.

$= \langle r\bar r|r\bar r\rangle - \langle r\bar r|\bar r r\rangle + \langle rb|rb\rangle - \langle rb|br\rangle + \langle r\bar b|r\bar b\rangle - \langle r\bar b|\bar b r\rangle + \langle\bar r b|\bar r b\rangle - \langle\bar r b|b\bar r\rangle$
$+ \langle\bar r\bar b|\bar r\bar b\rangle - \langle\bar r\bar b|\bar b\bar r\rangle + \langle b\bar b|b\bar b\rangle - \langle b\bar b|\bar b b\rangle$

$= (rr|rr) + (rr|bb) - (rb|br) + (rr|bb) + (rr|bb) + (rr|bb) - (rb|br) + (bb|bb)$

$= \frac12J_{22} + 2J_{12} - K_{12} + \frac12J_{11}$ 代入 $h_{11} = \varepsilon_1 - J_{11}$, $h_{22} = \varepsilon_2 - 2J_{12} + K_{12}$ 再得 $\langle\Psi_{a\bar a}^{r\bar r}|\mathcal H|\Psi_{a\bar a}^{s\bar s}\rangle = \frac12J_{22}$.

$\therefore \langle\Psi_{a\bar a}^{**}|\mathcal H - E_0|\Psi_{a\bar a}^{**}\rangle = 2h_{22} - 2h_{11} + \frac12J_{22} - \frac32J_{11} + 2J_{12} - K_{12} = 2(\varepsilon_2 - \varepsilon_1) + \frac12J_{22} + \frac12(J_{11} - 4J_{12} + 2K_{12})$ 回代即得

练习5.6. 只要证得 $e_{a\bar b}$ 满足与 $e_{a\bar a}$ 相同的方程,由线性方程组解的唯一性,则应有 $e_{a\bar b} = e_{a\bar a}$.

由教材式(5.9a),从而 $e_{a\bar b} = \langle\Psi_0|\mathcal H|\Psi_{a\bar b}^{**}\rangle = \frac1{\sqrt2}\langle\Psi_0|\mathcal H|\Psi_{a\bar b}^{r\bar s}\rangle + \frac1{\sqrt2}\langle\Psi_0|\mathcal H|\Psi_{a\bar b}^{s\bar r}\rangle$.

$\therefore e_{a\bar b} = \frac1{\sqrt2}\langle a\bar b||r\bar s\rangle + \frac1{\sqrt2}\langle a\bar b||s\bar r\rangle = \frac1{\sqrt2}[\langle a\bar b|r\bar s\rangle - \langle a\bar b|\bar s r\rangle] + \frac1{\sqrt2}[\langle a\bar b|s\bar r\rangle - \langle a\bar b|\bar r s\rangle] = \frac1{\sqrt2}K_{12}$

而由教材式(5.9b),从而 $\langle\Psi_{a\bar b}^{**}|\mathcal H|\Psi_0\rangle + \langle\Psi_{a\bar b}^{**}|\mathcal H - E_0|\Psi_{a\bar b}^{**}\rangle c = e_{a\bar b}c$ 同练习5.5处理

$\therefore \langle\Psi_{a\bar b}^{**}|\mathcal H|\Psi_{a\bar b}^{**}\rangle = \frac12\langle\Psi_{a\bar b}^{r\bar s}|\mathcal H|\Psi_{a\bar b}^{r\bar s}\rangle + \frac12\langle\Psi_{a\bar b}^{r\bar s}|\mathcal H|\Psi_{a\bar b}^{s\bar r}\rangle + \frac12\langle\Psi_{a\bar b}^{s\bar r}|\mathcal H|\Psi_{a\bar b}^{r\bar s}\rangle + \frac12\langle\Psi_{a\bar b}^{s\bar r}|\mathcal H|\Psi_{a\bar b}^{s\bar r}\rangle$.

而 $\langle\Psi_{a\bar b}^{r\bar s}|\mathcal H|\Psi_{a\bar b}^{r\bar s}\rangle = \frac12J_{11} + 2J_{12} + \frac12J_{12} - K_{12} = \langle\Psi_{a\bar b}^{s\bar r}|\mathcal H|\Psi_{a\bar b}^{s\bar r}\rangle$, $\langle\Psi_{a\bar b}^{r\bar s}|\mathcal H|\Psi_{a\bar b}^{s\bar r}\rangle = \langle\Psi_{a\bar b}^{s\bar r}|\mathcal H|\Psi_{a\bar b}^{r\bar s}\rangle = \frac12J_{22}$

$\therefore \langle\Psi_{a\bar b}^{**}|\mathcal H|\Psi_{a\bar b}^{**}\rangle = \frac12J_{11} + 2J_{12} + J_{22} - K_{12} + 2h_{11} + 2h_{22}$, 而 $E_0 = \langle\Psi_0|\mathcal H|\Psi_0\rangle$ ~~$2(\varepsilon_1 - J_{11}) + 2(\varepsilon_2 - 2J_{12} + K_{12})$~~ $= 4h_{11} + 2J_{11}$.(由练习5.5获得)

$\therefore \langle\Psi_{a\bar b}^{**}|\mathcal H - E_0|\Psi_{a\bar b}^{**}\rangle = 2h_{22} - 2h_{11} + J_{22} - \frac32J_{11} + 2J_{12} - K_{12} = 2(\varepsilon_2 - 2J_{12} + K_{12}) - 2(\varepsilon_1 - J_{11}) + J_{22} - \frac32J_{11} + 2J_{12} - K_{12} = 2$

其中，$2\Delta'$定义见式(5.31b)，从而代入式(5.96)，得 $\frac{1}{\sqrt2}K_{12}+2\Delta' C=e_{a\bar b}C$.

从而应有 $e_{a\bar i}=e_{a\bar a}$，由问题对称性应有 $e_{ab}=e_{a\bar b}=e_{a\bar a}$.

练习5.7 (a) 同前，应有 $\langle\Psi_0|\mathcal{H}-E_0|\Psi_0\rangle=0$. $\langle\Psi_0|\mathcal{H}-E_0|\Psi_{a\bar a}^{**}\rangle=\frac{1}{\sqrt2}\langle\Psi_0|\mathcal{H}|\Psi_{a\bar a}^{r\bar r}\rangle+\frac{1}{\sqrt2}\langle\Psi_0|\mathcal{H}|\Psi_{a\bar a}^{s\bar s}\rangle$

$\therefore \langle\Psi_0|\mathcal{H}-E_0|\Psi_{a\bar a}^{**}\rangle=\frac{1}{\sqrt2}\langle a\bar a||r\bar r\rangle+\frac{1}{\sqrt2}\langle a\bar a||s\bar s\rangle=\frac{1}{\sqrt2}\frac12K_{12}+\frac{1}{\sqrt2}\frac12K_{12}=\frac{1}{\sqrt2}K_{12}$.

同理，$\langle\Psi_0|\mathcal{H}-E_0|\Psi_{b\bar b}^{**}\rangle=\frac{1}{\sqrt2}K_{12}$. 由练习5.6. $\therefore\langle\Psi_0|\mathcal{H}-E_0|\Psi_{a\bar b}^{**}\rangle=\langle\Psi_0|\mathcal{H}|\Psi_{a\bar b}^{**}\rangle=\frac{1}{\sqrt2}K_{12}$

同理，$\langle\Psi_0|\mathcal{H}-E_0|\Psi_{\bar a b}^{**}\rangle=\frac{1}{\sqrt2}K_{12}$. 由练习5.5. $\therefore\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{a\bar a}^{**}\rangle=2\Delta'$，由练习5.6，$\langle\Psi_{a\bar b}^{**}|\mathcal{H}-E_0|\Psi_{a\bar b}^{**}\rangle=2\Delta'$

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

而 $\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{b\bar b}^{**}\rangle=\frac12[\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{b\bar b}^{r\bar r}\rangle+\langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{b\bar b}^{r\bar r}\rangle+\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{b\bar b}^{s\bar s}\rangle+\langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{b\bar b}^{s\bar s}\rangle]$.

$=\frac12[\langle r\bar r b\bar b|\mathcal{H}|a\bar a r\bar r\rangle+\langle s\bar s b\bar b|\mathcal{H}|a\bar a r\bar r\rangle+\langle r\bar r b\bar b|\mathcal{H}|a\bar a s\bar s\rangle+\langle s\bar s b\bar b|\mathcal{H}|a\bar a s\bar s\rangle]$

$=\frac12[\langle b\bar b||a\bar a\rangle+0+0+\langle b\bar b||a\bar a\rangle]=\langle b\bar b|a\bar a\rangle-\langle b\bar b|\bar a a\rangle=(ba|ba)=\frac12J_{11}$.

同理，$\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{a\bar b}^{**}\rangle=\frac12[\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{a\bar b}^{r\bar s}\rangle+\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{a\bar b}^{s\bar r}\rangle+\langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{a\bar b}^{r\bar s}\rangle+\langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{a\bar b}^{s\bar r}\rangle]$

$=\frac12[\langle r\bar r b\bar b|\mathcal{H}|r\bar a b\bar s\rangle+\langle r\bar r b\bar b|\mathcal{H}|s\bar a b\bar r\rangle+\langle s\bar s b\bar b|\mathcal{H}|r\bar a b\bar s\rangle+\langle s\bar s b\bar b|\mathcal{H}|s\bar a b\bar r\rangle]$

$=\frac12[\langle rb\bar r\bar b|\mathcal{H}|rb\bar a\bar s\rangle+\langle\bar r b r\bar b|\mathcal{H}|\bar r b\bar a s\rangle+\langle b\bar s s\bar b|\mathcal{H}|b\bar s\bar a r\rangle+\langle\bar s b s\bar b|\mathcal{H}|\bar a r s b\rangle]$

$=\frac12[\langle\bar r\bar b||\bar a\bar s\rangle+\langle r\bar b||\bar a s\rangle+\langle s\bar b||\bar a r\rangle+\langle\bar s\bar b||\bar a\bar r\rangle]$

$=\frac12[\langle\bar r\bar b|\bar a\bar s\rangle-\langle\bar r\bar b|\bar s\bar a\rangle+\langle r\bar b|\bar a s\rangle-\langle r\bar b|s\bar a\rangle+\langle s\bar b|\bar a r\rangle-\langle s\bar b|r\bar a\rangle+\langle\bar s\bar b|\bar a\bar r\rangle-\langle\bar s\bar b|\bar r\bar a\rangle]$

$=\frac12[\frac12K_{12}-\frac12J_{12}-\frac12J_{12}+\frac12K_{12}-\frac12J_{12}-\frac12J_{12}]=\frac12K_{12}-J_{12}$. 同理证明 $\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{\bar a b}^{**}\rangle=\frac12K_{12}-J_{12}$.

同理证明：$\langle\Psi_{b\bar b}^{**}|\mathcal{H}-E_0|\Psi_{a\bar b}^{**}\rangle=\frac12K_{12}-J_{12}$. 接下来证明 $\langle\Psi_{a\bar b}^{**}|\mathcal{H}-E_0|\Psi_{\bar a b}^{**}\rangle=\frac12K_{12}-J_{12}$.

$\langle\Psi_{a\bar b}^{**}|\mathcal{H}-E_0|\Psi_{\bar a b}^{**}\rangle=\frac12\langle\Psi_{a\bar b}^{r\bar s}|\mathcal{H}|\Psi_{\bar a b}^{\bar r s}\rangle+\frac12\langle\Psi_{a\bar b}^{r\bar s}|\mathcal{H}|\Psi_{\bar a b}^{\bar s r}\rangle+\frac12\langle\Psi_{a\bar b}^{s\bar r}|\mathcal{H}|\Psi_{\bar a b}^{\bar r s}\rangle+\frac12\langle\Psi_{a\bar b}^{s\bar r}|\mathcal{H}|\Psi_{\bar a b}^{\bar s r}\rangle$.

$=\frac12[\langle r\bar a b\bar s|\mathcal{H}|a\bar r s\bar b\rangle+\langle r\bar a b\bar s|\mathcal{H}|a\bar s r\bar b\rangle+\langle s\bar a b\bar r|\mathcal{H}|a\bar r s\bar b\rangle+\langle s\bar a b\bar r|\mathcal{H}|a\bar s r\bar b\rangle]$

$=\frac12[0+\langle r\bar s\bar a b|\mathcal{H}|r\bar s\bar b a\rangle+\langle s\bar r\bar a b|\mathcal{H}|s\bar r\bar b a\rangle+0]=\frac12[\langle\bar a b||\bar b a\rangle+\langle\bar a b||\bar b a\rangle]$

$=\langle\bar a b|\bar b a\rangle-\langle\bar a b|a\bar b\rangle=(ab|ba)=\frac12J_{11}$，从而再由 $\mathcal{H}-E_0$ 对应为Hermite矩阵，得

$$\begin{pmatrix} 0 & \frac{1}{\sqrt2}K_{12} & \frac{1}{\sqrt2}K_{12} & \frac{1}{\sqrt2}K_{12} & \frac{1}{\sqrt2}K_{12} \\ \frac{1}{\sqrt2}K_{12} & 2\Delta' & \frac12J_{11} & \frac12K_{12}-J_{12} & \frac12K_{12}-J_{12} \\ \frac{1}{\sqrt2}K_{12} & \frac12J_{11} & 2\Delta' & \frac12K_{12}-J_{12} & \frac12K_{12}-J_{12} \\ \frac{1}{\sqrt2}K_{12} & \frac12K_{12}-J_{12} & \frac12K_{12}-J_{12} & 2\Delta' & \frac12J_{11} \\ \frac{1}{\sqrt2}K_{12} & \frac12K_{12}-J_{12} & \frac12K_{12}-J_{12} & \frac12J_{11} & 2\Delta' \end{pmatrix}\begin{pmatrix}1\\C_1\\C_2\\C_3\\C_4\end{pmatrix}=E_{corr}(DCI)\begin{pmatrix}1\\C_1\\C_2\\C_3\\C_4\end{pmatrix}$$

(b) 由(a)中结论，$\frac{1}{\sqrt2}K_{12}+2\Delta'C_1+\frac12J_{11}C_2+(\frac12K_{12}-J_{12})C_3+(\frac12K_{12}-J_{12})C_4={}^2E_{corr}C_1$ (a)

$\frac{1}{\sqrt2}K_{12}+\frac12J_{11}C_1+2\Delta'C_2+(\frac12K_{12}-J_{12})C_3+(\frac12K_{12}-J_{12})C_4={}^2E_{corr}C_2$ (b)

$\frac{1}{\sqrt2}K_{12}+(\frac12K_{12}-J_{12})C_1+(\frac12K_{12}-J_{12})C_2+2\Delta'C_3+\frac12J_{11}C_4={}^2E_{corr}C_3$ (c)

$\frac{1}{\sqrt2}K_{12}+(\frac12K_{12}-J_{12})C_1+(\frac12K_{12}-J_{12})C_2+\frac12J_{11}C_3+2\Delta'C_4={}^2E_{corr}C_4$. (d)

5.11.

由式(a)及式(b),知 $c_1=c_2$;由式(c)及式(d),知 $c_3=c_4$ 从而式(b)与式(c)化简为

$$\frac{1}{\sqrt{2}}K_{12}+\left(\frac{1}{2}J_{11}+2\Delta'\right)c_1+(K_{12}-2J_{12})c_3={}^2E_{corr}c_1 \qquad (e)$$

$$\frac{1}{\sqrt{2}}K_{12}+(K_{12}-2J_{12})c_1+\left(\frac{1}{2}J_{11}+2\Delta'\right)c_3={}^2E_{corr}c_3 \qquad (f)$$

从式(e)及式(f),得 $c_1=c_3$. $\therefore c_1=c_2=c_3=c_4$. 将此式代入(a)中结论. $\frac{1}{\sqrt{2}}K_{12}(c_1+c_2+c_3+c_4)={}^2E_{corr}(DCI)$,得.

$${}^2E_{corr}(DCI)=2K_{12}c_1 \qquad (g)$$

代回式(e),得.

$$c_1=\frac{-\frac{1}{\sqrt{2}}K_{12}}{\frac{1}{2}J_{11}+2\Delta'+K_{12}-2J_{12}-{}^2E_{corr}(DCI)} \qquad (h)$$

(g)与(h)消去 c_1,得 $\quad ({}^2E_{corr}(DCI))^2-2\Delta({}^2E_{corr}(DCI))-2K_{12}^2=0$

此期间代入了 $2\Delta'=2\Delta-\frac{1}{2}J_{11}+2J_{12}-K_{12}$. 从而 ${}^2E_{corr}(DCI)=\Delta-\sqrt{\Delta^2+2K_{12}^2}$.

与之前的结果相同.

练习5.8 ${}^2E_{corr}(FO(D))=\frac{|\langle a\bar{a}||r\bar{r}\rangle|^2}{\varepsilon_a+\varepsilon_a-\varepsilon_r-\varepsilon_r}+\frac{|\langle a\bar{a}||s\bar{s}\rangle|^2}{\varepsilon_a+\varepsilon_a-\varepsilon_s-\varepsilon_s}+\frac{|\langle a\bar{a}||r\bar{s}\rangle|^2}{\varepsilon_a+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\frac{|\langle a\bar{a}||s\bar{r}\rangle|^2}{\varepsilon_a+\varepsilon_a-\varepsilon_s-\varepsilon_r}+\frac{|\langle b\bar{b}||r\bar{r}\rangle|^2}{\varepsilon_b+\varepsilon_b-\varepsilon_r-\varepsilon_r}+\frac{|\langle b\bar{b}||s\bar{s}\rangle|^2}{\varepsilon_b+\varepsilon_b-\varepsilon_s-\varepsilon_s}+$

$\frac{|\langle b\bar{b}||s\bar{r}\rangle|^2}{\varepsilon_b+\varepsilon_b-\varepsilon_s-\varepsilon_r}+\frac{|\langle b\bar{b}||r\bar{s}\rangle|^2}{\varepsilon_b+\varepsilon_b-\varepsilon_r-\varepsilon_s}+\frac{|\langle a\bar{b}||r\bar{r}\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_r}+\frac{|\langle a\bar{b}||s\bar{s}\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_s-\varepsilon_s}+\frac{|\langle a\bar{b}||r\bar{s}\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}+\frac{|\langle a\bar{b}||s\bar{r}\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}+$

$\frac{|\langle b\bar{a}||s\bar{r}\rangle|^2}{\varepsilon_b+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\frac{|\langle b\bar{a}||s\bar{s}\rangle|^2}{\varepsilon_b+\varepsilon_a-\varepsilon_s-\varepsilon_s}+\frac{|\langle b\bar{a}||r\bar{s}\rangle|^2}{\varepsilon_b+\varepsilon_a-\varepsilon_r-\varepsilon_s}+\frac{|\langle b\bar{a}||s\bar{r}\rangle|^2}{\varepsilon_b+\varepsilon_a-\varepsilon_s-\varepsilon_r}$.

$=\frac{1}{2(\varepsilon_1-\varepsilon_2)}\left[\frac14K_{12}^2+\frac14K_{12}^2+0+0+\frac14K_{12}^2+\frac14K_{12}^2+0+0+0+0+\frac14K_{12}^2+\frac14K_{12}^2+0+0+\frac14K_{12}^2+\frac14K_{12}^2\right]$.

$=\frac{2K_{12}^2}{2(\varepsilon_1-\varepsilon_2)}=2\left(\frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)}\right)$. 即式(5.46)结果

练习5.9 (a) $\langle\Psi_0|\mathscr{H}|\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle=\langle 1_1\bar{1}_1 1_2\bar{1}_2|\mathscr{H}|2_1\bar{2}_1 1_2\bar{1}_2\rangle=\langle 1_1\bar{1}_1||2_1\bar{2}_1\rangle=K_{12}$, $\langle\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}|\mathscr{H}|\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle=2h_{11}+2h_{22}+J_{11}+J_{22}$

$E_0=\langle 1_1|h|1_1\rangle+\langle\bar{1}_1|h|\bar{1}_1\rangle+\langle 1_2|h|1_2\rangle+\langle\bar{1}_2|h|\bar{1}_2\rangle+\langle 1_1\bar{1}_1||1_1\bar{1}_1\rangle+\langle 1_1 1_2||1_1 1_2\rangle+\langle 1_1\bar{1}_2||1_1\bar{1}_2\rangle$
$+\langle\bar{1}_1 1_2||\bar{1}_1 1_2\rangle+\langle\bar{1}_1\bar{1}_2||\bar{1}_1\bar{1}_2\rangle+\langle 1_2\bar{1}_2||1_2\bar{1}_2\rangle$

$=4h_{11}+2J_{11}$ $\quad\therefore\langle\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}|\mathscr{H}-E_0|\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle=2(\varepsilon_2-\varepsilon_1)-4J_{12}+2K_{12}+J_{11}+J_{22}=2\Delta$.

$\therefore e_{1_1\bar{1}_1}^{EN}=-\frac{|\langle\Psi_0|\mathscr{H}|\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle|^2}{\langle\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}|\mathscr{H}-E_0|\Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle}=-\frac{K_{12}^2}{2\Delta}$ 而 ${}^2E_{corr}(EN(L))=e_{1_1\bar{1}_1}^{EN}+e_{1_2\bar{1}_2}^{EN}=-\frac{K_{12}^2}{\Delta}$.

(b) $\langle\Psi_{a\bar{a}}^{r\bar{s}}|\mathscr{H}|\Psi_{a\bar{a}}^{r\bar{s}}\rangle=\langle b|h|b\rangle+\langle\bar{b}|h|\bar{b}\rangle+\langle r|h|r\rangle+\langle\bar{s}|h|\bar{s}\rangle+\langle r\bar{s}||r\bar{s}\rangle+\langle rb||rb\rangle+\langle r\bar{b}||r\bar{b}\rangle$
$+\langle\bar{s}b||\bar{s}b\rangle+\langle\bar{s}\bar{b}||\bar{s}\bar{b}\rangle+\langle b\bar{b}||b\bar{b}\rangle$

$=2h_{11}+2h_{22}+(rr|ss)+(rr|bb)-(rb|br)+(rr|bb)+(ss|bb)+(ss|bb)-(sb|bs)+(bb|bb)$

$=2h_{11}+2h_{22}+\frac12J_{11}+2J_{12}+\frac12J_{22}-K_{12}$.

$\langle\Psi_{a\bar{a}}^{r\bar{s}}|\mathscr{H}|\Psi_{a\bar{a}}^{s\bar{r}}\rangle=\langle r\bar{s}||s\bar{r}\rangle=(rs|rs)=\frac12J_{22}$. 同理. $\langle\Psi_{a\bar{a}}^{s\bar{r}}|\mathscr{H}|\Psi_{a\bar{a}}^{s\bar{r}}\rangle=\langle\Psi_{a\bar{a}}^{r\bar{s}}|\mathscr{H}|\Psi_{a\bar{a}}^{r\bar{s}}\rangle$.

$\therefore\langle\Psi_{a\bar{a}}^{**}|\mathscr{H}|\Psi_{a\bar{a}}^{**}\rangle=\frac12[\langle\Psi_{a\bar{a}}^{r\bar{s}}|\mathscr{H}|\Psi_{a\bar{a}}^{r\bar{s}}\rangle+\langle\Psi_{a\bar{a}}^{r\bar{s}}|\mathscr{H}|\Psi_{a\bar{a}}^{s\bar{r}}\rangle+\langle\Psi_{a\bar{a}}^{s\bar{r}}|\mathscr{H}|\Psi_{a\bar{a}}^{r\bar{s}}\rangle+\langle\Psi_{a\bar{a}}^{s\bar{r}}|\mathscr{H}|\Psi_{a\bar{a}}^{s\bar{r}}\rangle]$

$=2h_{11}+2h_{22}+\frac12J_{11}+2J_{12}+\frac12J_{22}-K_{12}+\frac12J_{22}\Rightarrow\langle\Psi_{a\bar{a}}^{**}|\mathscr{H}-E_0|\Psi_{a\bar{a}}^{**}\rangle=2(\varepsilon_2-\varepsilon_1)+\frac12J_{11}+\frac12J_{22}-2J_{12}+K_{12}=2\Delta'$

由教材练习5.6,或由教材式(5.38),得. ${}^2E_{corr}(EN(D))=4e_{a\bar{a}}^{EN}$, 而 $\langle\Psi_0|\mathscr{H}|\Psi_{a\bar{a}}^{**}\rangle=\frac{1}{\sqrt{2}}K_{12}$.

而 $e_{a\bar{a}}^{EN}=-\frac{|\langle\Psi_0|\mathscr{H}|\Psi_{a\bar{a}}^{**}\rangle|^2}{\langle\Psi_{a\bar{a}}^{**}|\mathscr{H}-E_0|\Psi_{a\bar{a}}^{**}\rangle}=-\frac{K_{12}^2/2}{2\Delta'}=-\frac{K_{12}^2}{4\Delta'}$ $\quad\therefore{}^2E_{corr}(EN(D))=-\frac{K_{12}^2}{\Delta'}$.

(c) 同(b). 只是 $\langle{}^B\Psi_{a\bar{b}}^{r\bar{s}}|\mathscr{H}-E_0|{}^B\Psi_{a\bar{b}}^{r\bar{s}}\rangle=2\Delta''$ 由教材式(5.42b)得. $\langle\Psi_0|\mathscr{H}|{}^B\Psi_{a\bar{b}}^{r\bar{s}}\rangle=K_{12}$ 由教材式(5.42a)得.

$\therefore e_{a\bar a}'' = -\frac{K_{12}^2}{2\Delta''}$. 而 $e_{a\bar a} = -\frac{K_{12}^2}{4\Delta'}$ 由(b)得, $e_{b\bar b} = -\frac{K_{12}^2}{4\Delta'}$ 同理.

从而 ${}^2E_{corr}^{singlet}(EN(D)) = -\frac{K_{12}^2}{2\Delta''} - \frac{K_{12}^2}{2\Delta'}$.

(d). $R=1.4$ a.u.时, $J_{11}=0.6746$ a.u., $J_{12}=0.6636$ a.u. $J_{22}=0.6975$ a.u. $K_{12}=0.1813$ a.u. $\varepsilon_1=-0.5782$ a.u. $\varepsilon_2=0.6703$ a.u.

$\therefore \Delta = \varepsilon_2-\varepsilon_1+\frac12 J_{11}+\frac12 J_{22}-2J_{12}+K_{12} = 0.78865$ a.u. $\Rightarrow {}^2E_{corr}(EN(L)) = -0.04168$ a.u.

$\Delta' = \varepsilon_2-\varepsilon_1+\frac12 J_{22}+\frac14(J_{11}-4J_{12}+2K_{12}) = 1.19295$ a.u. $\Rightarrow {}^2E_{corr}(EN(D)) = -0.02755$ a.u.

$\Delta'' = \varepsilon_2-\varepsilon_1+\frac12 J_{11}+\frac12 J_{22}-J_{12}+\frac12 K_{12} = 1.3616$ a.u. $\Rightarrow {}^2E_{corr}^{singlet}(EN(D)) = -0.02414$ a.u.

练习5.10 $\langle\Psi_0|\mathcal{H}-E_0|\Psi_0\rangle = 0$. $\langle\Psi_0|\mathcal{H}|\Psi_{a\bar a}^{**}\rangle = \frac{1}{\sqrt2}K_{12}$ (见练习5.5). $\langle\Psi_0|\mathcal{H}|\Psi_{b\bar b}^{**}\rangle = \frac{1}{\sqrt2}K_{12}$. 同理.

$\langle\Psi_0|\mathcal{H}-E_0|{}^1\Psi_{ab}^{rs}\rangle = \langle\Psi_0|\mathcal{H}|{}^1\Psi_{ab}^{rs}\rangle = K_{12}$, 即式(5.42a).

由练习5.5. $\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{a\bar a}^{**}\rangle = 2\Delta'$. 由练习5.6. $\langle\Psi_{b\bar b}^{**}|\mathcal{H}-E_0|\Psi_{b\bar b}^{**}\rangle = 2\Delta'$. 由教材式(5.42b)得.

$$\langle{}^1\Psi_{ab}^{rs}|\mathcal{H}-E_0|{}^1\Psi_{ab}^{rs}\rangle = 2\Delta''.$$

又 $\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|\Psi_{b\bar b}^{**}\rangle = \frac12[\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{b\bar b}^{r\bar r}\rangle + \langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{b\bar b}^{s\bar s}\rangle + \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{b\bar b}^{r\bar r}\rangle + \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{b\bar b}^{s\bar s}\rangle]$

$= \frac12[\langle r\bar r b\bar b|\mathcal{H}|a\bar a r\bar r\rangle + \langle r\bar r b\bar b|\mathcal{H}|a\bar a s\bar s\rangle + \langle s\bar s b\bar b|\mathcal{H}|a\bar a r\bar r\rangle + \langle s\bar s b\bar b|\mathcal{H}|a\bar a s\bar s\rangle] = \frac12 J_{11}$.

$\langle\Psi_{a\bar a}^{**}|\mathcal{H}-E_0|{}^1\Psi_{ab}^{**}\rangle = \frac{1}{2\sqrt2}[\langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{a\bar b}^{r\bar s}\rangle + \langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{\bar a b}^{\bar r s}\rangle + \langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{a\bar b}^{s\bar r}\rangle + \langle\Psi_{a\bar a}^{r\bar r}|\mathcal{H}|\Psi_{\bar a b}^{\bar s r}\rangle$

$+ \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{a\bar b}^{r\bar s}\rangle + \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{\bar a b}^{\bar r s}\rangle + \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{a\bar b}^{s\bar r}\rangle + \langle\Psi_{a\bar a}^{s\bar s}|\mathcal{H}|\Psi_{\bar a b}^{\bar s r}\rangle]$

$= \frac{1}{2\sqrt2}[\langle r\bar r b\bar b|\mathcal{H}|a s r\bar b\rangle + \langle r\bar r b\bar b|\mathcal{H}|a r s\bar b\rangle + \langle r\bar r b\bar b|\mathcal{H}|r a b\bar s\rangle + \langle r\bar r b\bar b|\mathcal{H}|s a b\bar r\rangle$

$+ \langle s\bar s b\bar b|\mathcal{H}|a s r\bar b\rangle + \langle s\bar s b\bar b|\mathcal{H}|a r s\bar b\rangle + \langle s\bar s b\bar b|\mathcal{H}|r a b\bar s\rangle + \langle s\bar s b\bar b|\mathcal{H}|s a b\bar r\rangle]$

$= \frac{1}{2\sqrt2}[\langle\bar r b||a\bar s\rangle + \langle\bar r b||a s\rangle + \langle\bar r b||\bar a\bar s\rangle + \langle r b||\bar a s\rangle + \langle s b||a r\rangle + \langle b s||\bar r a\rangle + \langle s b||\bar a r\rangle + \langle\bar s b||a\bar r\rangle]$

$= \frac{1}{2\sqrt2}[-(rs|ba)+(ra|bs)-(rs|ba)+(ra|bs)-(rs|ba)-(rs|ba)+(sa|br)-(sr|ba)-(ba|sr)-(sr|ba)+(sa|br)-(sr|ba)]$

$= \frac{1}{2\sqrt2}[2(ra|bs)+2(sa|br)-8(sr|ba)] = \frac{1}{2\sqrt2}(2\cdot\frac12 K_{12}+2\cdot\frac12 K_{12}-8\cdot\frac12 J_{12}) = \frac{1}{\sqrt2}(K_{12}-2J_{12})$.

同理得 $\langle\Psi_{b\bar b}^{**}|\mathcal{H}|{}^1\Psi_{ab}^{**}\rangle = \frac{1}{\sqrt2}(K_{12}-2J_{12})$. 从而同教材4.1.1节排列矩阵为

$$\begin{pmatrix} 0 & \frac{1}{\sqrt2}K_{12} & \frac{1}{\sqrt2}K_{12} & K_{12} \\ \frac{1}{\sqrt2}K_{12} & 2\Delta' & \frac12 J_{11} & \frac{1}{\sqrt2}(K_{12}-2J_{12}) \\ \frac{1}{\sqrt2}K_{12} & \frac12 J_{11} & 2\Delta' & \frac{1}{\sqrt2}(K_{12}-2J_{12}) \\ K_{12} & \frac{1}{\sqrt2}(K_{12}-2J_{12}) & \frac{1}{\sqrt2}(K_{12}-2J_{12}) & 2\Delta'' \end{pmatrix}\begin{pmatrix}1\\c_1\\c_2\\c_3\end{pmatrix} = {}^2E_{corr}(DCI)\begin{pmatrix}1\\c_1\\c_2\\c_3\end{pmatrix}$$

由 $\frac{1}{\sqrt2}K_{12}+2\Delta' c_1+\frac12 J_{11}c_2+\frac{1}{\sqrt2}(K_{12}-2J_{12})c_3 = {}^2E_{corr}(DCI)c_1$ 及 $\frac{1}{\sqrt2}K_{12}+\frac12 J_{11}c_1+2\Delta' c_2+\frac{1}{\sqrt2}(K_{12}-2J_{12})c_3 = {}^2E_{corr}(DCI)c_2$.

从而 $c_1=c_2$. 将此代入 $K_{12}+\frac{1}{\sqrt2}(K_{12}-2J_{12})c_1+\frac{1}{\sqrt2}(K_{12}-2J_{12})c_2+2\Delta'' c_3 = {}^2E_{corr}(DCI)c_3$. 得

$$\sqrt2(K_{12}-2J_{12})c_1+(2\Delta''-E)c_3 = -K_{12}.\quad E\equiv{}^2E_{corr}(DCI) \qquad (1)$$

与式回本身有

$$(2\Delta''+\frac12 J_{11}-E)c_1+\frac{1}{\sqrt2}(K_{12}-2J_{12}) = -\frac{1}{\sqrt2}K_{12} \qquad (2)$$

联立(1),(2)得

$$c_1 = \frac{-K_{12}}{\sqrt2(2\Delta-{}^2E_{corr}(DCI))},\quad c_3 = -\frac{K_{12}}{2\Delta-{}^2E_{corr}(DCI)} \qquad (3)$$

将$C_1=C_2$，及式(3)代入$\frac{1}{\sqrt{2}}K_{12}C_1+\frac{1}{\sqrt{2}}K_{12}C_2+K_{12}C_3={}^2E_{corr}(DCI)$，得

$$({}^2E_{corr}(DCI))^2-2\Delta\,{}^2E_{corr}(DCI)-2K_{12}^2=0.$$

从而${}^2E_{corr}(DCI)=\Delta-\sqrt{\Delta^2+2K_{12}^2}$.

5.2.2节(波函数的簇展开)习题解析

习题5.11 $|\Phi\rangle = e^{\tau_1+\tau_2}|1_1\bar{1}_1 1_2\bar{1}_2\rangle = (1+\tau_1)(1+\tau_2)|1_1\bar{1}_1 1_2\bar{1}_2\rangle$ $\left(\tau_1 = C_{1_1\bar{1}_1}^{2_1\bar{2}_1} a^\dagger_{2_1} a^\dagger_{\bar{2}_1} a_{\bar{1}_1} a_{1_1},\ \tau_2 = C_{1_2\bar{1}_2}^{2_2\bar{2}_2} a^\dagger_{2_2} a^\dagger_{\bar{2}_2} a_{\bar{1}_2} a_{1_2}\right)$.

$= (1+\tau_1+\tau_2+\tau_1\tau_2)|1_1\bar{1}_1 1_2\bar{1}_2\rangle = |1_1\bar{1}_1 1_2\bar{1}_2\rangle + C_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1 1_2\bar{1}_2\rangle + C_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1 2_2\bar{2}_2\rangle + C_{1_1\bar{1}_1}^{2_1\bar{2}_1} C_{1_2\bar{1}_2}^{2_2\bar{2}_2}|2_1\bar{2}_1 2_2\bar{2}_2\rangle$.

为何 $e^{\tau_1} = 1+\tau_1$ 呢？因为对双独立H_2模型来讲，多了没意义(湮灭不存在的电子不可行)。

5.2.3节 线性CCA方法及耦合电子对近似(CEPA)习题解析.

练习5.12. (a). $E_{corr}(L\text{-}CCA) = -\sum_{r<s}\sum_{a<b}\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle^{-1}\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle = \sum_{a<b}\left(-\sum_{r<s}\frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle}\right)$

从而记 $e_{ab} = -\sum_{r<s}\frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle}$，即得 $E_{corr}(L\text{-}CCA) = \sum_{a<b} e_{ab}$. 此即为式(5.15)及式(5.16).

(b) 设 $|\Phi\rangle = |\Psi_0\rangle + c_1|\Psi_{a\bar a}^{**}\rangle + c_2|\Psi_{b\bar b}^{**}\rangle + c_3|\Psi_{a\bar b}^{**}\rangle + c_4|\Psi_{\bar a b}^{**}\rangle$. 则由L-CCA方法应得

$$E_{corr} = c_1\langle\Psi_0|\mathscr{H}|\Psi_{a\bar a}^{**}\rangle + c_2\langle\Psi_0|\mathscr{H}|\Psi_{b\bar b}^{**}\rangle + c_3\langle\Psi_0|\mathscr{H}|\Psi_{a\bar b}^{**}\rangle + c_4\langle\Psi_0|\mathscr{H}|\Psi_{\bar a b}^{**}\rangle \quad (1)$$

$$\langle\Psi_{a\bar a}^{**}|\mathscr{H}|\Psi_0\rangle + c_1\langle\Psi_{a\bar a}^{**}|\mathscr{H}-E_0|\Psi_{a\bar a}^{**}\rangle + c_2\langle\Psi_{a\bar a}^{**}|\mathscr{H}-E_0|\Psi_{b\bar b}^{**}\rangle + c_3\langle\Psi_{a\bar a}^{**}|\mathscr{H}-E_0|\Psi_{a\bar b}^{**}\rangle + c_4\langle\Psi_{a\bar a}^{**}|\mathscr{H}-E_0|\Psi_{\bar a b}^{**}\rangle = 0. \quad (2)$$

式(2)有4个，依次换 $\langle\Psi_{a\bar a}^{**}|$ 为 $\langle\Psi_{b\bar b}^{**}|$, $\langle\Psi_{a\bar b}^{**}|$, $\langle\Psi_{\bar a b}^{**}|$ 即得其余3式. 排成矩阵并代入元素(由练习5.7 a结论)，得

$$\begin{pmatrix} 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12}-J_{12} & \frac{1}{2}K_{12}-J_{12} \\ \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12}-J_{12} & \frac{1}{2}K_{12}-J_{12} \\ \frac{1}{2}K_{12}-J_{12} & \frac{1}{2}K_{12}-J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ \frac{1}{2}K_{12}-J_{12} & \frac{1}{2}K_{12}-J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = -\frac{K_{12}}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}.$$

由矩阵前二行知 $c_1 = c_2$，后二行知 $c_3 = c_4$. 从而矩阵化简为

$$\begin{pmatrix} 2\Delta' + \frac{1}{2}J_{11} & K_{12}-2J_{12} \\ K_{12}-2J_{12} & 2\Delta'+\frac{1}{2}J_{11} \end{pmatrix}\begin{pmatrix} c_1 \\ c_3 \end{pmatrix} = -\frac{K_{12}}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

从而知 $c_1 = c_3$. 从而

$$\left(2\Delta' + \frac{1}{2}J_{11} + K_{12} - 2J_{12}\right)c_1 = 2\Delta c_1 = -\frac{K_{12}}{\sqrt{2}} \Rightarrow c_1 = -\frac{K_{12}}{2\sqrt{2}\Delta}.$$

从而

$$E_{corr}(L\text{-}CCA(D)) = c_1\cdot\frac{1}{\sqrt{2}}K_{12} + c_2\cdot\frac{K_{12}}{\sqrt{2}} + c_3\cdot\frac{K_{12}}{\sqrt{2}} + c_4\cdot\frac{K_{12}}{\sqrt{2}} = -\frac{K_{12}^2}{\Delta}.$$

而使用定域轨道时同理. 设 $|\Phi_0\rangle = |\Psi_0\rangle + c_1|\Psi_{1\bar 1}^{2\bar 2}\rangle + c_2|\Psi_{\bar 1 \bar 2}^{2\bar 2}\rangle$. 相应方程为

$$\begin{pmatrix} 2\Delta & 0 \\ 0 & 2\Delta \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = -K_{12}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$\therefore c_1 = c_2 = -K_{12}/2\Delta$. 代入到 ${}^2E_{corr}(L\text{-}CCA(L)) = K_{12}\cdot c_1 + K_{12}\cdot c_2 = -K_{12}^2/2\Delta - K_{12}^2/2\Delta = -K_{12}^2/\Delta$.

5.3.0节（单粒子Hamilton量的多电子理论）习题解析.

练习5.13 方程为 $H_{12}C^2+(H_{11}-H_{22})C-H_{21}=0$. $\therefore \Delta=(H_{11}-H_{22})^2+4H_{12}H_{21}>0$.

$\therefore C_{1,2}=\frac{1}{2H_{12}}\left[H_{22}-H_{11}\pm\sqrt{(H_{11}-H_{22})^2+4H_{12}H_{21}}\right]$ $\quad\therefore E_R=\frac{1}{2}\left[H_{22}-H_{11}-\sqrt{(H_{11}-H_{22})^2+4H_{12}H_{21}}\right]=\varepsilon_1-H_{11}$

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

5.3.1节(CI. IEPA, CEPA及CCA中的迟豫能)

练习5.14 (a) $\langle\Psi_0|\mathcal{H}|\Psi_b^s\rangle=\sum_{i=1}^{N}\langle\Psi_0|h(i)|\Psi_b^s\rangle+\sum_{i=1}^{N}\langle\Psi_0|v(i)|\Psi_b^s\rangle=\langle\chi_b^{(0)}|v|\chi_s^{(0)}\rangle=V_{bs}$.

(b) $\langle\Psi_a^r|\mathcal{H}|\Psi_0\rangle=\sum_{i=1}^{N}\langle\Psi_a^r|h(i)|\Psi_0\rangle+\sum_{i=1}^{N}\langle\Psi_a^r|v(i)|\Psi_0\rangle=\langle\chi_r^{(0)}|v|\chi_a^{(0)}\rangle=V_{ra}$

(c). $\langle\Psi_a^r|\mathcal{H}|\Psi_a^r\rangle=\sum_{i=1}^{N\setminus a}\langle\chi_i|h(i)+v(i)|\chi_i^{(0)}\rangle+\langle\chi_r^{(0)}|h+v|\chi_r\rangle=E_0+\varepsilon_r^{(0)}+V_{rr}-\varepsilon_a^{(0)}-V_{aa}$

而 $E_0\langle\Psi_a^r|\Psi_a^r\rangle=E_0\Rightarrow\langle\Psi_a^r|\mathcal{H}-E_0|\Psi_a^r\rangle=\varepsilon_r^{(0)}+V_{rr}-\varepsilon_a^{(0)}-V_{aa}$.

当 $r\neq s, a\neq b$ 时, 由于$\mathcal{H}$是单粒子变换之和, 从而 $\langle\Psi_a^r|\mathcal{H}-E_0|\Psi_b^s\rangle=0-0=0$;

当 $r=s, a\neq b$ 时, 由于$\mathcal{H}$中一次只有一个对应a, 则 $\langle\Psi_a^r|\mathcal{H}|\Psi_b^r\rangle=\langle\cdots r\cdots b\cdots|\mathcal{H}|\cdots a\cdots r\cdots\rangle$

交换b与r. 则 $\langle\Psi_a^r|\mathcal{H}|\Psi_b^r\rangle=-\langle\cdots b\cdots r\cdots|\mathcal{H}|\cdots a\cdots r\cdots\rangle=-V_{ba}$; 从而 $\langle\Psi_a^r|\Psi_b^r\rangle=0$.

从而 $\langle\Psi_a^r|\mathcal{H}-E_0|\Psi_b^r\rangle=-V_{ba}(r\neq s)$;

当 $r\neq s, a=b$ 时. 同理, $\langle\Psi_a^r|\mathcal{H}|\Psi_a^s\rangle=\langle\cdots r\cdots b\cdots|\mathcal{H}|\cdots s\cdots b\cdots\rangle=\langle\chi_r^{(0)}|v|\chi_s^{(0)}\rangle=V_{rs}$. $\therefore\langle\Psi_a^r|\mathcal{H}-E_0|\Psi_a^s\rangle=V_{rs}$;

综上, 有

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

(d) $\langle\Psi_a^r|\mathcal{H}|\Psi_{ab}^{rs}\rangle$大抵相当于$\langle\Psi_0|\mathcal{H}|\Psi_a^r\rangle$, 只是(a, r)与(b, s)有重合可能. 计及此处只需注意 $|\Psi_{aa}^{rs}\rangle=0$.

$|\Psi_{aa}^{rs}\rangle=0$. (激发同一电子到二相异电子态不被允许). $|\Psi_{ab}^{rr}\rangle=0$ (激发两电子到同态违反不相容原理). 从而

$$\langle\Psi_a^r|\mathcal{H}|\Psi_{ab}^{rs}\rangle=\begin{cases}V_{bs} & a\neq b\wedge r\neq s\\ 0. & a=b\vee r=s.\end{cases}$$

练习5.15. (a) $|\Phi_0\rangle=|(a_1\chi_1^{(0)}+a_2\chi_2^{(0)}+a_3\chi_3^{(0)}+a_4\chi_4^{(0)})(b_1\chi_1^{(0)}+b_2\chi_2^{(0)}+b_3\chi_3^{(0)}+b_4\chi_4^{(0)})\rangle$

$$\begin{aligned}&=(a_1b_2-a_2b_1)|\chi_1^{(0)}\chi_2^{(0)}\rangle+(a_1b_3-a_3b_1)|\chi_1^{(0)}\chi_3^{(0)}\rangle+(a_1b_4-a_4b_1)|\chi_1^{(0)}\chi_4^{(0)}\rangle\\&\quad+(a_2b_3-a_3b_2)|\chi_2^{(0)}\chi_3^{(0)}\rangle+(a_2b_4-a_4b_2)|\chi_2^{(0)}\chi_4^{(0)}\rangle+(a_3b_4-a_4b_3)|\chi_3^{(0)}\chi_4^{(0)}\rangle.\\&=(a_1b_2-a_2b_1)|\Psi_0\rangle+(a_1b_3-a_3b_1)|\Psi_2^3\rangle+(a_1b_4-a_4b_1)|\Psi_2^4\rangle-(a_2b_3-a_3b_2)|\Psi_1^3\rangle-(a_2b_4-a_4b_2)|\Psi_1^4\rangle+(a_3b_4-a_4b_3)|\Psi_{12}^{34}\rangle.\end{aligned}$$

经中间归一化后, 得

$$|\Phi_0\rangle=|\Psi_0\rangle+\frac{1}{a_1b_2-a_2b_1}\left[(a_1b_1-a_3b_1)|\Psi_2^3\rangle+(a_1b_4-a_4b_1)|\Psi_2^4\rangle-(a_2b_3-a_3b_2)|\Psi_1^3\rangle-(a_2b_4-a_4b_2)|\Psi_1^4\rangle+(a_3b_4-a_4b_3)|\Psi_{12}^{34}\rangle\right]$$

从而 $C_{12}^{34}=\frac{a_3b_4-a_4b_3}{a_1b_2-a_2b_1}$, $C_1^3C_2^4-C_1^4C_2^3=\frac{-(a_2b_3-a_3b_2)}{a_1b_2-a_2b_1}\cdot\frac{(a_1b_4-a_4b_1)}{a_1b_2-a_2b_1}-\frac{-(a_2b_4-a_4b_2)}{a_1b_2-a_2b_1}\cdot\frac{a_1b_3-a_3b_1}{a_1b_2-a_2b_1}=\frac{a_3b_4-a_4b_3}{a_1b_2-a_2b_1}=C_{12}^{34}$.

(b) $U_{AA}^{-1}=\frac{1}{a_1b_2-b_1a_2}\begin{pmatrix}b_2 & -b_1\\ -a_2 & a_1\end{pmatrix}$ $U_{BA}=\begin{pmatrix}a_3 & b_3\\ a_4 & b_4\end{pmatrix}$ $\therefore(U_{BA}U_{AA}^{-1})_{11}=(U_{BA})_{11}(U_{AA}^{-1})_{11}+(U_{BA})_{12}(U_{AA}^{-1})_{21}=\frac{b_2a_3-a_2b_3}{a_1b_2-a_2b_1}=C_1^3$.

确与(a)中得 $|\Psi_1^3\rangle$ 系数相同.

5.3.2节（Hückel理论中苯的共轭能）习题解析

练习5.16　苯的Hückel矩阵为

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

$\therefore \det(H-EI)=(\alpha'-2\beta)(\alpha'-\beta)^2(\alpha'+\beta)^2(\alpha'+2\beta)=0.\ \alpha'=\alpha-E.$

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

$\therefore E_0=6\alpha+8\beta.$

练习5.17

$\langle i|j\rangle=\frac{1}{2}[\langle\phi_{2i-1}|\phi_{2j-1}\rangle+\langle\phi_{2i-1}|\phi_{2j}\rangle+\langle\phi_{2i}|\phi_{2j-1}\rangle+\langle\phi_{2i}|\phi_{2j-1}\rangle]=\frac{1}{2}[\delta_{ij}+0+0+\delta_{ij}]=\delta_{ij}.$

$\langle i^*|j^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|\phi_{2j-1}\rangle-\langle\phi_{2i-1}|\phi_{2j}\rangle-\langle\phi_{2i}|\phi_{2j-1}\rangle+\langle\phi_{2i}|\phi_{2j}\rangle]=\frac{1}{2}[\delta_{ij}-0-0-\delta_{ij}]=\delta_{ij}.$

$\langle i|j^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|\phi_{2j-1}\rangle-\langle\phi_{2i-1}|\phi_{2j}\rangle+\langle\phi_{2i}|\phi_{2j-1}\rangle-\langle\phi_{2i}|\phi_{2j}\rangle]=\frac{1}{2}[\delta_{ij}-0+0-\delta_{ij}]=0.$

$\langle i|h_{eff}|i\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i-1}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i-1}\rangle+\langle\phi_{2i-1}|h_{eff}|\phi_{2i}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i}\rangle]=\alpha+\beta.$

$\langle i^*|h_{eff}|i^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i-1}\rangle-\langle\phi_{2i-1}|h_{eff}|\phi_{2i}\rangle-\langle\phi_{2i}|h_{eff}|\phi_{2i-1}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i}\rangle]=\alpha-\beta.$

$\langle i|h_{eff}|i-1\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i-3}\rangle+\langle\phi_{2i-1}|h_{eff}|\phi_{2i-2}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i-3}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i-2}\rangle]=\frac{1}{2}\beta.$

$\langle i|h_{eff}|i+1\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i+1}\rangle+\langle\phi_{2i-1}|h_{eff}|\phi_{2i+2}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i+1}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i+2}\rangle]=\frac{1}{2}\beta.$

$\langle i^*|h_{eff}|(i+1)^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i+1}\rangle-\langle\phi_{2i-1}|h_{eff}|\phi_{2i+2}\rangle-\langle\phi_{2i}|h_{eff}|\phi_{2i+1}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i+2}\rangle]=\frac{1}{2}[0-0-\beta+0]=-\frac{1}{2}\beta.$

$\langle i^*|h_{eff}|(i-1)^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i-3}\rangle-\langle\phi_{2i-1}|h_{eff}|\phi_{2i-2}\rangle-\langle\phi_{2i}|h_{eff}|\phi_{2i-3}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i-2}\rangle]=\frac{1}{2}[0-\beta-0+0]=-\frac{1}{2}\beta.$

$\langle i|h_{eff}|(i+1)^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i+1}\rangle-\langle\phi_{2i-1}|h_{eff}|\phi_{2i+2}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i+1}\rangle-\langle\phi_{2i}|h_{eff}|\phi_{2i+2}\rangle]=\frac{1}{2}[0-0+\beta-0]=\frac{1}{2}\beta.$

$\langle i|h_{eff}|(i-1)^*\rangle=\frac{1}{2}[\langle\phi_{2i-1}|h_{eff}|\phi_{2i-3}\rangle-\langle\phi_{2i-1}|h_{eff}|\phi_{2i-2}\rangle+\langle\phi_{2i}|h_{eff}|\phi_{2i-3}\rangle-\langle\phi_{2i}|h_{eff}|\phi_{2i-2}\rangle]=\frac{1}{2}[0-\beta+0-0]=-\frac{1}{2}\beta.$

$\langle(i+1)|h_{eff}|i^*\rangle=\frac{1}{2}[\langle\phi_{2i+1}|h_{eff}|\phi_{2i-1}\rangle-\langle\phi_{2i+1}|h_{eff}|\phi_{2i}\rangle+\langle\phi_{2i+2}|h_{eff}|\phi_{2i-1}\rangle-\langle\phi_{2i+2}|h_{eff}|\phi_{2i}\rangle]=-\frac{1}{2}\beta.$

$\langle(i-1)|h_{eff}|i^*\rangle=\frac{1}{2}[\langle\phi_{2i-3}|h_{eff}|\phi_{2i-1}\rangle-\langle\phi_{2i-3}|h_{eff}|\phi_{2i}\rangle+\langle\phi_{2i-2}|h_{eff}|\phi_{2i-1}\rangle-\langle\phi_{2i-2}|h_{eff}|\phi_{2i}\rangle]=\frac{1}{2}\beta.$

练习5.18

$\langle\Psi_0|\mathcal{H}|{}^*_1\rangle=\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_1^{2^*}\rangle-\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_1^{3^*}\rangle=\frac{1}{\sqrt{2}}\left(\frac{\beta}{2}\right)-\frac{1}{\sqrt{2}}\left(-\frac{\beta}{2}\right)=\frac{1}{\sqrt{2}}\beta.$

$\langle{}^*_1|\mathcal{H}-E_0|{}^*_1\rangle=\frac{1}{2}[\langle\Psi_1^{2^*}|\mathcal{H}-E_0|\Psi_1^{2^*}\rangle-\langle\Psi_1^{2^*}|\mathcal{H}|\Psi_1^{3^*}\rangle-\langle\Psi_1^{3^*}|\mathcal{H}|\Psi_1^{2^*}\rangle+\langle\Psi_1^{3^*}|\mathcal{H}-E_0|\Psi_1^{3^*}\rangle]$

$=\frac{1}{2}[\varepsilon_{2^*}^{(0)}+V_{2^*2^*}-\varepsilon_1^{(0)}-V_{11}-V_{2^*3^*}-V_{3^*2^*}+\varepsilon_{3^*}^{(0)}+V_{3^*3^*}-\varepsilon_1^{(0)}-V_{11}]$

$=\frac{1}{2}[\alpha+\beta-(\alpha-\beta)-(-\beta/2)-(-\beta/2)+\alpha+\beta-(\alpha-\beta)]=\frac{3}{2}\beta.$

从而式(5.148)化为

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

解本征方程为 $E^2+\frac{3}{2}\beta E-\frac{1}{2}\beta^2=0.\ \Delta_E=\frac{17}{4}\beta^2$

$\therefore e_{1,1}=\frac{\beta}{4}(-3+\sqrt{17}),\ e_{1,2}=-\frac{\beta}{4}(-3-\sqrt{17}).$　取 $e_1=\frac{1}{4}(-3+\sqrt{17})\beta=0.2808\beta.$

$\therefore$ E(⌬). $|E(PA)|=6e_1=1.6846\beta.$

练习5.19 (a) $\langle\Psi_0|\mathcal{H}|{}^{*}_{1}\rangle = \frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_1^{2*}\rangle - \frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_1^{m*}\rangle = \frac{1}{\sqrt{2}}\left(\frac{\beta}{2}\right) - \frac{1}{\sqrt{2}}\left(-\frac{\beta}{2}\right) = \frac{1}{\sqrt{2}}\beta$

$\langle{}^{*}_{1}|\mathcal{H}-E_0|{}^{*}_{1}\rangle = \frac{1}{2}\left[\langle\Psi_1^{2*}|\mathcal{H}-E_0|\Psi_1^{2*}\rangle - \langle\Psi_1^{2*}|\mathcal{H}|\Psi_1^{m*}\rangle - \langle\Psi_1^{m*}|\mathcal{H}|\Psi_1^{2*}\rangle + \langle\Psi^{m*}|\mathcal{H}-E_0|\Psi^{m*}\rangle\right]$

$= \frac{1}{2}\left[(\alpha-\beta)-(\alpha+\beta)-0-0+(\alpha-\beta)-(\alpha+\beta)\right] = -2\beta.$

不同的原因在于$N>6$时，$\langle\Psi_1^{2*}|\mathcal{H}|\Psi_1^{m*}\rangle = 0$，而非$N=6$时的$\langle\Psi_1^{2*}|\mathcal{H}|\Psi_1^{3*}\rangle = v_{2^*3^*} = -\beta/2$.

从而得到$\mathcal{H}$的矩阵方程.

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

本征方程为 $E^2+2\beta E-\frac{1}{2}\beta^2=0$. $\Delta_E = 4\beta^2+2\beta^2 = 6\beta^2$ $\therefore E = \frac{1}{2}[-2\beta+\sqrt{6}\beta] = \left(\sqrt{\frac{3}{2}}-1\right)\beta = 0.2247\beta.$

$\therefore E_R(⬡, \text{IEPA}) = Ne_1 = 0.2247N\beta.$

(b) $\langle\Psi_0|\mathcal{H}|\Psi_1^{3*}\rangle = \langle 1|h_{eff}|3^*\rangle = \langle 1|h|3^*\rangle + \langle 1|v|3^*\rangle = 0.$ 同理，$\langle\Psi_0|\mathcal{H}|\Psi_1^{4*}\rangle = 0.$

$\langle\Psi_1^{3*}|\mathcal{H}-E_0|\Psi_1^{3*}\rangle = \varepsilon_{3^*}^{(0)} - \varepsilon_1^{(0)} = (\alpha-\beta)-(\alpha+\beta) = -2\beta.$ 同理，$\langle\Psi_1^{4*}|\mathcal{H}-E_0|\Psi_1^{4*}\rangle = -2\beta.$

$\langle\Psi_1^{3*}|\mathcal{H}|\Psi_1^{4*}\rangle = \langle 3^*|h_{eff}|4^*\rangle = \langle 3^*|v|4^*\rangle = -\beta/2$ $\therefore \langle\Psi_1^{3*}|\mathcal{H}-E_0|\Psi_1^{4*}\rangle = -\beta/2.$

$\langle{}^{*}_{1}|\mathcal{H}|\Psi_1^{3*}\rangle = \frac{1}{\sqrt{2}}\langle\Psi_1^{2*}|\mathcal{H}|\Psi_1^{3*}\rangle - \frac{1}{\sqrt{2}}\langle\Psi_1^{m*}|\mathcal{H}|\Psi_1^{3*}\rangle = \frac{1}{\sqrt{2}}\left(-\frac{\beta}{2}\right) - \frac{1}{\sqrt{2}}\cdot 0 = -\frac{\beta}{2\sqrt{2}} \Rightarrow \langle{}^{*}_{1}|\mathcal{H}-E_0|\Psi_1^{3*}\rangle = -\frac{\beta}{2\sqrt{2}}$

$\langle{}^{*}_{1}|\mathcal{H}|\Psi_1^{4*}\rangle = \frac{1}{\sqrt{2}}\langle\Psi_1^{2*}|\mathcal{H}|\Psi_1^{4*}\rangle - \frac{1}{\sqrt{2}}\langle\Psi_1^{m*}|\mathcal{H}|\Psi_1^{4*}\rangle = \frac{1}{\sqrt{2}}\cdot 0 - \frac{1}{\sqrt{2}}\left(-\frac{\beta}{2}\right) = \frac{\beta}{2\sqrt{2}} \Rightarrow \langle{}^{*}_{1}|\mathcal{H}-E_0|\Psi_1^{4*}\rangle = \frac{\beta}{2\sqrt{2}}$

从而矩阵方程为

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

从而本征多项式为 $\frac{1}{4}(e_1-\frac{3}{2}\beta)(4e_1^3+14e_1^2\beta+9\beta^2e_1-3\beta^3)=0.$ $e_1 = 0.2387\beta.$ $e_2 = -1.2760\beta.$ $e_3 = -2.4267\beta.$ $e_4 =$

$\therefore E(N=10, \text{IEPA}) = 10\cdot 0.2387\beta = 2.387\beta.$

练习5.20 $\langle{}^{*}_{1}|\mathcal{H}|{}^{*}_{2}\rangle = \frac{1}{2}\left[\langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{3*}\rangle - \langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{1*}\rangle - \langle\Psi_1^{3*}|\mathcal{H}|\Psi_2^{3*}\rangle + \langle\Psi_1^{2*}|\mathcal{H}|\Psi_2^{1*}\rangle\right]$

$= -\frac{1}{2}\langle\Psi_1^{3*}|\mathcal{H}|\Psi_2^{3*}\rangle = -\frac{1}{2}(-v_{12}) = \frac{1}{2}\cdot\frac{\beta}{2} = \frac{1}{4}\beta.$

$\langle{}^{*}_{1}|\mathcal{H}|{}^{*}_{3}\rangle = \frac{1}{2}\left[\langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{1*}\rangle - \langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{2*}\rangle - \langle\Psi_1^{3*}|\mathcal{H}|\Psi_3^{1*}\rangle + \langle\Psi_1^{3*}|\mathcal{H}|\Psi_3^{2*}\rangle\right]$

$= -\frac{1}{2}\langle\Psi_1^{2*}|\mathcal{H}|\Psi_3^{2*}\rangle = -\frac{1}{2}(-v_{13}) = \frac{1}{2}v_{13} = \frac{1}{2}\cdot\frac{1}{2}\beta = \frac{1}{4}\beta.$

$\langle{}^{*}_{2}|\mathcal{H}|{}^{*}_{3}\rangle = \frac{1}{2}\left[\langle\Psi_2^{3*}|\mathcal{H}|\Psi_3^{1*}\rangle - \langle\Psi_2^{3*}|\mathcal{H}|\Psi_3^{2*}\rangle - \langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{1*}\rangle + \langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{2*}\rangle\right]$

$= -\frac{1}{2}\langle\Psi_2^{1*}|\mathcal{H}|\Psi_3^{1*}\rangle = -\frac{1}{2}(-v_{23}) = \frac{1}{2}\cdot\frac{1}{2}\beta = \frac{1}{4}\beta.$

从而式(5.152c)得证.

由于 $c_1=c_2=c_3=\bar{c}_1=\bar{c}_2=\bar{c}_3=c$. $\therefore |\Psi_{SCI}\rangle = |\Psi_0\rangle + c\left(\sum_{i=1}^{3}|{}^{*}_{i}\rangle + |{}^{\bar{*}}_{i}\rangle\right)$. 从而矩阵方程为

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

$\sum_{i=1}^{3}\langle\Psi_i^{*}|\mathcal{H}-E_0|\Psi_i^{*}\rangle + \sum_{i=1}^{3}\langle\Psi_i^{*}|\mathcal{H}-E_0|\Psi_i^{\bar{*}}\rangle = -\frac{3}{2}\beta + \frac{1}{4}\beta\cdot 2 + 0\cdot 3 = -\beta.$ 其余同.

5.3.2

从而本征多项式为 $c^2+\beta c-3\beta^2=0$. 从而 $E_R(SCI)=\frac{1}{2}(\sqrt{13}-1)\beta=1.3028\beta$.

练习5.21 $\langle\Psi_0|\mathcal{H}|{}^{*}_{i}\rangle=\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i+1)*}\rangle-\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i-1)*}\rangle=\frac{1}{\sqrt{2}}\frac{1}{2}\beta-\frac{1}{\sqrt{2}}(-\frac{1}{2}\beta)=\frac{1}{\sqrt{2}}\beta$.

$\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{i}\rangle=\frac{1}{2}[\langle\Psi_i^{(i+1)*}|\mathcal{H}-E_0|\Psi_i^{(i+1)*}\rangle-\langle\Psi_i^{(i+1)*}|\mathcal{H}-E_0|\Psi_i^{(i-1)*}\rangle-\langle\Psi_i^{(i-1)*}|\mathcal{H}-E_0|\Psi_i^{(i+1)*}\rangle+\langle\Psi_i^{(i-1)*}|\mathcal{H}-E_0|\Psi$

$=\frac{1}{2}[-2\beta+0+0-2\beta]=-2\beta$.

当 $N>6$ 时, $i\neq j$ 时, $i+1\neq j$ 且 $i\pm1\neq j\mp1$ 是可能的, 但 ~~此时 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=0$~~ 此时 $i=j+2$ 或 $j=i+2$.

从而势能积分为0. 从而 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=0$. 从而综上. $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=\delta_{ij}(-2\beta)$.

不同的原因是 $N>6$ 时 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=-2\beta\delta_{ij}$. 从而同练习5.20.

$$Nc\cdot\frac{1}{\sqrt{2}}\beta=E_R(SCI)$$

$$\frac{1}{\sqrt{2}}\beta-2\beta\cdot c=E_R(SCI)c.$$

同理, 得本征多项式为 $\varepsilon^2+2\beta\varepsilon-\frac{1}{2}N\beta^2=0$. $\therefore E_R(SCI)=(\sqrt{\beta^2+N\beta^2/2}-\beta)=(\sqrt{1+N/2}-1)\beta$.

$\therefore\lim_{N\to\infty}\frac{E_R(SCI)}{N^{1/2}}=\frac{1}{4}\beta$