4.1.1节(中间体归一化与相关能表达式)习题解析

练习4.1 $\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle\neq0 \Leftrightarrow t=r,\ a=c \vee r=u,\ a=d \vee r=v,\ a=e$.(不同电子跃迁至同一虚轨道显然没可能,反之亦然).

$$\therefore \sum_{\substack{c<d<e\\t<u<v}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle=\sum_{\substack{r<u<v\\a<d<e}}\langle\Psi_a^r|\mathscr{H}|\Psi_{ade}^{ruv}\rangle+\sum_{\substack{t<r<v\\c<a<e}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cae}^{trv}\rangle+\sum_{\substack{t<u<r\\c<d<a}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{tur}\rangle.$$

故当添加系数项后,有(注意a,r相当于常值,仅提至首位即可)

$$\therefore \sum_{\substack{c<d<e\\t<u<v}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle=\sum_{\substack{u<v\\d<e}}C_{ade}^{ruv}\langle\Psi_a^r|\mathscr{H}|\Psi_{ade}^{ruv}\rangle+\sum_{\substack{v<t\\e<c}}C_{aec}^{rvt}\langle\Psi_a^r|\mathscr{H}|\Psi_{aec}^{rvt}\rangle+\sum_{\substack{t<u\\c<d}}C_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle$$

$$=\sum_{\substack{t<u\\c<d}}C_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle-\sum_{\substack{t<u\\c<d}}C_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle+\sum_{\substack{t<u\\c<d}}C_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle=\sum_{\substack{t<u\\c<d}}C_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle.$$

练习4.2. $|H-E\mathbf{1}|=E^2-2\Delta E-K_{12}^2=0$, $\Delta_E=4(\Delta^2+K_{12}^2)$ $\therefore E_{1,2}=\Delta\pm\sqrt{\Delta^2+K_{12}^2}$. 由于相关能是负值,从而.

$E=\Delta-\sqrt{\Delta^2+K_{12}^2}$ 此即教材式(4.23).

练习4.3 $R=1.4$ a.u.时, $\varepsilon_1=-0.5782$ a.u. $\varepsilon_2=0.6703$ a.u. $J_{11}=0.6746$ a.u. $J_{12}=0.6636$ a.u. $J_{22}=0.6975$ a.u. $K_{12}=0.1813$ a.u.

$\therefore \Delta=\frac{1}{2}[2(\varepsilon_2-\varepsilon_1)+J_{11}+J_{22}-4J_{12}+2K_{12}]=0.78865$ a.u. $E_{corr}=\Delta-\sqrt{\Delta^2+K_{12}^2}=-0.02057$ a.u.

$\therefore c=E_{corr}/K_{12}=-0.1135$.

$R\to\infty$时, $\lim\limits_{R\to\infty}\Delta=\frac{1}{2}\lim\limits_{R\to\infty}[h_{22}-h_{11}+J_{22}-J_{11}]=0$. $\therefore \lim\limits_{R\to\infty}c=\lim\limits_{R\to\infty}\frac{E_{corr}}{K_{12}}=\lim\limits_{R\to\infty}\frac{\Delta-\sqrt{\Delta^2+K_{12}^2}}{K_{12}}=\lim\limits_{R\to\infty}\frac{\Delta}{K_{12}}-\lim\limits_{R\to\infty}\sqrt{\left(\frac{\Delta}{K_{12}}\right)^2+1}=-1$.

可代入$R\to\infty$时, $\varepsilon_1=-0.0793$ a.u. $\varepsilon_2=-0.0793$ a.u. $J_{11}=0.3873$ a.u. $J_{12}=0.3873$ a.u. $J_{22}=0.3873$ a.u. $K_{12}=0.3873$ a.u.

验证得 $\lim\limits_{R\to\infty}\Delta=0$. 从而 $\lim\limits_{R\to\infty}c=-1$. 从数值方法亦得此结论,从而 $\lim\limits_{R\to\infty}|\Phi_0\rangle=|\Psi_0\rangle-|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$

代入 $|\Psi_0\rangle=|\psi_1\bar{\psi}_1\rangle$, $|\Psi_{1\bar{1}}^{2\bar{2}}\rangle=|\psi_2\bar{\psi}_2\rangle$, $\psi_1=C_1(\phi_1+\phi_2)$, $\psi_2=C_2(\phi_1-\phi_2)$ $C_1=\frac{1}{\sqrt{2(1+S_{12})}}$, $C_2=\frac{1}{\sqrt{2(1-S_{12})}}$

从而 $|\Phi_0\rangle=C_1^2[|\phi_1\bar{\phi}_1\rangle+|\phi_1\bar{\phi}_2\rangle+|\bar{\phi}_2\phi_1\rangle+|\phi_2\bar{\phi}_2\rangle]-C_2^2[|\phi_1\bar{\phi}_1\rangle-|\phi_1\bar{\phi}_2\rangle-|\bar{\phi}_2\phi_1\rangle+|\phi_2\bar{\phi}_2\rangle]$

而 $\lim\limits_{R\to\infty}S_{12}=0\Rightarrow\lim\limits_{R\to\infty}C_1=\lim\limits_{R\to\infty}\frac{1}{\sqrt{2(1+S_{12})}}=\frac{1}{\sqrt{2}}$. 同理, $\lim\limits_{R\to\infty}C_2=\frac{1}{\sqrt{2}}$.

$\therefore \lim\limits_{R\to\infty}|\Phi_0\rangle=\lim\limits_{R\to\infty}|\Psi_0\rangle-|\Psi_{1\bar{1}}^{2\bar{2}}\rangle=\lim\limits_{R\to\infty}|\phi_1\bar{\phi}_2\rangle+|\phi_2\bar{\phi}_1\rangle$, 而 $\lim\limits_{R\to\infty}\langle\Phi_0|\Phi_0\rangle=2$.

$\therefore \lim\limits_{R\to\infty}|\Phi\rangle=\lim\limits_{R\to\infty}\frac{1}{\sqrt{\langle\Phi_0|\Phi_0\rangle}}|\Phi_0\rangle=\lim\limits_{R\to\infty}\frac{1}{\sqrt{2}}[|\phi_1\bar{\phi}_2\rangle+|\phi_2\bar{\phi}_1\rangle]$ 即 $|\Phi\rangle_{CI}\longrightarrow\frac{1}{\sqrt{2}}[|\phi_1\bar{\phi}_2\rangle+|\phi_2\bar{\phi}_1\rangle]$

4.4节（自然轨道和单粒子约化密度矩阵）习题解析

练习4.4 $\gamma^*(x_1,x_1')=N\int_{\Omega_{2\sim N}}dx_2dx_3\cdots dx_N\,\Phi^*(x_1,x_2,\cdots,x_N)\Phi(x_1',x_2,\cdots,x_N)=N\int_{\Omega_{2\sim N}}dx_2\cdots dx_N\,\Phi(x_1',x_2,\cdots,x_N)\Phi^*(x_1,x_2,\cdots,x_N)=\gamma(x_1',x_1)$.

$\therefore \gamma_{ji}^*=\int_{\Omega_{1,1'}}dx_1dx_1'\,\chi_j(x_1)\gamma^*(x_1,x_1')\chi_i^*(x_1')=\int_{\Omega_{1,1'}}dx_1dx_1'\,\chi_i^*(x_1')\gamma(x_1',x_1)\chi_j(x_1)=\int_{\Omega_{1,1'}}dx_1'dx_1\,\chi_i^*(x_1)\gamma(x_1,x_1')\chi_j(x_1')=\gamma_{ij}$.

从而 γ 是一个Hermite矩阵.

练习4.5 $N=\int_{\Omega_1}dx_1\,\rho(x_1)=\sum_{i=1}^{N}\sum_{j=1}^{N}\int_{\Omega_1}dx_1\,\chi_i(x_1)\chi_j^*(x_1)\gamma_{ij}=\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{ij}\gamma_{ij}=\sum_{i=1}^{N}\gamma_{ii}=\mathrm{tr}\,\gamma$.

练习4.6 (a) $\langle\Phi|\mathcal{O}_1|\Phi\rangle=\sum_{i=1}^{N}\langle\Phi|h(i)|\Phi\rangle=N\langle\chi_i|h|\chi_i\rangle=N\int_{\Omega_1}dx_1\,\chi_i^*(x_1)h(x_1)\chi_i(x_1)=\int_{\Omega_1}dx_1\,N\,h(x_1)|\chi_i(x_1)|^2$

$=\int_{\Omega_1}dx_1\left[h(x_1)\gamma(x_1,x_1')\right]\Big|_{x_1'=x_1}$. 因 $\left[h(x_1)\gamma(x_1,x_1')\right]\Big|_{x_1'=x_1}=h(x_1)N\int_{\Omega_{2\sim N}}dx_2\cdots dx_N\,\Phi(x_1,\cdots,x_N)\Phi^*(x_1,\cdots,x_N)=Nh(x_1)|\chi_i(x_1)|^2$.

(b). $\mathrm{tr}\,h\gamma=\sum_{i=1}^{N}\sum_{j=1}^{N}h_{ij}\gamma_{ji}=\sum_{i=1}^{N}\sum_{j=1}^{N}\int_{\Omega_1}dx_1\,\chi_i^*(x_1)h(x_1)\chi_j(x_1)\gamma_{ji}=\int_{\Omega_1}dx_1\,h(x_1)\sum_{i=1}^{N}\sum_{j=1}^{N}\chi_j(x_1)\gamma_{ji}\chi_i^*(x_1)=\int_{\Omega_1}dx_1\left[h(x_1)\gamma(x_1,x_1')\right]\Big|_{x_1'=x_1}$

由(a)中结论. $\therefore\langle\Phi|\mathcal{O}_1|\Phi\rangle=\mathrm{tr}\,h\gamma$.

练习4.7 (a) $\gamma_{ij}=\int_{\Omega_1}dx_1\int_{\Omega_1'}dx_1'\,\chi_i^*(x_1)\gamma(x_1,x_1')\chi_j(x_1')=\int_{\Omega_1}dx_1\int_{\Omega_1'}dx_1'\,\chi_i^*(x_1)N\int_{\Omega_{2\sim N}}dx_2\cdots dx_N\,\Phi(x_1,x_2,\cdots,x_N)\Phi^*(x_1',x_2,\cdots,x_N)\chi_j(x_1')$

$=\int_{\Omega_{2\sim N}}dx_2\cdots dx_N\int_{\Omega_1}dx_1\,\chi_i^*(x_1)\Phi(x_1,x_2,\cdots,x_N)\int_{\Omega_1'}dx_1'\,\chi_j(x_1')\Phi^*(x_1',x_2,\cdots,x_N)=\int_{\Omega_{2\sim N}}\Phi(\cdots i-1,i+1,\cdots)\Phi^*(\cdots j-1,j+1\cdots)dx_2\cdots dx_N$

$=\langle\Phi|a_j^\dagger a_i|\Phi\rangle$.

(b). $\gamma_{ij}=\langle\Phi|a_j^\dagger a_i|\Phi\rangle=\langle\Phi|\Phi\rangle\delta_{ij}-\langle\Phi|a_ia_j^\dagger|\Phi\rangle=\delta_{ij}$.

~~最后一步理由是：若增设电子有不被之前占据，则必正交，否则应有 $a_j^\dagger|\Phi\rangle=0$.~~

练习4.8 注意体系是双电子系统，从而最多到双激发. 可写全组态相互作用为：

$$|\Phi_0\rangle=c_0|1\bar{1}\rangle+\sum_{r=2}^{k}c_1^r|{}^1\Psi_1^r\rangle+\frac{1}{4}\sum_{r=2}^{k}\sum_{s=2}^{k}c_{11}^{rs}|{}^1\Psi_{11}^{rs}\rangle.$$

(a). 化简 $|{}^1\Psi_1^r\rangle$ 与 $|{}^1\Psi_{11}^{rs}\rangle$.

$|{}^1\Psi_1^r\rangle=\frac{1}{\sqrt{2}}(|\Psi_1^{\bar{r}}\rangle+|\Psi_{\bar{1}}^{r}\rangle)\equiv\frac{1}{\sqrt{2}}(|1\bar{r}\rangle+|r\bar{1}\rangle)$

$|{}^1\Psi_{11}^{rr}\rangle=|r\bar{r}\rangle$. $|{}^1\Psi_{11}^{rs}\rangle=\frac{1}{\sqrt{2}}(|r\bar{s}\rangle-|\bar{r}s\rangle)=\frac{1}{\sqrt{2}}(|r\bar{s}\rangle+|s\bar{r}\rangle)$.

从而 $|\Phi_0\rangle=c_0|1\bar{1}\rangle+\sum_{r=2}^{k}c_1^r\cdot\frac{1}{\sqrt{2}}(|1\bar{r}\rangle+|r\bar{1}\rangle)+\frac{1}{2}\sum_{r=2}^{k}c_{11}^{rr}|r\bar{r}\rangle+\frac{1}{2}\sum_{r=2}^{k}\sum_{s=2}^{k}{}'\frac{c_{11}^{rs}}{\sqrt{2}}(|r\bar{s}\rangle+|s\bar{r}\rangle)$.

$C_{11}=c_0$. $C_{1r}=C_{r1}=\frac{1}{\sqrt{2}}c_1^r$. $C_{rr}=\frac{1}{2}c_{11}^{rr}$. $C_{ij}=\frac{1}{2\sqrt{2}}(c_{11}^{ij}+c_{11}^{ji})$. 从而 $\forall i,j\in I_1^k$. $C_{ij}=C_{ji}$.

即 C 是实对称阵.

(b) 将(a)中结果代入教材式(4.35)，得

$$\gamma=2\int_{\Omega_2}dx_2\,\Phi(x_1,x_2)\Phi^*(x_1',x_2)=2\int_{\Omega_2}dx_2\cdot\frac{1}{\sqrt{2}}\sum_{i=1}^{k}\sum_{j=1}^{k}C_{ij}\left(\psi_i(x_1)\overline{\psi_j(x_2)}-\psi_i(x_2)\overline{\psi_j(x_1)}\right)\cdot\frac{1}{\sqrt{2}}\sum_{k=1}^{k}\sum_{l=1}^{k}C_{kl}^*\left(k^*(1')\overline{l^*(2)}-k^*(2)\overline{l^*(1')}\right)$$

$$=\sum_{i=1}^{k}\sum_{j=1}^{k}\sum_{k=1}^{k}\sum_{l=1}^{k}C_{ij}C_{kl}^*\int_{\Omega_2}dx_2\left(\psi_i(x_1)\overline{\psi_j(x_2)}-\psi_i(x_2)\overline{\psi_j(x_1)}\right)\left(\psi_k(1')\overline{\psi_l(2)}-\overline{\psi_k(2)}\,\overline{\psi_l(1')}\right)^*$$

$$=\sum_{i=1}^{k}\sum_{j=1}^{k}\sum_{k=1}^{k}\sum_{l=1}^{k}C_{ij}C_{kl}^*\left(\psi_i(x_1)\psi_k^*(x_1')\delta_{jl}+\overline{\psi_j(x_1)}\,\overline{\psi_l^*(x_1')}\delta_{ik}\right)=\sum_{i=1}^{k}\sum_{j=1}^{k}\sum_{k=1}^{k}C_{ij}C_{kj}^*\psi_i(1)\psi_k^*(1')+\sum_{i=1}^{k}\sum_{j=1}^{k}\sum_{l=1}^{k}C_{ij}C_{il}^*\overline{\psi_j(1)}\,\overline{\psi_l^*(1')}$$

$$=\sum_{i=1}^{k}\sum_{k=1}^{k}(CC^\dagger)_{ik}\psi_i(1)\psi_k^*(1')+\sum_{j=1}^{k}\sum_{l=1}^{k}(CC^\dagger)_{jl}\overline{\psi_j(1)}\,\overline{\psi_l^*(1')}=\sum_{i=1}^{k}\sum_{j=1}^{k}(CC^\dagger)_{ij}\left[\psi_i(1)\psi_j^*(1')+\overline{\psi_i(1)}\,\overline{\psi_j^*(1')}\right].$$

(c) 由于C是实对称阵. 从而d为实矩阵. 从而$d^\dagger = d$.

$\therefore U^\dagger C C^\dagger U = (U^\dagger C U)(U^\dagger C U) = d d^\dagger = d^2$.

(d) 由(c). 从而 $CC^\dagger = U d^2 U^\dagger \Leftrightarrow (CC^\dagger)_{ij} = (U d U^\dagger)_{ij}$ 由(b)结论,

$\therefore \gamma(x_1, x_1') = \sum_{i=1}^{K}\sum_{j=1}^{K} (CC^\dagger)_{ij}[\psi_i(1)\psi_j^*(1') + \overline{\psi_i(1)}\,\overline{\psi_j^*(1')}] = \sum_{i=1}^{K}\sum_{j=1}^{K} (U d U^\dagger)_{ij}[\psi_i(1)\overline{\psi_j^*}(1') + \psi_i(1)\overline{\psi_j^*}(1')]$

$= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K} U_{ik} d_k^2 U_{jk}^* [\psi_i(1)\psi_j^*(1') + \overline{\psi_i(1)}\,\overline{\psi_j(1')}] = \sum_{k=1}^{K} d_k^2 [\sum_{i=1}^{K}\psi_i(1) U_{ik}\sum_{j=1}^{K}\psi_j^*(1) U_{jk}^* + \sum_{i=1}^{K}\overline{\psi_i(1)} U_{ik}\sum_{j=1}^{K}\overline{\psi_j^*(1')} U_{jk}^*]$

$= \sum_{k=1}^{K} d_k^2 [\zeta(1)\zeta^*(1') + \overline{\zeta(1)}\,\overline{\zeta^*(1')}]$.

(e). $|\Phi_0\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K} c_{ij}|\psi_i\overline{\psi}_j\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K}(\sum_{k=1}^{K} U_{ik} d_k U_{jk}^*)|\psi_i\overline{\psi}_j\rangle = \sum_{k=1}^{K} d_k |(\sum_{i=1}^{K}\psi_i U_{ik})(\sum_{j=1}^{K}\overline{\psi}_j U_{jk}^*)\rangle = \sum_{k=1}^{K} d_k |\zeta_k\overline{\zeta}_k\rangle$.

4.5节(多组态自洽场方法(MCSCF)及推广价键方法(GVB))习题解析

练习4.9　(a) $\langle u|u\rangle=\frac{1}{a^2+b^2}[a^2\langle\psi_A|\psi_A\rangle+ab\langle\psi_A|\psi_B\rangle+ab\langle\psi_B|\psi_A\rangle+b^2\langle\psi_B|\psi_B\rangle]=\frac{1}{a^2+b^2}[a^2\cdot1+ab\cdot0+ab\cdot0+b^2\cdot1]=1$.

同理, $\langle v|v\rangle=1$. 而 $\langle u|v\rangle=\frac{1}{a^2+b^2}[a^2\langle\psi_A|\psi_B\rangle-ab\langle\psi_A|\psi_B\rangle+ab\langle\psi_A|\psi_B\rangle-b^2\langle\psi_B|\psi_B\rangle=\frac{a^2-b^2}{a^2+b^2}$. 即 $S=\frac{a^2-b^2}{a^2+b^2}$

(b) 代入 $S=\frac{a^2-b^2}{a^2+b^2}$ 到教材式(4.52).

$$|\Psi_{GVB}\rangle=\frac{1}{\sqrt{2[1+(\frac{a^2-b^2}{a^2+b^2})^2}}[\frac{1}{a^2+b^2}[a\psi_A(1)+b\psi_B(1)][a\psi_A(2)-b\psi_B(2)]+\frac{1}{a^2+b^2}[a\psi_A(2)+b\psi_B(2)][a\psi_A(1)-b\psi_B(1)]\frac{1}{\sqrt2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$$

$$=\frac{a^2+b^2}{2\sqrt{2(a^4+b^4)}}\cdot\frac{1}{a^2+b^2}[(a\psi_A(1)+b\psi_B(1))(a\psi_A(2)-b\psi_B(2))+(a\psi_A(2)+b\psi_B(2))(a\psi_A(2)-b\psi_B(1))](\alpha(1)\beta(2)-\alpha(2)\beta(1)).$$

$$=\frac{1}{\sqrt{2(a^4+b^4)}}[a^2\psi_A(1)\psi_A(2)-b^2\psi_B(1)\psi_B(2)][\alpha(1)\beta(2)-\alpha(2)\beta(1)]=\frac{a^2}{\sqrt{a^4+b^4}}|\psi_A\bar{\psi}_A\rangle-\frac{b^2}{\sqrt{a^4+b^2}}|\psi_B\bar{\psi}_B\rangle.$$

由教材式(4.48), 从而 $C_A=\frac{a^2}{\sqrt{a^4+b^4}}$, $C_B=-\frac{b^2}{\sqrt{a^4+b^4}}$.

4.6节（截断组态相互作用计算及大小广延性问题

练习4.10 $\langle\Psi_0|\mathscr{H}|1_1\bar{1}_1 2_2\bar{2}_1\rangle = \langle 1_1\bar{1}_1 2_2\bar{2}_2|\mathscr{H}|1_1\bar{1}_1 2_1\bar{2}_1\rangle = \langle 1_2\bar{1}_2||2_1\bar{2}_1\rangle = [1_2 2_1|\bar{1}_2\bar{2}_1] = (1_2 2_1|1_2 2_1)$

由于两原子体系相距无穷远，从而 $\lim_{r_{12}\to\infty}\frac{1}{r_{12}}=0 \Rightarrow (1_2 2_1|1_2 2_1)=0$.

同理，$\langle 1_1\bar{1}_1 2_2\bar{2}_2|\mathscr{H}|1_1\bar{1}_1 2_1\bar{2}_1\rangle = \langle 2_2\bar{2}_2||2_1\bar{2}_1\rangle = (2_2 2_1|2_2 2_1)=0$，$\langle 2_2\bar{2}_2 1_2\bar{1}_2|1_1 1_1 2_1\bar{2}_1\rangle = 0$.

练习4.11 $R=1.4\,\text{a.u.}$时，$\varepsilon_1=-0.5782\,\text{a.u.}$ $\varepsilon_2=0.6703\,\text{a.u.}$ $J_{11}=0.6746\,\text{a.u.}$ $J_{12}=0.6636\,\text{a.u.}$ $J_{22}=0.6975\,\text{a.u.}$ $K_{12}=0.1813\,\text{a.u.}$

$\therefore \Delta=\varepsilon_2-\varepsilon_1+\frac{1}{2}(J_{11}+J_{22}-4J_{12})+K_{12}=0.78865\,\text{a.u.}$ 从而

$$\left[\frac{{}^N E_{corr}(DCI)}{N}\right]_{N=1} = -0.4849,\quad \left[\frac{{}^N E_{corr}(DCI)}{N}\right]_{N=10} = -0.9242,\quad \left[\frac{{}^N E_{corr}(DCI)}{N}\right]_{N=100} = -0.9921.$$

练习4.12. $\langle\Psi_0|\mathscr{H}-E_0|\Psi_0\rangle=0$. $\langle\Psi_0|\mathscr{H}-E_0|2_1\bar{2}_1 1_2\bar{1}_2\rangle = \langle\Psi_0|2_1\bar{2}_1 1_2\bar{1}_2\rangle = \langle 1_1\bar{1}_1||2_1\bar{2}_1\rangle = (1_1 2_1|1_1 2_1) = K_{12}$.

$\langle\Psi_0|\mathscr{H}-E_0|1_1\bar{1}_1 2_2\bar{2}_2\rangle = \langle\Psi_0|1_1\bar{1}_1 2_2\bar{2}_2\rangle = \langle 1_2\bar{1}_2||2_2\bar{2}_2\rangle = (1_2 2_2|1_2 2_2) = K_{12}$.

$\langle\Psi_0|\mathscr{H}-E_0|2_1\bar{2}_1 2_2\bar{2}_2\rangle = \langle 1_1\bar{1}_1 1_2\bar{1}_2||2_1\bar{2}_1 2_2\bar{2}_2\rangle = 0$. 从而在 $(\mathscr{H}-E_0)|\Phi_0\rangle = (\mathcal{E}-E_0)|\Phi_0\rangle = {}^2E_{corr}|\Phi_0\rangle$ 两边同乘 $\langle\Psi_0|$，并代入 $|\Phi_0\rangle$ 的Full CI表达式有 $K_{12}C_1+K_{12}C_2={}^2E_{corr}$.

记 $\langle 2_1\bar{2}_1 1_2\bar{1}_2|\mathscr{H}-E_0|2_1\bar{2}_1 1_2\bar{1}_2\rangle = 2\Delta$，$\langle 2_1\bar{2}_1 1_2\bar{1}_2|\mathscr{H}-E_0|2_1\bar{2}_1 2_2\bar{2}_2\rangle = \langle 1_2\bar{1}_2||2_2\bar{2}_2\rangle = K_{12}$.

从而 $\langle 2_1\bar{2}_1 1_2\bar{1}_2|$ 同乘于 $(\mathscr{H}-E_0)|\Phi_0\rangle={}^2E_{corr}|\Phi_0\rangle$，得 $K_{12}\cdot 1 + C_1\cdot 2\Delta + 0\cdot C_2 + C_3\cdot K_{12} = C_1\cdot {}^2E_{corr}$

同理再得 $K_{12}\cdot 1 + 0\cdot C_1 + 2\Delta\cdot C_2 + K_{12}\cdot C_3 = C_2\,{}^2E_{corr}$.

~~$\langle 2_1\bar{2}_1 2_2\bar{2}_2|\mathscr{H}-E_0|2_1\bar{2}_1 2_2\bar{2}_2\rangle = 4h_{22}+2J_{22}$（因为两分子间不计相互作用，同理 $2\Delta = 2h_{11}+2h_{22}+J_{11}+J_{22}$）~~

而 $E_0=4h_{11}+2J_{11}$（因分子间无相互作用，无交换积分，$\langle 2_1\bar{2}_1 1_2\bar{1}_2|\mathscr{H}|2_1\bar{2}_1 1_2\bar{1}_2\rangle = 2h_{11}+2h_{22}+J_{11}+J_{22}$

$\therefore 2\Delta = 2h_{22}-2h_{11}+J_{22}-J_{11}$，同理，$\langle 2_1\bar{2}_1 2_2\bar{2}_2|\mathscr{H}-E_0|2_1\bar{2}_1 2_2\bar{2}_2\rangle = (4h_{22}+2J_{22})-(4h_{11}+2J_{11}) = 2(2h_{22}-2h_{11}+J_{22}-J_{11})$

$\therefore \langle 2_1\bar{2}_1 2_2\bar{2}_2|\mathscr{H}-E_0|2_1\bar{2}_1 2_2\bar{2}_2\rangle = 4\Delta$. 从而得到全组态相互作用矩阵方程为

$$\begin{pmatrix} 0 & K_{12} & K_{12} & 0 \\ K_{12} & 2\Delta & 0 & K_{12} \\ K_{12} & 0 & 2\Delta & K_{12} \\ 0 & K_{12} & K_{12} & 4\Delta \end{pmatrix}\begin{pmatrix} 1 \\ C_1 \\ C_2 \\ C_3 \end{pmatrix} = {}^2E_{corr}\begin{pmatrix} 1 \\ C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

此思路即4.1.1节推导思路.

(b) 由(a)，有 $K_{12}+2\Delta C_1+K_{12}\cdot C_3={}^2E_{corr}C_1$，$K_{12}+2\Delta C_2+K_{12}\cdot C_3={}^2E_{corr}C_2$，

从而 $C_1=C_2$，将之代入 $K_{12}\cdot C_1+K_{12}\cdot C_2={}^2E_{corr}$ $\quad\therefore {}^2E_{corr}=2K_{12}C_1$

(c) 代入(b)中结果至 $K_{12}\cdot C_1+K_{12}\cdot C_2+4\Delta\cdot C_3={}^2E_{corr}C_3$. $\quad\therefore C_3=\frac{{}^2E_{corr}}{{}^2E_{corr}-4\Delta}$.

(d) 将(c)中结果代入(b)，即可化简得 $C_1=\frac{2K_{12}}{{}^2E_{corr}-4\Delta}$.

(e) 将(d)中结果代入(b)，得 $({}^2E_{corr})^2-4\Delta\,{}^2E_{corr}-4K_{12}^2=0$ $\quad\therefore E_{corr}=2\Delta-2\sqrt{\Delta^2+K_{12}^2}$

练习4.13. ${}^1E_{corr}(\text{exact}) = \Delta\left(1-\sqrt{1+K_{12}^2/\Delta^2}\right) \doteq \Delta\left(1-\left(1+\frac{K_{12}^2}{2\Delta^2}\right)\right) = -\frac{K_{12}^2}{2\Delta}$.（if $\frac{K_{12}^2}{\Delta^2}\ll 1$）.

练习4.14. (a) ${}^N E_{corr}(DCI) = \Delta\left[1-\sqrt{1+NK_{12}^2/\Delta^2}\right] \doteq \Delta\left[1-\left(1+\frac{NK_{12}^2}{2\Delta^2}-\frac{N^2K_{12}^4}{8\Delta^4}\right)\right] = -\frac{NK_{12}^2}{2\Delta}+\frac{N^2K_{12}^4}{8\Delta^3}+\cdots$

(b) 在DCI下，有 $|\Phi_0\rangle = |\Psi_0\rangle + \sum_{i=1}^{2} C_i|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle$. 从而 $\langle\Phi_0|\Phi_0\rangle = 1+NC_1^2$. $\therefore |\Phi\rangle = \frac{1}{\sqrt{\langle\Phi_0|\Phi_0\rangle}}|\Phi_0\rangle$

$\therefore |\Phi\rangle = \frac{1}{\sqrt{1+NC_1^2}}\left(|\Psi_0\rangle + \sum_{i=1}^{N} C_i|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle\right)$ 即 $C_0=\frac{1}{\sqrt{1+NC_1^2}}$ $\quad\therefore 1-C_0^2 = 1-\frac{1}{1+NC_1^2} = \frac{NC_1^2}{1+NC_1^2}$

(c) 由教材式(4.64),及结论(a),有.

$$C_1=\frac{K_{12}}{{}^{N}E_{corr}(DCI)-2\Delta}=\frac{K}{-2\Delta-\frac{-NK_{12}^2}{2\Delta}+\frac{N^2K_{12}^4}{8\Delta^3}+o(N^3)}=-\frac{K_{12}}{2\Delta}\frac{1}{1+\frac{NK_{12}^2}{4\Delta^2}+\frac{N^2K_{12}^4}{16\Delta^4}+\cdots}\doteq-\frac{K_{12}}{2\Delta}.$$

(d) 由教材式(4.65). ${}^{N}E_{corr}(DCI)=NK_{12}C_1$, 再由(b)中结论及(c)中结论

$$\therefore \Delta E_{Davidson}=(1-C_0^2)E_{corr}(DCI)=\frac{NC_1^2}{1+NC_1^2}\cdot \cancel{NK_{12}C_1}=\frac{N^2K_{12}(-K_{12}/2\Delta)^3}{1+N(-K_{12}/2\Delta)^2}\doteq-\frac{N^2K_{12}^4}{8\Delta^3}$$

(e) 在(d)中, 代入 $C_1={}^{N}E_{corr}(DCI)/NK_{12}$. $\therefore \Delta E_{Davidson}=[{}^{N}E_{corr}(DCI)]^3/[NK_{12}^2+[{}^{N}E_{corr}(DCI)]^2]$

$R=1.4a.u.$ 时, 同前得 $\Delta=0.78865a.u.$ 用codeblocks编写程序运行结果如下:

代码为

```
#include <iostream>
#include <iomanip>        // 用之是为了控制输出整齐
#include <math.h>         // 用之是为了调用pow及sqrt函数.
using namespace std;

const double dia = 0.78865, K12 = 0.1813;
const double dia_2 = row( 0.78865, 2), K12_2 = row( 0.1813, 2);

int main()
{   double energyDCI, energyExact, energyDavidson, erro1, error2;
    cout << setw(3) << "□□N\t" << setw(1) << "energyDCI/energyExact\t" << setw(12) << "erro1\t"
        << setw(10) << "energyTotal/energyExact\t" << setw(18) << "error2 " << endl;
    for( unsigned N = 1; N != 101 ; ++N){
        energyDCI = dia - sqrt( dia_2 + N * K12_2);
        energyExact = N*( dia - sqrt( dia_2 + K12_2));
        energyDavidson = pow( energyDCI, 3)/ (N* K12_2 + pow( energyDCI, 2));
        erro1 = (energyDCI - energyExact)/ energyExact;
        erro2 = ( energyDavidson + energyDCI - energyExact)/ energyExact;
        cout << setw(3) << N << "\t" << setw(21) << energyDCI/ energyExact << "\t" << setw(10)
            << 100 * erro1 << "%\t" << setw(23) << ( energyDavidson + energyDCI)/ energyExact
            << "\t" << setw(17) << 100 * error2 << "%" << endl;
        if ( N == 20)
            N += 79;
    }
    return 0;
}
```

通过运行程序可以验证题干中的结论，在此不列表表述结果.

f. 略.

练习4.15 $\langle \Psi_0 | \Phi_0 \rangle = \frac{1}{(1+c^2)^{N/2}} \prod_{i=1}^{N} \prod_{j=1}^{N} [\langle 1_i \bar{1}_i | 1_j \bar{1}_j \rangle + \langle 1_i \bar{1}_i | 2_j \bar{2}_j \rangle] = \frac{1}{(1+c^2)^{N/2}} \prod_{i=1}^{N} \prod_{j=1}^{N} \delta_{ij} = \frac{1}{(1+c^2)^{N/2}}$.

$c = \frac{N E_{corr}}{K_{12}} = \frac{N}{K_{12}} [\Delta - \sqrt{\Delta^2 + K_{12}^2}]$. 代入$N=1, 10, 100$, 得 $\langle \Psi_0 | \Phi_0 \rangle|_{n=1} = 0.9936$, $\langle \Psi_0 | \Phi_0 \rangle|_{n=10} = 0.01$[illegible] $\langle \Psi_0 | \Phi_0 \rangle|_{n=100} = 2.22 \times 10^{-106}$.