3.1.2节（Fock算符）习题解析

练习3.1 $\langle i|f|j\rangle = \langle i|h|j\rangle + \sum_b \langle i|\mathcal{J}_b - \mathcal{K}_b|j\rangle = \langle i|h|j\rangle + \sum_b \langle i|\mathcal{J}_b|j\rangle - \langle i|\mathcal{K}_b|j\rangle$.

$\langle i|\mathcal{J}_b|j\rangle = \int_{\Omega_1} dx_1\, \chi_i^*(1)\chi_j(1) \int_{\Omega_2} dx_2\, \chi_b^*(2) r_{12}^{-1} \chi_b(2) = \langle ib|jb\rangle$.

$\langle i|\mathcal{K}_b|j\rangle = \int_{\Omega_1} dx_1\, \chi_i^*(1)\chi_j(1) \int_{\Omega_2} dx_2\, \chi_b^*(2) r_{12}^{-1} \mathcal{P}_{12} \chi_b(2) = \int_{\Omega_1} dx_1\, \chi_i^*(1)\chi_b(1) \int_{\Omega_2} dx_2\, \chi_b^*(2) r_{12}^{-1} \chi_j(2) = \langle ib|bj\rangle$.

$\therefore \langle i|f|j\rangle = \langle i|h|j\rangle + \sum_b \langle ib|jb\rangle - \langle ib|bj\rangle = \langle i|h|j\rangle + \sum_b \langle ib||jb\rangle = \langle i|h|j\rangle + \sum_b [ij|bb] - [ib|bj]$.

3.2.2节(单Slater行列式的能量最小化)习题解析

练习3.2　由于Lagrange 辅助函数 $\mathscr{L}$ 为实函数 则 $\mathscr{L}^*[\{\chi_a\}]=\mathscr{L}[\{\chi_a\}]=E_0[\{\chi_a\}]-\sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}([a|b]-\delta_{ab})$

$$\therefore E_0^*[\{\chi_a\}]-\sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}^*([a|b]^*-\delta_{ab}^*)=E_0[\{\chi_a\}]-\sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}^*([b|a]-\delta_{ab})=E_0[\{\chi_a\}]-\sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ab}^*([a|b]-\delta_{ab}).$$

$\therefore \sum_{a=1}^{N}\sum_{b=1}^{N}(\varepsilon_{ba}-\varepsilon_{ab}^*)([a|b]-\delta_{ab})=0$. 由 $[a|b]-\delta_{ab}\ (a\in I_1^N,\ b\in I_1^N)$ 间线性无关　$\therefore \varepsilon_{ab}^*=\varepsilon_{ba}$.

练习3.3　注意到求和指标的对称性及双电子积分对偶标的对称性. 首先 $\sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_a\chi_a|\delta\chi_b\chi_b]=\sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_b\chi_b|\delta\chi_a\chi_a]$.

而 $[\chi_b\chi_b|\delta\chi_a\chi_a]=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\,\chi_b^*(1)\chi_b(1)\delta\chi_a^*(1)\chi_a(1)r_{12}^{-1}=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\,\chi_b^*(2)\chi_b(2)\delta\chi_a^*(2)\chi_a(2)r_{12}^{-1}=[\delta\chi_a\chi_a|\chi_b\chi_b]$.

$\therefore \sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_a\chi_a|\delta\chi_b\chi_b]=\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_a|\chi_b\chi_b]$. 同理论证后面.

$$[\chi_a\chi_b|\delta\chi_b\chi_a]=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\,\chi_a^*(1)\chi_b(1)r_{12}^{-1}\delta\chi_b^*(2)\chi_a(2)=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\,\chi_a^*(2)\chi_b(2)r_{12}^{-1}\delta\chi_b^*(1)\chi_a(1)=[\delta\chi_b\chi_a|\chi_a\chi_b]$$

$\therefore \sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_b\chi_a|\chi_a\chi_b]=\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_b|\chi_b\chi_a]=\sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_a\chi_b|\delta\chi_b\chi_a]$. 由教材式(3.44)

$$\begin{aligned}\therefore \delta E_0 &= \sum_{a=1}^{N}[\delta\chi_a|h|\chi_a]+\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_a|\chi_b\chi_b]+[\chi_a\chi_a|\delta\chi_b\chi_b]-\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_b|\chi_b\chi_a]+[\chi_a\chi_b|\delta\chi_b\chi_a]\\ &\quad+\sum_{a=1}^{N}[\chi_a|h|\delta\chi_a]+\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_a\delta\chi_a|\chi_b\chi_b]+[\chi_a\chi_a|\chi_b\delta\chi_b]-\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\chi_a\delta\chi_b|\chi_b\chi_a]+[\chi_a\chi_b|\chi_b\delta\chi_a]\\ &=\sum_{a=1}^{N}[\delta\chi_a|h|\chi_a]+\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_a|\chi_b\chi_b]-\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_b|\chi_b\chi_a]+\text{complex conjugate.}\end{aligned}$$

3.3.1节(轨道能及Koopman定理)习题解析.

练习3.4 $\langle j|f|i\rangle^* = \langle j|h|i\rangle^* + \sum_b \langle jb|ib\rangle^* - \langle jb|bi\rangle^* = \langle i|h|j\rangle + \sum_b \langle ib|jb\rangle - \langle ib|bj\rangle = \langle i|f|j\rangle$.

故Fock算符f是Hermite变换.

练习3.5 $IP_{cd}^{2} = {}^{N-2}E_{c,d} - {}^{N}E_0 = \left[\sum_a'' \langle a|h|a\rangle + \frac{1}{2}\sum_a'' \sum_b'' \langle ab||ab\rangle\right] - \left[\sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a \sum_b \langle ab||ab\rangle\right]$.

注:$\sum''$表示去掉了c.d外对其他情形全体结果求和,$\sum$表示对全体情形求和

$\therefore IP_{cd}^{2} = -\langle c|h|c\rangle - \langle d|h|d\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle - \frac{1}{2}\sum_b \langle cb||cb\rangle - \frac{1}{2}\sum_b \langle db||db\rangle + \frac{1}{2}\langle cc||cc\rangle$

$+ \frac{1}{2}\langle cd||cd\rangle + \frac{1}{2}\langle dc||dc\rangle + \frac{1}{2}\langle dd||dd\rangle$.

$= -\langle c|h|c\rangle - \langle d|h|d\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle + \langle cd||cd\rangle$

$= -\left[\langle c|h|c\rangle + \sum_a \langle ac||ac\rangle\right] - \left[\langle d|h|d\rangle + \sum_a \langle ad||ad\rangle\right] + \langle cd||cd\rangle = -\varepsilon_c - \varepsilon_d + \langle cd|cd\rangle - \langle cd|dc\rangle$.

练习3.6 $EA = {}^{N}E_0 - {}^{N+1}E^r = \left[\sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a \sum_b \langle ab||ab\rangle\right] - \left[\sum_{a+r} \langle a|h|a\rangle + \frac{1}{2}\sum_{a+r} \sum_{b+r} \langle ab||ab\rangle\right]$

$= -\langle r|h|r\rangle - \frac{1}{2}\sum_b \langle rb||rb\rangle - \frac{1}{2}\sum_a \langle ar||ar\rangle + \frac{1}{2}\langle rr||rr\rangle = -\langle r|h|r\rangle - \frac{1}{2}\sum_b \langle rb||rb\rangle - \frac{1}{2}\sum_b \langle rb||rb\rangle = -\langle r|h|r\rangle - \sum_b \langle rb||rb\rangle$

3.3.3 节（Hartree-Fock 哈密顿量）习题解析

练习3.7

$$\mathscr{H}|\Psi_0\rangle=\sum_{i=1}^{N}f(i)\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)=\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\sum_{i=1}^{N}f(i)\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)$$

$$=\sum_{i_1i_2\cdots i_N}\frac{1}{\sqrt{N!}}(-1)^{\tau(i_1i_2\cdots i_N)}\sum_{i=1}^{N}\varepsilon_i\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)=\left(\sum_{i=1}^{N}\varepsilon_i\right)\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)=\left(\sum_{i=1}^{N}\varepsilon_i\right)|\Psi_0\rangle$$

练习3.8

$$\langle\Psi_0|\mathscr{V}|\Psi_0\rangle=\langle\Psi_0|\sum_{i=1}^{N}\sum_{j>i}^{N}r_{ij}^{-1}|\Psi_0\rangle-\sum_{i}\langle\Psi_0|v^{HF}(i)|\Psi_0\rangle=\langle\Psi_0|\mathscr{O}_2|\Psi_0\rangle-\sum_{a}\sum_{b}\langle i|\mathscr{J}_b(1)|i\rangle-\langle i|\mathscr{K}_b(1)|i\rangle$$

$$=\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\langle ab||ab\rangle-\sum_{a}^{N}\sum_{b}^{N}\langle ab|ab\rangle-\langle ab|ba\rangle=-\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\langle ab||ab\rangle.$$

3.4.1节（闭壳层Hartree-Fock方法：对受限自旋轨道）习题解析

练习3.9

$$\varepsilon_i = \langle i|h|i\rangle + \sum_b^N \langle ib||ib\rangle = \langle i|h|i\rangle + \sum_b^N \langle ib|ib\rangle - \langle ib|bi\rangle = \langle i|h|i\rangle + \sum_b^N [ii|bb] - [ib|bi]$$

$$= (i|h|i) + \sum_b^{N/2} [ii|bb] - [ib|bi] + \sum_b^{N/2} [ii|\bar{b}\bar{b}] - [i\bar{b}|\bar{b}i] = (i|h|i) + \sum_b^{N/2} (ii|bb) - (ib|bi) + \sum_b^{N/2} (ii|bb) - 0$$

$$= h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib}.$$

3.4.2节(基的引入:Roothaan方程)习题解析

练习3.10　只要证明对应矩阵元相等 则 $C^\dagger SC(i;j) = I(i;j) \Leftrightarrow C^\dagger SC = I$. $i \in I_1^K, j \in I_1^K$.

$\therefore C^\dagger SC(i;j) = \cancel{\sum_{\mu=1}^{K} C_{\mu i}^* S_{\mu\nu} C_{\nu j}} = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_{\mu i}^* S_{\mu\nu} C_{\nu j} = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_{\mu i}^* \int dr_1\, \phi_\mu^*(1)\phi_\nu(1) C_{\nu j} = \int dr_1 \left(\sum_{\mu=1}^{K} C_{\mu i}^* \phi_\mu^*(1)\right)\left(\sum_{\nu=1}^{K} C_{\nu j}\phi_\nu(1)\right)$

$= \int dr_1\, \psi_i^*(1)\psi_j(1) = \delta_{ij} = I(i;j)$. 故 $C^\dagger SC = I$. (本行因为使用正交分子轨道得到).

3.4.3节(电子态密度)习题解析

练习3.11 $\rho(\vec{r})=\langle\Psi_0|\hat{\rho}(\vec{r})|\Psi_0\rangle=\sum_{i=1}^{N}\langle\Psi_0|\delta(\vec{r}-\vec{r}_i)|\Psi_0\rangle=\sum_{i=1}^{N}\langle\Psi_i(\vec{r})|\Psi_i(\vec{r})\rangle=2\sum_{i=1}^{N/2}(\psi_a(\vec{r})|\psi_a(\vec{r}))=2\sum_{a=1}^{N/2}|\psi_a(\vec{r})|^2$

练习3.12 $(PSP)_{\mu\nu}=\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K}P_{\mu\lambda}S_{\lambda\sigma}P_{\sigma\nu}=\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K}\left(2\sum_{a=1}^{N/2}C_{\mu a}C_{\lambda a}^*\right)\int_{\Omega}dr\,\phi_\lambda^*(r)\phi_\sigma(r)\left(2\sum_{b=1}^{N/2}C_{\sigma b}C_{\nu b}^*\right)$

$=4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\int_{\Omega}dr\left(\sum_{\lambda=1}^{K}C_{\lambda a}^*\phi_\lambda^*(r)\right)\left(\sum_{\sigma=1}^{K}C_{\sigma b}\phi_\sigma(r)\right)=4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\int_{\Omega}dr\,\psi_a^*(r)\psi_b(r)=4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\delta_{ab}$

$=4\sum_{a=1}^{N/2}C_{\mu a}C_{\nu a}^*=2\left(2\sum_{a=1}^{N/2}C_{\mu a}C_{\nu a}^*\right)=2P_{\mu\nu}$ 即证得 $PSP=2P$. 波浪线处是因为取用分子轨道正交.

而 $[(\frac{1}{2}P)^2]_{\mu\nu}=\frac{1}{4}P_{\mu\nu}^2=\frac{1}{4}\sum_{\lambda=1}^{K}P_{\mu\lambda}P_{\lambda\nu}=\frac{1}{4}\sum_{\lambda=1}^{K}\left(2\sum_{a=1}^{N/2}C_{\mu a}C_{\lambda a}^*\right)\left(2\sum_{b=1}^{N/2}C_{\lambda b}C_{\nu b}^*\right)=\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\left(\sum_{\lambda=1}^{K}C_{\lambda a}^*C_{\lambda b}\right)$.

由于选用 $\psi_i=\sum_{a=1}^{K}C_{ai}\phi_a$ 亦满足 $\langle\psi_i|\psi_j\rangle=\delta_{ij}$. $\therefore\sum_{\lambda=1}^{K}C_{\lambda a}^*C_{\lambda b}=\delta_{ab}$.

$\therefore[(\frac{1}{2}P)^2]_{\mu\nu}=\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\delta_{ab}=\frac{1}{2}\left(2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}C_{\mu a}C_{\nu b}^*\right)=\frac{1}{2}P_{\mu\nu}$. $\therefore(\frac{1}{2}P)^2=\frac{1}{2}P$. 从而 $\frac{1}{2}P$ 为幂等矩阵.

练习3.13: $f(r_1)=h(r_1)+\sum_{a=1}^{N/2}\int_{\Omega_2}dr_2\,\psi_a^*(r_2)(2-P_{12})r_{12}^{-1}\psi_a(r_2)=h(r_1)+\sum_{a=1}^{N/2}\int_{\Omega_2}dr_2\sum_{\sigma=1}^{K}C_{\sigma a}^*\phi_\sigma^*(r_2)(2-P_{12})r_{12}^{-1}\sum_{\lambda=1}^{K}C_{\lambda a}\phi_\lambda(r_2)\psi_a(r_2)$

$=h(r_1)+\sum_{a=1}^{N/2}\int_{\Omega_2}dr_2\sum_{\sigma=1}^{K}\sum_{\lambda=1}^{K}C_{\sigma a}^*C_{\lambda a}\phi_\sigma^*(r_2)(2-P_{12})r_{12}^{-1}\phi_\lambda(r_2)\psi_a(r_2)$

$=h(r_1)+\frac{1}{2}\sum_{\sigma=1}^{K}\sum_{\lambda=1}^{K}\left(2\sum_{a=1}^{N/2}C_{\sigma a}^*C_{\lambda a}\right)\phi_\sigma^*(r_2)(2-P_{12})r_{12}^{-1}\phi_\lambda(r_2)\psi_a(r_2)=h(r_1)+\frac{1}{2}\sum_{\sigma=1}^{K}\sum_{\lambda=1}^{K}P_{\sigma\lambda}\left[\int_{\Omega_2}dr_2\,\phi_\sigma^*(r_2)(2-P_{12})r_{12}^{-1}\phi_\lambda(r_2)\right]$

3.4.4节（Fock矩阵的表达）习题解析

练习3.14　此题按构成双电子积分所需的基函数数目可进行分类。为下述方便，用不同的数字表示。

若构成的双电子积分只用了1种基函数（设为1），则显然只有100种（C_{100}^{1}种）；

若构成的双电子积分用了两种基函数（设为1、2），则独立种类有(12|11)、(11|22)及(12|21)三类。

对(12|11)来讲，1与2地位不平等，故也需计入(21|22)类，故独立种有$4C_{100}^{2}=19800$种；

若构成的双电子积分用了三种基函数（设为1,2,3）则独立大类有(11|23)及(12|13)两大类，但它们均有内部1,2,3间地位不平等情况，从而独立种有$2C_3^1C_2^2C_{100}^{3}=970200$种。

若构成的四电子积分用了四种基函数（设为1,2,3,4），则独立大类有(12|34)、(13|24)及(14|23)三大类（或认为有$A_4^4/(A_2^2A_2^2C_2^1)=3$大类），它们内部1,2,3,4地位平等，从而有$3C_{100}^{4}=11763675$种。

综上，独立的双电子积分有$3C_{100}^{4}+6C_{100}^{3}+4C_{100}^{2}+C_{100}^{1}=12753775$种

若只进行阶估计，则可只计入第四种情形，因其数目远大于前三类之和，约为$O(K^4/8)$。

3.4.5节(基的标准正交化)习题解析

练习3.15　由教材式(3.166)　$\therefore SU = sU \Leftrightarrow \therefore (SU)(\mu;i) = (Us)(\mu;i) \Leftrightarrow \sum_{\nu=1}^{K} S_{\mu\nu} C_\nu^i = \sum_{\nu=1}^{K} C_\mu^\nu s_{\nu i} = \sum_{\nu=1}^{K} C_\mu^\nu \delta_{\nu i} s_i = C_\mu^i s_i$.

两边左侧同乘 $\sum_{\mu=1}^{K} C_\mu^{i*}$. 得　$\sum_{\mu=1}^{K} C_\mu^{i*} \left(\sum_{\nu=1}^{K} S_{\mu\nu} C_\nu^i\right) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} S_{\mu\nu} C_\mu^{i*} C_\nu^i = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_\mu^{i*} C_\nu^i \int_\Omega dr\, \phi_\mu^*(r)\phi_\nu(r)$

$\therefore \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_\mu^{i*} C_\nu^i \int_\Omega dr\, \phi_\mu^*(r)\phi_\nu(r) = \int_\Omega dr \left(\sum_{\mu=1}^{K} C_\mu^i \phi_\mu(r)\right)^* \left(\sum_{\nu=1}^{K} C_\nu^i \phi_\nu(r)\right) = \int_\Omega dr\, \phi_i^*(r)\phi_i(r) = \int_\Omega dr |\phi_i(r)|^2 > 0.$

而 $\sum_{\mu=1}^{K} C_\mu^{i*} C_\mu^i s_i = s_i \sum_{\mu=1}^{K} |C_\mu^i|^2$, $\sum_{\mu=1}^{K} |C_\mu^i|^2 > 0$, 因为不能所有 $C_\mu^i = 0$. ($\mu \in I_1^K$). 否则 $\phi_i(r) \equiv 0$. 从而 $s_i = \dfrac{\int_\Omega dr |\phi_i(r)|^2}{\sum_{\mu=1}^{K} |C_\mu^i|^2} > 0$.

对一切 $i \in I_1^K$ 成立, 从而 S 是正定的.

练习3.16　由教材式(3.179), $\psi_i = \sum_{\mu=1}^{K} C'_{\mu i} \phi'_\mu = \sum_{\mu=1}^{K} C'_{\mu i} \left(\sum_{\nu=1}^{K} X_{\nu\mu} \phi_\nu\right) = \sum_{\nu=1}^{K}\left(\sum_{\mu=1}^{K} C'_{\mu i} X_{\nu\mu}\right)\phi_\nu = \sum_{\nu=1}^{K} C_{\nu i}\phi_\nu$

由 $\{\phi_\nu\}$ ($\nu \in I_1^K$) 线性无关.　$\therefore C_{\nu i} = \sum_{\mu=1}^{K} C'_{\mu i} X_{\nu\mu}$　　$\therefore C = XC' \Leftrightarrow C' = X^{-1}C$. 此即式(3.174)

由教材式(3.180), $F'_{\mu\nu} = \int_\Omega dr_1\, \phi'^*_\mu(1) f(1) \phi'_\nu(1) = \int_\Omega dr \left(\sum_{i=1}^{K} X_{i\mu}^* \phi_i^*(1)\right) f(1) \left(\sum_{j=1}^{K} X_{j\nu}\phi_j(1)\right) = \sum_{i=1}^{K}\sum_{j=1}^{K} X_{i\mu}^* X_{j\nu} F_{ij} = (X^\dagger F X)(\mu;\nu)$

$\therefore F' = X^\dagger F X$. 此即式(3.177)

3.4.7节(期望值与布居分析)习题解析

练习3.17　由教材式(3.183).

$$E_0=\sum_{a=1}^{N/2}(f_{aa}+h_{aa})=\sum_{a=1}^{N/2}\left[\int_{\Omega_1}dr_1\,\psi_a^*(1)f(1)\psi_a(1)+\int_{\Omega_1}dr_1\,\psi_a^*(1)h(1)\psi_a(1)\right]$$

$$=\sum_{a=1}^{N/2}\left[\int_{\Omega_1}dr_1\left(\sum_{\mu=1}^{K}\phi_\mu^*(1)C_{\mu a}^*\right)f(1)\left(\sum_{\nu=1}^{K}\phi_\nu(1)C_{\nu a}\right)+\int_{\Omega_1}dr_1\left(\sum_{\mu=1}^{K}\phi_\mu^*(1)C_{\mu a}^*\right)h(1)\left(\sum_{\nu=1}^{K}\phi_\nu(1)C_{\nu a}\right)\right]$$

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\left(\int_{\Omega_1}dr_1\,\phi_\mu^*(1)h(1)\phi_\nu(1)+\int_{\Omega_1}dr_1\,\phi_\mu^*(1)f(1)\phi_\nu(1)\right)\sum_{a=1}^{N/2}C_{\mu a}^*C_{\nu a}=\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}P_{\nu\mu}(H_{\mu\nu}^{core}+F_{\mu\nu}).$$ 此即式(3.184)

练习3.18　由教材式(3.144)

$$\rho(r)=\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K}P_{\lambda\sigma}\phi_\lambda(r)\phi_\sigma^*(r)=\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}(S^{1/2}PS^{+1/2})_{\mu\nu}(S^{-1/2})_{\lambda\mu}\phi_\lambda(r)(S^{-1/2})^*_{\sigma\nu}\phi_\sigma(r)$$. 由教材式(3.200)

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}P'_{\mu\nu}\phi'_\mu(r)\phi'^*_\nu(r).$$ 由基$\{\phi'_\mu(r)\phi'^*_\nu(r)\}$的线性无关性. $\therefore P'_{\mu\nu}=(S^{1/2}PS^{+1/2})_{\mu\nu}\Leftrightarrow P'=S^{1/2}PS^{+1/2}$.

3.5.1节(最小基STO-3G基)

练习3.19　从$\phi_{1s}^{GF}(p,\vec{r}-\vec{R}_p)$中凑出$\phi_{1s}^{GF}(\alpha,\vec{r}-\vec{R}_A)$及$\phi_{1s}^{GF}(\beta,\vec{r}-\vec{R}_A)$形式即可得解.

$$\phi_{1s}^{GF}(p,\vec{r}-\vec{R}_p)=\left(\frac{2p}{\pi}\right)^{\frac{3}{4}}e^{-p|\vec{r}-\vec{R}_p|^2}=\left(\frac{2(\alpha+\beta)}{\pi}\right)^{\frac{3}{4}}e^{-(\alpha+\beta)|\vec{r}-\frac{\alpha\vec{R}_A+\beta\vec{R}_B}{\alpha+\beta}|}$$

先化简指数项的幂次.

$$(\alpha+\beta)|\vec{r}-\frac{\alpha\vec{R}_A+\beta\vec{R}_B}{\alpha+\beta}|=\frac{1}{\alpha+\beta}|(\alpha+\beta)\vec{r}-(\alpha\vec{R}_A+\beta\vec{R}_B)|^2=\frac{1}{\alpha+\beta}|\alpha(\vec{r}-\vec{R}_A)+\beta(\vec{r}-\vec{R}_B)|^2$$

$$=\frac{1}{\alpha+\beta}[\alpha^2|\vec{r}-\vec{R}_A|^2+\beta^2|r-R_B|^2+2\alpha\beta(\vec{r}-\vec{R}_A)(\vec{r}-\vec{R}_B)]=\frac{1}{\alpha+\beta}[\alpha(\alpha+\beta)|\vec{r}-\vec{R}_A|^2+\beta(\beta+\alpha)|\vec{r}-\vec{R}_B|^2+2\alpha\beta(\vec{r}-\vec{R}_A)(\vec{r}-\vec{R}_B)-\alpha|\vec{r}-\vec{R}_A|^2-\beta|$$

$$=\alpha|\vec{r}-\vec{R}_A|^2+\beta|\vec{r}-\vec{R}_B|^2+\alpha\beta(2r^2-2\vec{r}\cdot\vec{R}_B-2\vec{r}\cdot\vec{R}_A+2\vec{R}_A\cdot\vec{R}_B-r^2+2\vec{r}\cdot\vec{R}_A-\vec{R}_A^2-r^2+2\vec{r}\cdot\vec{R}_B-\vec{R}_B^2)\cdot\frac{1}{\alpha+\beta}$$

$$=\alpha|\vec{r}-\vec{R}_A|^2+\beta|\vec{r}-\vec{R}_B|^2+\frac{-\alpha\beta}{\alpha+\beta}(\vec{R}_A^2-2\vec{R}_A\cdot\vec{R}_B+\vec{R}_B^2)=\alpha|\vec{r}-\vec{R}_A|^2+\beta|\vec{r}-\vec{R}_B|^2-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2$$，代入此结果

$$\therefore\phi_{1s}^{GF}(p,\vec{r}-\vec{R}_p)=\left(\frac{2(\alpha+\beta)\pi}{2\alpha\cdot2\beta}\right)^{\frac{3}{4}}\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}}\left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}}e^{-\alpha|\vec{r}-\vec{R}_A|^2-\beta|\vec{r}-\vec{R}_B|^2+\frac{\alpha\beta}{\alpha+\beta}|R_A-R_B|^2}=\left(\frac{\pi(\alpha+\beta)}{2\alpha\beta}\right)^{\frac{3}{4}}e^{\frac{\alpha\beta}{\alpha+\beta}|R_A-R_B|^2}\phi_{1s}^{GF}(\alpha,\vec{r}-\vec{R}_A)\phi_{1s}^{GF}(\beta,\vec{r}-$$

$$\therefore\phi_{1s}^{GF}(\alpha,\vec{r}-\vec{R}_A)\phi_{1s}^{GF}(\beta,\vec{r}-\vec{R}_B)=\left(\frac{2\alpha\beta}{\pi(\alpha+\beta)}\right)^{\frac{3}{4}}e^{-\frac{\alpha\beta}{\alpha+\beta}|R_A-R_B|^2}\phi_{1s}^{GF}(p,\vec{r}-\vec{R}_p)$$，此即教材式(3.208)代入式(3.207)结果.

练习3.20　$\phi_{1s}^{CGF}(\zeta=1.0,STO-1G)|_{r=0}=\sqrt[4]{\left(\frac{2\cdot0.270950}{\pi}\right)^3}\doteq0.267656.$

$\phi_{2s}^{CGF}(\zeta=1.0,STO-2G)|_{r=0}=0.678914\cdot\left(\frac{2\cdot0.151623}{\pi}\right)^{\frac{3}{4}}+0.430129\cdot\left(\frac{2\cdot0.851819}{\pi}\right)^{\frac{3}{4}}=0.389383$

$\phi_{3s}^{CGF}(\zeta=1.0,STO-3G)|_{r=0}=0.444635\cdot\left(\frac{2\cdot0.109818}{\pi}\right)^{\frac{3}{4}}+0.535328\cdot\left(\frac{2\cdot0.405771}{\pi}\right)^{\frac{3}{4}}+0.154329\cdot\left(\frac{2.222766}{\pi}\right)^{\frac{3}{4}}=0.454986.$

3.5.2节(H_2的STO-3G基)习题解析

练习3.21　先修正$\zeta=1.24$，有$\phi_{1s}^{CGF}(\zeta=1.24, STO-1G) = \phi_{1s}^{GF}(0.416613)$，$0.416613 = 1.24^2 \cdot 0.270950$。

$\therefore S_{12} = \int_{\mathbb{R}^3} \phi_{1s}^{GF}(0.416613)\phi_{1s}^{GF}(0.416613)d\tau$，记为$\phi_{1s}^{GF}(\alpha, \vec{r}-\vec{R}_A)$，$\phi_{1s}^{GF}(\beta, \vec{r}-\vec{R}_B)$。

$$\therefore S_{12} = \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi}\right)^{3/4} K \int_{\mathbb{R}^3} \phi_{1s}^{GF}(\alpha+\beta, \vec{r}-\vec{R}_p)d\tau = \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi}\right)^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2} \cdot 4\pi \int_0^{+\infty} r_p^2 e^{-(\alpha+\beta)r_p^2} dr_p$$

$$= \left(\frac{4\alpha\beta}{(\alpha+\beta)^2}\right)^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2}$$

代入$\alpha=\beta=0.416613$，$|\vec{R}_A-\vec{R}_B|=1.4\,a.u.$　$\therefore S_{12} \doteq 0.664792 \doteq 0.6648$。

练习3.22.　可参考练习2.6，两题实质相同。

练习3.23　由式(3.234)得

$$\begin{pmatrix} H_{11}^{core} & H_{12}^{core} \\ H_{21}^{core} & H_{22}^{core} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix}\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$

计算完矩阵乘法，由矩阵相等之定义，$C_1H_{11}^{core}+C_1H_{12}^{core} = \varepsilon_1(S_{11}C_1+S_{12}C_1)$，$C_2H_{11}^{core}-C_2H_{12}^{core} = \varepsilon_2(S_{11}C_2-S_{12}C_2)$。

$$\therefore \varepsilon_1 = \frac{H_{11}^{core}+H_{12}^{core}}{S_{11}+S_{12}} = \frac{H_{11}^{core}+H_{12}^{core}}{1+S_{12}} = \frac{-1.1204-0.9584}{1+0.6593}a.u. = -1.2528\,a.u.$$

$$\varepsilon_2 = \frac{H_{11}^{core}-H_{12}^{core}}{S_{11}-S_{12}} = \frac{H_{11}^{core}-H_{12}^{core}}{1-S_{12}} = \frac{-1.1204+0.9584}{1-0.6593}a.u. = -0.4755\,a.u.$$

练习3.24　$C_{11} = \frac{1}{\sqrt{2(1+S_{12})}}$，$C_{21} = \frac{1}{\sqrt{2(1+S_{12})}}$　$\therefore P_{11} = 2C_{11}C_{11}^* = \frac{1}{1+S_{12}}$，$P_{12} = 2C_{11}C_{21}^* = \frac{1}{1+S_{12}}$，$P_{21} = 2C_{21}C_{11}^* = \frac{1}{1+S_{12}}$，$P_{22} = 2C_{21}C_{21}^* = \frac{1}{1+S_{12}}$。

$$\therefore P_{H_2} = \begin{pmatrix} \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \\ \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \end{pmatrix} = \frac{1}{1+S_{12}}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

而H_2^+相比于H_2，少了一半电子，由H_2结构的对称性及H_2^+结构对称性。

$$\therefore P_{H_2^+} = \frac{1}{2(1+S_{12})}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

练习3.25　由于$F = H^{core}+G$，先计算G，教材式(3.154)给出$G_{\mu\nu} = \sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda)-\frac{1}{2}(\mu\lambda|\sigma\nu)]$。

$$\therefore G_{11} = \sum_{\lambda=1}^{2}\sum_{\sigma=1}^{2} P_{\lambda\sigma}[(11|\sigma\lambda)-\frac{1}{2}(1\lambda|\sigma1)]$$

$$= P_{11}[(11|11)-\frac{1}{2}(11|11)]+P_{12}[(11|21)-\frac{1}{2}(11|21)]+P_{21}[(11|12)-\frac{1}{2}(12|11)]+P_{22}[(11|22)-\frac{1}{2}(12|21)]$$

$$= \frac{1}{1+S_{12}}[\frac{1}{2}(11|11)+(11|12)+(11|22)-\frac{1}{2}(12|21)]$$，代入式(3.233)，式(3.235)及$S_{12}=0.6593$(式(3.229))。

$$\therefore F_{11} = H_{11}^{core}+G_{11} = H_{11}^{core}+\frac{1}{1+S_{12}}[\frac{1}{2}(11|11)+(11|22)+(11|12)-\frac{1}{2}(12|21)] = -0.3655\,a.u.$$

同理，$G_{12} = \sum_{\lambda=1}^{2}\sum_{\sigma=1}^{2} P_{\lambda\sigma}[(12|\sigma\lambda)-\frac{1}{2}(1\lambda|\sigma2)]$　注意到$(11|12)=(22|21)$

$$\therefore G_{12} = P_{11}[(12|11)-\frac{1}{2}(11|12)]+P_{12}[(12|21)-\frac{1}{2}(11|22)]+P_{21}[(12|12)-\frac{1}{2}(12|12)]+P_{22}[(12|22)-\frac{1}{2}(12|22)]$$

$$= \frac{1}{1+S_{12}}[\frac{1}{2}(11|12)+\frac{3}{2}(12|12)-\frac{1}{2}(11|22)+\frac{1}{2}(12|22)] = \frac{1}{1+S_{12}}[-\frac{1}{2}(11|22)+(11|12)+\frac{3}{2}(12|12)]$$

$$\therefore F_{12} = H_{12}^{core}+G_{12} = H_{12}^{core}+\frac{1}{1+S_{12}}[-\frac{1}{2}(11|22)+(11|12)+\frac{3}{2}(12|12)] = -0.5939\,a.u.$$

$$G_{21} = P_{11}[(21|11)-\frac{1}{2}(21|11)]+P_{12}[(21|21)-\frac{1}{2}(21|21)]+P_{21}[(21|12)-\frac{1}{2}(22|11)]+P_{22}[(21|22)-\frac{1}{2}(22|21)]$$

$$= \frac{1}{1+S_{12}}[\frac{3}{2}(12|12)-\frac{1}{2}(11|22)+(11|12)] = 0.3645\,a.u.\quad F_{21} = H_{21}^{core}+G_{21} = -0.5939\,a.u.$$

$$G_{22} = P_{11}[(22|11)-\frac{1}{2}(12|12)]+P_{12}[(22|21)-\frac{1}{2}(21|22)]+P_{21}[(22|12)-\frac{1}{2}(22|12)]+P_{22}[(22|22)-\frac{1}{2}(22|22)]$$

$$= \frac{1}{1+S_{12}}[(22|11)-\frac{1}{2}(12|12)+(11|22)+\frac{1}{2}(22|22)] = 0.7549\,a.u.\quad \therefore F_{22} = H_{22}^{core}+G_{22} = -0.3655\,a.u.$$

练习3.26　同练习3.23. 由 $FC=SC\varepsilon$. 得

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix}=\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} C_1 & C_2 \\ C_1 & -C_2 \end{pmatrix}\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}$$

$\therefore F_{11}C_1+F_{12}C_1=(S_{11}C_1+S_{12}C_1)\varepsilon_1$，$F_{11}C_2-F_{12}C_2=(S_{11}C_2-S_{12}C_2)\varepsilon_2$. 代入练习3.25结果及 $S_{12}=0.6593\,a.u.$

$\therefore \varepsilon_1=\dfrac{F_{11}+F_{12}}{1+S_{12}}=-0.5782\,a.u.$　$\varepsilon_2=\dfrac{F_{11}-F_{12}}{1-S_{12}}=0.6704\,a.u.$

练习3.27　由式(3.184), 得 $E_0=\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}P_{\mu\nu}(H_{\mu\nu}^{core}+F_{\mu\nu})$, 代入式(3.239). 式(3.239)及练习3.25结果

$\therefore E_0=\frac{1}{2}[P_{11}(H_{11}^{core}+F_{11})+P_{12}(H_{12}^{core}+F_{12})+P_{21}(H_{21}^{core}+F_{21})+P_{22}(H_{22}^{core}+F_{22})]=\frac{1}{1+S_{12}}[F_{11}+H_{11}^{core}+F_{12}+H_{12}^{core}]=-1.8310\,a.u.$

$\therefore E_{total}=E_0+\frac{1\cdot 1}{R}=-1.1167\,a.u.$

3.5.3节（对HeH^+ STO-3G基的自洽场计算）习题解析.

练习3.28 $\phi_1' = X_{11}\phi_1 + X_{21}\phi_2 = \phi_1$，$\phi_2' = X_{12}\phi_2 + X_{22}\phi_2 = -\frac{S_{12}}{\sqrt{1-S_{12}^2}}\phi_1 + \frac{1}{\sqrt{1-S_{12}^2}}\phi_2$

$\therefore \langle\phi_1'|\phi_1'\rangle = \langle\phi_1|\phi_1\rangle = 1$. $\langle\phi_1'|\phi_2'\rangle = \langle\phi_2'|\phi_1'\rangle = \langle\phi_1| -\frac{S_{12}}{\sqrt{1-S_{12}^2}}\phi_1\rangle + \langle\phi_1|\frac{1}{\sqrt{1-S_{12}^2}}\phi_2\rangle = -\frac{S_{12}}{\sqrt{1-S_{12}^2}} + \frac{S_{12}}{\sqrt{1-S_{12}^2}} = 0.$

$\therefore \langle\phi_2'|\phi_2'\rangle = \langle -\frac{S_{12}}{\sqrt{1-S_{12}^2}}\phi_1 + \frac{1}{\sqrt{1-S_{12}^2}}\phi_2 | -\frac{S_{12}}{\sqrt{1-S_{12}^2}}\phi_1 + \frac{1}{\sqrt{1-S_{12}^2}}\phi_2\rangle = \frac{1+S_{12}^2}{1-S_{12}^2} - 2\frac{S_{12}}{\sqrt{1-S_{12}^2}}\langle\phi_1|\phi_2\rangle = \frac{1-S_{12}^2}{1-S_{12}^2} = 1.$

从而ϕ_1', ϕ_2'构成一个标准正交基.

练习3.29 $G_{11} = \sum_{\lambda=1}^{2}\sum_{\sigma=1}^{2} P_{\lambda\sigma}[(11|\sigma\lambda) - \frac{1}{2}(1\lambda|\sigma 1)] = P_{11}[(11|11) - \frac{1}{2}(11|11)] = 2\cdot\frac{1}{2}(11|11) = (11|11)$

$E_0 = \frac{1}{2}\sum_{\lambda=1}^{2}\sum_{\sigma=1}^{2} P_{\lambda\sigma}(2H_{\mu\nu}^{core} + G_{\mu\nu}) = \frac{1}{2}P_{11}(2H_{11}^{core} + G_{11}) = \frac{1}{2}\cdot 2\cdot(2T_{11} + 2V_{11}' + (11|11)) = 2T_{11} + 2V_{11}' + (11|11).$

3.6.3节 双Zeta基：4-31G|习题解析

练习3.30　He的1s轨道为 $\psi_{1s} = 0.51380\, g_{1s}(0.298073, r) + 0.46954\, g_{1s}(1.242567) + 0.15457\, g_{1s}(5.782948) + 0.02373\, g_{1s}(38.47497)$.

取内层轨道为 $\phi_{1s}''(r) = g_{1s}(0.298073, r)$. ~~外层轨道 $\phi_{1s}'(r) = N[0.51380\, g_{1s}(0.298073, r) + 0.46954\, g_{1s}(1.242567) + 0.15457$~~

外层轨道为 $\phi_{1s}'(r) = N[0.46954\, g_{1s}(1.242567) + 0.15457\, g_{1s}(5.782948) + 0.02373\, g_{1s}(38.47497)]$.

从而由 $\langle \phi_{1s}' | \phi_{1s}' \rangle = 1$ 定出N，从而完全确定 $\phi_{1s}'(r)$. 由以下引理确定：

$$\langle g_{1s}(\alpha_i, r) | g_{1s}(\alpha_j, r) \rangle = \left(\frac{4\alpha_i \alpha_j}{(\alpha_i + \alpha_j)^2} \right)^{3/4}$$

$\therefore \langle g_{1s}(1.242567) | g_{1s}(5.782948) \rangle = 0.666622$. $\langle g_{1s}(1.242567) | g_{1s}(38.47497) \rangle = 0.205445$.

$\langle g_{1s}(5.782948) | g_{1s}(38.47497) \rangle = 0.553419$. 　从而定出 $N \doteq 1.689528$

$\therefore \phi_{1s}'(r) = 0.79330\, g_{1s}(1.242597) + 0.26115\, g_{1s}(5.782948) + 0.04009\, g_{1s}(38.47497)$.

从而 $\phi_{1s}'(r)$ 与 $\phi_{1s}''(r)$ 构成He的一个4-31G基.

3.6.4节（极化基组：6-31G*和6-31G**）习题解析

练习3.31　使用未并缩基组情况：

H的STO-3G使用了3个Gaussian Functions，4-31G使用了4个Gaussian Functions，6-31G*使用了4个Gaussian Functions，6-31G**使用了$4+1\times3=7$个Gaussian Functions（增加了p型的三个轨道）；C的STO-3G使用了$3+3+3\times3=15$个函数，C的4-31G使用了$4+4+4\times3=20$ Gaussian Functions，6-31G*使用了$6+4\times4+1\times6=28$个Gaussian Functions，6-31G**使用了与6-31G*相同数的Gaussian Functions。

苯的化学式为C_6H_6，则STO-3G下使用Gaussian函数$6\times(3+15)=108$个Gaussian Functions，4-31G基下使用了$6\times(4+20)=144$ Gaussian Functions，6-31G*使用了$6\times(4+28)=192$个Gaussian Functions，6-31G**使用了186个Gaussian Functions，6-31G**使用了$6\times(7+28)=210$个Gaussian Functions。

使用并缩基组情况：

H的STO-3G使用了1个Gaussian Functions，4-31G使用了2个Gaussian Functions，6-31G*使用了2个Gaussian Functions，6-31G**使用了$2+1\times3=5$个Gaussian Functions；C的STO-3G使用5个Gaussian Functions，4-31G使用了9个Gaussian Functions，6-31G*使用15个Gaussian Functions，6-31G**使用15个Gaussian Functions。

从而苯在STO-3G下使用了$6\times(1+5)=36$ Gaussian Functions，4-31G下使用了$6\times(2+9)=66$个Gaussian Functions，6-31G*使用了$6\times(2+15)=102$ Gaussian Functions，6-31G**使用了$6\times(5+15)=120$个Gaussian Functions。

3.7.1节(总能量)习题解析

练习3.32　先将本题用到的所有数据列表.

计算水平/	H_2	N_2	NH_3	CO	CH_4	H_2O	
STO-3G	-1.117	-107.496	-55.454	-111.225	-39.727	-74.963	
4-31G	-1.127	-108.754	-56.102	-112.552	-40.140	-75.907	
6-31G*	-1.127	-108.942	-56.184	-112.737	-40.195	-76.011	
6-31G**	-1.131	-108.942	-56.195	-112.737	-40.202	-76.023	
HF-limit	-1.134	-108.997	-56.225	-112.791	-40.225	-76.065	

$\Delta E(\text{reaction1, STO-3G}) = 2\times(-55.454\,a.u.) - 1\times(-107.496\,a.u.) - 3\times(1.117\,a.u.) = -0.061\,a.u. = -38.28\,kcal\cdot mol^{-1}$

同理, 有 $\Delta E(\text{reaction1, 4-31G}) = -0.069\,a.u.\ (-43.30\,kcal\cdot mol^{-1})$

$\Delta E(\text{reaction1, 6-31G*}) = -0.045\,a.u.\ (-28.24\,kcal\cdot mol^{-1})$

$\Delta E(\text{reaction1, 6-31G**}) = -0.055\,a.u.\ (-34.51\,kcal\cdot mol^{-1})$

$\Delta E(\text{reaction, HF-limit}) = -0.051\,a.u.\ (-32.00\,kcal\cdot mol^{-1})$.

$\Delta E(\text{reaction2, STO-3G}) = 1\times(-39.727\,a.u.) + 1\times(-74.963\,a.u.) - 1\times(-111.225\,a.u.) - 3\times(-1.117\,a.u.) = -0.114\,a.u. = -71.54\,kcal\cdot mol^{-1}$

同理; $\Delta E(\text{reaction2, 4-31G}) = -0.114\,a.u. = -71.54\,kcal\cdot mol^{-1}$.

$\Delta E(\text{reaction2, 6-31G*}) = -0.088\,a.u. = -55.22\,kcal\cdot mol^{-1}$

$\Delta E(\text{reaction2, 6-31G**}) = -0.095\,a.u. = -59.61\,kcal\cdot mol^{-1}$

$\Delta E(\text{reaction2, }\cancel{\text{6-31}}\text{HF-limit}) = -0.097\,a.u. = -60.87\,kcal\cdot mol^{-1}$.

$\frac{1}{2}h\nu(\text{reaction1}) = 2\times 1.35 - 3\times 6.18 - 1\times 3.35 = -19.19\,kcal\cdot mol^{-1}$

$\frac{1}{2}h\nu(\text{reaction2}) = 1\times 1.86 + 1\times 2.28 - 3\times 6.18 - 1\times 3.08 = -17.48\,kcal\cdot mol^{-1}$

显然, 零点能不宜被忽略.

3.8.1节(开壳层结构的HF方法:未限制自旋轨道)习题解析

练习3.33 同3.4.1节正文推导的方法处理即可. 可以做为3.4.1节理解的证明. 具体如下:

$$f^{\alpha}(1)\psi_j(1)=h(1)\psi_j(1)+\sum_{c=1}^{N}\int_{\Omega_{x_2}}dx_2\int_{\Omega_{\omega_1}}d\omega_1\,\alpha^*(1)\chi_c^*(2)r_{12}^{-1}\chi_c(2)\alpha(1)\psi_j(1)-\sum_{c=1}^{N}\int_{\Omega_{x_2}}dx_2\int_{\Omega_{\omega_1}}d\omega_1\,\alpha^*(1)\chi_c^*(2)r_{12}^{-1}\chi_c(1)\alpha(2)\psi_j(2)$$

$$=h(1)\psi_j(1)+\sum_{c=1}^{N^{\alpha}}\int_{\Omega_2}dr_2\int_{\Omega_{\omega_1}}d\omega_1\int_{\Omega_{\omega_2}}d\omega_2\,\alpha^*(1)\alpha^*(2)\psi_c^*(2)r_{12}^{-1}\psi_c(2)\alpha^*(2)\alpha(1)\psi_j(1)-\int_{\Omega_2}dr_2\int_{\Omega_{\omega_1}}d\omega_1\int_{\Omega_{\omega_2}}d\omega_2\,\alpha^*(1)\psi_c^*(2)\alpha^*(2)r_{12}^{-1}\psi_c(1)\alpha^*(2)\alpha(1)\psi_j(2)$$

$$+\sum_{c=1}^{N^{\beta}}\int_{\Omega_2}dr_2\int_{\Omega_{\omega_1}}d\omega_1\int_{\Omega_{\omega_2}}d\omega_2\,\alpha^*(1)\psi_c(2)\beta^*(2)r_{12}^{-1}\psi_c(2)\beta^*(2)\alpha(1)\psi_j(1)-\int_{\Omega_2}dr_2\int_{\Omega_1}d\omega_1\int_{\Omega_2}d\omega_2\,\alpha^*(1)\psi_c^*(2)\beta^*(2)r_{12}^{-1}\psi_c(1)\beta(1)\alpha(2)\psi_j(2)$$

$$=h(1)\psi_j(1)+\sum_{c=1}^{N^{\alpha}}\int_{\Omega_2}dr_2\,\psi_c^*(2)r_{12}^{-1}\psi_c(2)\psi_j(1)-\int_{\Omega_2}dr_2\,\psi_c^*(2)r_{12}^{-1}\psi_c(1)\psi_j(2)+\sum_{c=1}^{N^{\beta}}\int_{\Omega_2}dr_2\,\psi_c^*(2)r_{12}^{-1}\psi_c(2)\psi_j(1)$$

$$=\{h(1)+\sum_{c=1}^{N^{\alpha}}[J_c^{\alpha}(1)-K_c^{\alpha}(1)]+\sum_{c=1}^{N^{\beta}}J_c^{\beta}(1)\}\psi_j(1).$$ 由$\psi_j(1)$的独立性. $\therefore f^{\alpha}(1)=h(1)+\sum_{c=1}^{N^{\alpha}}[J_c^{\alpha}(1)-K_c^{\alpha}(1)]+\sum_{c=1}^{N^{\beta}}J_c^{\beta}(1).$

练习3.34. 利用式(3.327)直接得到(Li原子视作有α电子2个, β电子1个)

$$E_0=\sum_{a=1}^{2}h_{aa}^{\alpha}+\sum_{a=1}^{1}h_{aa}^{\beta}+\frac{1}{2}\sum_{a=1}^{2}\sum_{b=1}^{2}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})+\frac{1}{2}\sum_{a=1}^{1}\sum_{b=1}^{1}(J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta})+\sum_{a=1}^{2}\sum_{b=1}^{1}J_{ab}^{\alpha\beta}$$

$$=h_{11}^{\alpha}+h_{22}^{\alpha}+h_{11}^{\beta}+\frac{1}{2}(J_{12}^{\alpha\alpha}-K_{12}^{\alpha\alpha})+\frac{1}{2}(J_{21}^{\alpha\alpha}-K_{21}^{\alpha\alpha})+\frac{1}{2}(J_{11}^{\beta\beta}-K_{11}^{\beta\beta}\cancel{+J_{21}^{\beta\beta}-K_{21}^{\beta\beta}})+J_{11}^{\alpha\beta}+J_{21}^{\alpha\beta}$$

$$=h_{11}^{\alpha}+h_{22}^{\alpha}+h_{11}^{\beta}+J_{12}^{\alpha\alpha}-K_{12}^{\alpha\alpha}+J_{11}^{\alpha\beta}+J_{21}^{\alpha\beta}.$$

练习3.35

$$\varepsilon_i^{\alpha}=(\psi_i^{\alpha}|f^{\alpha}|\psi_j^{\alpha})=(\psi_i^{\alpha}|h^{\alpha}|\psi_i^{\alpha})+\sum_{a=1}^{N^{\alpha}}(\psi_i^{\alpha}|J_a^{\alpha}(1)|\psi_i^{\alpha})-(\psi_i^{\alpha}|K_a^{\alpha}(1)|\psi_i^{\alpha})+\sum_{a=1}^{N^{\beta}}(\psi_i^{\alpha}|J_a^{\beta}(1)|\psi_i^{\alpha})$$

$$=h_{ii}^{\alpha}+\sum_{a=1}^{N^{\alpha}}(\psi_i^{\alpha}\psi_i^{\alpha}|\psi_a^{\alpha}\psi_a^{\alpha})-(\psi_i^{\alpha}\psi_a^{\alpha}|\psi_a^{\alpha}\psi_i^{\alpha})+\sum_{a=1}^{N^{\beta}}(\psi_i^{\alpha}\psi_i^{\alpha}|\psi_a^{\beta}\psi_a^{\beta})$$

$$=h_{ii}^{\alpha}+\sum_{a=1}^{N^{\alpha}}J_{ia}^{\alpha\alpha}-K_{ia}^{\alpha\alpha}+\sum_{a=1}^{N^{\beta}}J_{ia}^{\alpha\beta}$$ 同理, $\varepsilon_i^{\beta}=h_{ii}^{\beta}+\sum_{a=1}^{N^{\beta}}(J_{ia}^{\beta\beta}-K_{ia}^{\beta\beta})+\sum_{a=1}^{N^{\alpha}}J_{ia}^{\beta\alpha}$

$$\therefore \cancel{E_0}\sum_{a=1}^{N^{\alpha}}\varepsilon_a^{\alpha}+\sum_{a=1}^{N^{\beta}}\varepsilon_a^{\beta}=\sum_{a=1}^{N^{\alpha}}(h_{aa}^{\alpha}+\sum_{b=1}^{N^{\alpha}}J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha}+\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta})+\sum_{a=1}^{N^{\beta}}(h_{aa}^{\beta}+\sum_{b=1}^{N^{\beta}}J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta}+\sum_{b=1}^{N^{\alpha}}J_{ab}^{\beta\alpha})$$

$$=\sum_{a=1}^{N^{\alpha}}h_{aa}^{\alpha}+\sum_{a=1}^{N^{\beta}}h_{aa}^{\beta}+\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\alpha}}J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha}+\sum_{a=1}^{N^{\beta}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta}+2\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta}$$ (利用式(3.327))

$$=\Big(\sum_{a=1}^{N^{\alpha}}h_{aa}^{\alpha}+\sum_{a=1}^{N^{\beta}}h_{aa}^{\beta}+\frac{1}{2}\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\alpha}}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})+\frac{1}{2}\sum_{a=1}^{N^{\beta}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta}+\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta}\Big)$$

$$+\frac{1}{2}\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\alpha}}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})+\frac{1}{2}\sum_{a=1}^{N^{\beta}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta}+\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta}$$

$$=E_0+\frac{1}{2}\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\alpha}}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})+\frac{1}{2}\sum_{a=1}^{N^{\beta}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta}+\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta}$$

$$\therefore E_0=\sum_{a=1}^{N^{\alpha}}\varepsilon_a^{\alpha}+\sum_{a=1}^{N^{\beta}}\varepsilon_a^{\beta}-\frac{1}{2}\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\alpha}}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})-\frac{1}{2}\sum_{a=1}^{N^{\beta}}\sum_{b=1}^{N^{\beta}}(J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta})-\sum_{a=1}^{N^{\alpha}}\sum_{b=1}^{N^{\beta}}J_{ab}^{\alpha\beta}.$$

3.8.3节(不受限态密度矩阵)习题解析

练习3.36 $\int_\Omega dr\,\rho^s(r) = \int_\Omega dr\,\rho^\alpha(r) - \rho^\beta(r) = N^\alpha - N^\beta = \frac{1}{2}(N^\alpha - N^\beta)\cdot 2 = 2\langle S_z\rangle.$

练习3.37 $\rho^\alpha(r) = \sum_{a=1}^{N^\alpha}|\psi_a^\alpha(r)|^2 = \sum_{a=1}^{N^\alpha}\left(\sum_{\mu=1}^{K} C_{\mu a}^\alpha\phi_\mu(r)\right)\left(\sum_{\nu=1}^{K} C_{\nu a}^\alpha\phi_\nu(r)\right)^* = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\left(\sum_{a=1}^{N^\alpha} C_{\mu a}^\alpha C_{\nu a}^{\alpha *}\right)\phi_\mu(r)\phi_\nu^*(r) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} P_{\mu\nu}^\alpha\phi_\mu(r)\phi_\nu^*(r)$

由$\{\phi_\mu(r)\}(\mu\in I_1^K)$的线性无关性，从而$\{\phi_\mu(r)\phi_\nu^*(r)\}$线性无关，从而 $P_{\mu\nu}^\alpha = \sum_{a=1}^{N^\alpha} C_{\mu a}^\alpha C_{\nu a}^{\alpha *}$，此即式(3.342)。

同理，由式(3.341)可得式(3.343)。

练习3.38 $\langle \mathscr{O}_1\rangle = \langle\Psi|\sum_{i=1}^{N} h(i)|\Psi\rangle = \sum_{i=1}^{N}\langle\chi_i|h(i)|\chi_i\rangle = \sum_{i=1}^{N}(i|h|i) = \sum_{i=1}^{N}\left(\sum_{\nu=1}^{N} C_{\nu i}\phi_\nu|h|\sum_{\mu=1}^{N} C_{\mu i}\phi_\mu\right) = \sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\sum_{i=1}^{N} C_{\mu i}C_{\nu i}^*\right)(\nu|h|\mu).$

$= \sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\left(\sum_{i=1}^{N^\alpha} C_{\mu i}^\alpha C_{\nu i}^{\alpha *} + \sum_{i=1}^{N^\beta} C_{\mu i}^\beta C_{\nu i}^{\beta *}\right)(\nu|h|\mu) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K}(P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta)(\nu|h|\mu) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} P_{\mu\nu}^T(\nu|h|\mu).$

练习3.39 $\langle\hat{\rho}^s\rangle = \langle\Psi|2\sum_{i=1}^{N}\delta(r_i - R)S_z(i)|\Psi\rangle = 2\sum_{i=1}^{N}\langle\chi_i(R)|S_z(i)|\chi_i(R)\rangle = 2\left[\sum_{i=1}^{N^\alpha}\langle\chi_i^\alpha(R)|S_z(i)|\chi_i^\alpha(R)\rangle + \sum_{i=1}^{N^\beta}\langle\chi_i^\beta(R)|S_z(i)|\chi_i^\beta(R)\rangle\right]$

$= 2\left[\frac{1}{2}\sum_{i=1}^{N^\alpha}(\psi_i^\alpha(R)|\psi_i^\alpha(R)) - \frac{1}{2}\sum_{i=1}^{N^\beta}(\psi_i^\beta(R)|\psi_i^\beta(R))\right] = \sum_{i=1}^{N^\alpha}|\psi_i^\alpha(R)|^2 - \sum_{i=1}^{N^\alpha}|\psi_i^\beta(R)|^2 = \rho^\alpha(R) - \rho^\beta(R) = \rho^s(R).$

而 $\mathrm{tr}(P^sA) = \sum_{i=1}^{K}(P^sA)_{ii} = \sum_{i=1}^{K}\sum_{j=1}^{K} P_{ij}^s A_{ji} = \sum_{i,j=1}^{K}(P_{ij}^\alpha - P_{ij}^\beta)\phi_j^*(R)\phi_i(R) = \sum_{i=1}^{K}\sum_{j=1}^{K}\left(\sum_{a=1}^{N^\alpha} C_{ia}^\alpha C_{ja}^{\alpha *} - \sum_{a=1}^{N^\beta} C_{ia}^\beta C_{ja}^{\beta *}\right)\phi_j^*(R)\phi_i(R).$

$= \sum_{a=1}^{N^\alpha}\left(\sum_{i=1}^{K} C_{ia}^\alpha\phi_i(R)\right)\left(\sum_{j=1}^{K} C_{ja}^{\alpha *}\phi_j^*(R)\right) - \sum_{a=1}^{N^\beta}\left(\sum_{i=1}^{K} C_{ia}^\beta\phi_i(R)\right)\left(\sum_{j=1}^{K} C_{ja}^{\beta *}\phi_j^*(R)\right) = \sum_{a=1}^{N^\alpha}|\psi_a^\alpha(R)|^2 - \sum_{a=1}^{N^\beta}|\psi_a^\beta(R)|^2 = \rho^\alpha(R) - \rho^\beta(R) = \rho^s(R).$

即证得 $\langle\hat{\rho}^s\rangle = \rho^s(R) = \mathrm{tr}(P^sA).$

3.8.5节(不限制自洽场方程的求解)习题解析

练习3.40　由教材式(3.327).(不再特别写出自旋,自旋由求和上限表示足够清晰,除非有可能有歧义)

$$E_0=\sum_{a=1}^{N^\alpha}h_{aa}^\alpha+\sum_{a=1}^{N^\beta}h_{aa}^\beta+\frac{1}{2}\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\alpha}(J_{ab}^{\alpha\alpha}-K_{ab}^{\alpha\alpha})+\frac{1}{2}\sum_{a=1}^{N^\beta}\sum_{b=1}^{N^\beta}(J_{ab}^{\beta\beta}-K_{ab}^{\beta\beta})+\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\beta}J_{ab}^{\alpha\beta}$$

$$=\sum_{a=1}^{N^\alpha}(a|h|a)+\sum_{a=1}^{N^\beta}(a|h|a)+\frac{1}{2}\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\alpha}(aa|bb)-(ab|ba)+\frac{1}{2}\sum_{a=1}^{N^\beta}\sum_{b=1}^{N^\beta}(aa|bb)-(ab|ba)+\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\beta}(\psi_a^\alpha\psi_a^\alpha|\psi_b^\beta\psi_b^\beta)$$

$$=\sum_{a=1}^{N^\alpha}\Big(\sum_{\mu=1}^{K}C_{\mu a}\phi_\mu\Big|h\Big|\sum_{\nu=1}^{K}C_{\nu a}\phi_\nu\Big)+\sum_{a=1}^{N^\beta}\Big(\sum_{\mu=1}^{K}C_{\mu a}\phi_\mu\Big|h\Big|\sum_{\nu=1}^{K}C_{\nu a}\phi_\nu\Big)+\frac{1}{2}\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\alpha}\Big(aa\Big|\sum_{\mu=1}^{K}C_{\mu b}^{\alpha*}\phi_\mu\sum_{\nu=1}^{K}C_{\nu b}^{\alpha}\phi_\nu\Big)-$$

$$\Big(a\sum_{\nu=1}^{K}C_{\nu b}^{\alpha}\phi_\nu\Big|\sum_{\mu=1}^{K}C_{\mu b}^{\alpha}\phi_\mu a\Big)+\frac{1}{2}\sum_{a=1}^{N^\beta}\sum_{b=1}^{N^\beta}\Big(aa\Big|\sum_{\mu=1}^{K}C_{\mu b}^{\beta*}\phi_\mu^*\sum_{\nu=1}^{K}C_{\nu b}^{\beta}\phi_\nu\Big)-\Big(a\sum_{\nu=1}^{K}C_{\nu b}^{\beta}\phi_\nu\Big|\sum_{\mu=1}^{K}C_{\mu b}^{\beta*}\phi_\mu a\Big)$$

$$+\frac{1}{2}\sum_{a=1}^{N^\alpha}\sum_{b=1}^{N^\beta}\Big(aa\Big|\sum_{\mu=1}^{K}C_{\mu b}^{\beta*}\phi_\mu^*\sum_{\nu=1}^{K}C_{\nu b}^{\beta}\phi_\nu\Big)+\frac{1}{2}\sum_{b=1}^{N^\beta}\sum_{a=1}^{N^\alpha}\Big(\sum_{\mu=1}^{K}C_{\mu a}^{\alpha}\phi_\mu^*\sum_{\nu=1}^{K}C_{\nu a}^{\alpha}\phi_\nu\Big|bb\Big)$$

$$\cancel{=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big[\sum_{a=1}^{N^\alpha}h_{aa}+\sum_{a=1}^{N^\beta}h_{aa}+\frac{1}{2}\sum_{a=1}^{N^\alpha}(aa|\mu\nu)-(a\nu|\mu a)+\frac{1}{2}\sum_{a=1}^{N^\beta}}$$

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big(\sum_{a=1}^{N^\alpha}C_{\nu a}^{\alpha}C_{\mu a}^{\alpha*}\Big)(\mu|h|\nu)+\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big(\sum_{a=1}^{N^\beta}C_{\nu a}^{\beta}C_{\mu a}^{\beta*}\Big)(\mu|h|\nu)+\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\sum_{a=1}^{N^\alpha}\Big[\Big(\sum_{b=1}^{N^\alpha}C_{\nu b}^{\alpha}C_{\mu b}^{\alpha*}\Big)\Big][(aa|\mu\nu)-$$

$$(a\nu|\mu a)+\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\sum_{a=1}^{N^\beta}\Big(\sum_{b=1}^{N^\beta}C_{\mu b}^{\beta*}C_{\nu b}^{\beta}\Big)[(aa|\mu\nu)-(a\nu|\mu a)]+\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big(\sum_{b=1}^{N^\beta}C_{\mu b}^{\beta*}C_{\nu b}^{\beta}\Big)\sum_{a=1}^{N^\alpha}(aa|\mu\nu)$$

$$+\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big(\sum_{a=1}^{N^\alpha}C_{\mu a}^{\alpha}C_{\nu a}^{\alpha*}\Big)\sum_{b=1}^{N^\beta}(\mu\nu|bb)$$

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big[P_{\nu\mu}^{\alpha}H_{\mu\nu}^{core}+P_{\nu\mu}^{\beta}H_{\mu\nu}^{core}+\frac{1}{2}\sum_{a=1}^{N^\alpha}P_{\nu\mu}^{\alpha}[(aa|\mu\nu)-(a\nu|\mu a)]+\sum_{a=1}^{N^\beta}P_{\nu\mu}^{\beta}[(aa|\mu\nu)-(a\nu|\mu a)]$$

$$+\frac{1}{2}\sum_{a=1}^{N^\alpha}P_{\nu\mu}^{\beta}(aa|\mu\nu)+\frac{1}{2}\sum_{a=1}^{N^\beta}P_{\nu\mu}^{\alpha}(aa|\mu\nu)\Big]$$

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big[\frac{1}{2}(P_{\nu\mu}^{\alpha}+P_{\nu\mu}^{\beta})H_{\mu\nu}^{core}+\frac{1}{2}P_{\nu\mu}^{\alpha}\Big(H_{\mu\nu}^{core}+\sum_{a=1}^{N^\alpha}(aa|\mu\nu)-(a\nu|\mu a)+\sum_{a=1}^{N^\beta}(\mu\nu|aa)\Big)+\frac{1}{2}P_{\nu\mu}^{\beta}\Big(H_{\mu\nu}^{core}+\sum_{a=1}^{N^\beta}(aa|\mu\nu)-$$

$$(a\nu|\mu a)+\frac{1}{2}\sum_{a=1}^{N^\alpha}(aa|\mu\nu)\Big]$$

$$=\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\Big(\frac{1}{2}P_{\nu\mu}^{T}H_{\mu\nu}^{core}+\frac{1}{2}P_{\nu\mu}^{\alpha}F_{\mu\nu}^{\alpha}+\frac{1}{2}P_{\nu\mu}^{\beta}F_{\mu\nu}^{\beta}\Big)=\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}(P_{\nu\mu}^{T}H_{\mu\nu}^{core}+P_{\nu\mu}^{\alpha}F_{\mu\nu}^{\alpha}+P_{\nu\mu}^{\beta}F_{\mu\nu}^{\beta}).$$

即证得　$E_0=\frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K}[P_{\nu\mu}^{T}H_{\mu\nu}^{core}+P_{\nu\mu}^{\alpha}F_{\mu\nu}^{\alpha}+P_{\nu\mu}^{\beta}F_{\mu\nu}^{\beta}).$

3.8.6节（闭壳层不受限HF方法计算）习题解析

练习3.41 $\langle S^2\rangle_{UHF} = \langle\Psi_{UHF}|S^2|\Psi_{UHF}\rangle = C_1^2\langle{}^2\Psi|S^2|{}^2\Psi\rangle + C_1^*C_2\langle{}^2\Psi|S^2|{}^4\Psi\rangle + C_1C_2^*\langle{}^4\Psi|S^2|{}^2\Psi\rangle + C_2^2\langle{}^4\Psi|S^2|{}^4\Psi\rangle.$

$= |C_1|^2\frac{1}{2}\left(\frac{1}{2}+1\right) + |C_2|^2\frac{3}{2}\left(\frac{3}{2}+1\right) = \frac{3}{4}|C_1|^2 + \frac{15}{4}|C_2|^2 = \frac{3}{4} + 3|C_2|^2.$ $\therefore |C_2|^2 = \frac{1}{3}(\langle S^2\rangle_{UHF} - 3/4)$

$\therefore w = 100|C_2|^2/(|C_1|^2+|C_2|^2)\% = 100(\langle S^2\rangle_{UHF} - 3/4)/3(\%).$

分别代入教材表3.26中数据得到 $w(\text{STO-3G}) = 0.51\%$, $w(\text{4-31G}) = 0.41\%$, $w(\text{6-31G}^*) = 0.39\%$, $w(\text{6-31G}^{**}) = 0.38\%$.

3.8.7节(解离问题及它的未限制解)

练习3.42 $\langle\psi_1^\alpha|\psi_1^\alpha\rangle = \langle\cos\theta\psi_1+\sin\theta\psi_2|\cos\theta\psi_1+\sin\theta\psi_2\rangle = \cos^2\theta\langle\psi_1|\psi_1\rangle+2\cos\theta\sin\theta\langle\psi_1|\psi_2\rangle+\sin^2\theta\langle\psi_2|\psi_2\rangle=1.$

$\langle\psi_1^\alpha|\psi_2^\alpha\rangle = \langle\cos\theta\psi_1+\sin\theta\psi_2|-\sin\theta\psi_1+\cos\theta\psi_2\rangle = -\cos\theta\sin\theta\langle\psi_1|\psi_2\rangle+\cos\theta\sin\theta\langle\psi_2|\psi_2\rangle+(\cos^2\theta-\sin^2\theta)\langle\psi_1|\psi_2\rangle=0.$

同理,$\langle\psi_2^\alpha|\psi_2^\alpha\rangle=1$. 从而$\{\psi_1^\alpha,\psi_2^\alpha\}$构成一个标准正交基.

同理,$\{\psi_1^\beta,\psi_2^\beta\}$构成一个标准正交基.

练习3.43 $R=1.4\text{a.u.}$时. $\varepsilon_1=-0.5782\text{ a.u.}$ $\varepsilon_2=0.6703\text{ a.u.}$ $h_{11}=\varepsilon_1-J_{11}=-1.2529\text{ a.u.}$ $h_{22}=\varepsilon_2-2J_{12}+K_{12}=-0.4756\text{ a.u.}$

$J_{11}=0.6746\text{a.u.}$ $J_{12}=0.6636\text{ a.u.}$ $J_{22}=0.6975\text{ a.u.}$ $K_{12}=0.1813\text{ a.u.}$ 代入教材式(3.376).得 $\cos2\theta\doteq1.51>1$. 不可能

从而未限制解在$R=1.4\text{a.u.}$时不存在;

同理$R=4.0\text{a.u.}$时. $\varepsilon_1=-0.2542\text{ a.u.}$ $\varepsilon_2=0.0916\text{ a.u.}$ $h_{11}=-0.7568\text{ a.u.}$ $h_{22}=-0.6675\text{a.u.}$ $J_{11}=0.5026\text{ a.u.}$ $J_{12}=0.5121\text{a.u.}$

$J_{22}=0.5259\text{a.u.}$ $K_{12}=0.2651\text{a.u.}$ 得 $\cos2\theta=0.5965$. $\therefore\theta\doteq39.44°$. 即此时未限制解存在.

练习3.44. $|\psi_1\bar{\psi}_1\rangle=\frac{1}{2}|(\phi_1+\phi_2)(\bar{\phi}_1+\bar{\phi}_2)\rangle=\frac{1}{2}[|\phi_1\bar{\phi}_1\rangle+|\phi_1\bar{\phi}_2\rangle+|\phi_2\bar{\phi}_1\rangle+|\phi_2\bar{\phi}_2\rangle]$, 同理, $|\psi_2\bar{\psi}_2\rangle=\frac{1}{2}[|\phi_1\bar{\phi}_1\rangle-|\phi_1\bar{\phi}_2\rangle-|\phi_2\bar{\phi}_1\rangle+|\phi_2\bar{\phi}_2\rangle]$

而$|{}^3\Psi_1^2\rangle=\frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle-|\phi_2\bar{\phi}_1\rangle)$ $\therefore |\psi_1\bar{\psi}_1\rangle-|\psi_2\bar{\psi}_2\rangle+\sqrt{2}|{}^3\Psi_1^2\rangle=2|\phi_1\bar{\phi}_2\rangle$. 从而$\frac{1}{2}[|\psi_1\bar{\psi}_1\rangle-|\psi_2\bar{\psi}_2\rangle-\sqrt{2}|{}^3\Psi_1^2\rangle]=|\phi_1\bar{\phi}_2\rangle$.

即有$\lim\limits_{R\to\infty}|\Psi_0\rangle=\frac{1}{2}[|\psi_1\bar{\psi}_1\rangle-|\psi_2\bar{\psi}_2\rangle-\sqrt{2}|{}^3\Psi_1^2\rangle]=|\phi_1(1)\bar{\phi}_2(2)\rangle$.