1. 应用量子化学作业

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1.

$$H\vec{x} = \lambda\vec{x}, \tag{1.1.}$$

$$\det[H - \lambda I] = 0 \implies \tag{1.2.}$$

$$\begin{vmatrix} E_1^{\text{BO}} - \lambda & V_{12} \\ V_{21} & E_2^{\text{BO}} - \lambda \end{vmatrix} = 0 \implies \tag{1.3.}$$

$$\lambda^2 - (E_1^{\text{BO}} + E_2^{\text{BO}})\lambda + E_1^{\text{BO}} E_2^{\text{BO}} - V_{12}V_{21} = 0 \implies \tag{1.4.}$$

$$\lambda = \frac{E_1^{\text{BO}} + E_2^{\text{BO}} \pm \sqrt{(E_1^{\text{BO}} + E_2^{\text{BO}})^2 - 4(E_1^{\text{BO}} E_2^{\text{BO}} - V_{12}V_{21})}}{2}, \tag{1.5.}$$

$$H = H^\dagger \implies V_{12} = V_{21}^* \implies \tag{1.6.}$$

$$\lambda = \frac{E_1^{\text{BO}} + E_2^{\text{BO}} \pm \sqrt{(E_1^{\text{BO}} - E_2^{\text{BO}})^2 + 4\|V_{12}\|^2}}{2}. \tag{1.7.}$$

2.

Slater 波函数电子满足全同性:

$$\langle\Psi|\frac{1}{r_{12}}|\Psi\rangle = \langle\Psi|\frac{1}{r_{ij}}|\Psi\rangle \implies \tag{1.8.}$$

$$\langle\Psi|\hat{O}_2|\Psi\rangle = \frac{N(N-1)}{2}\langle\Psi|\frac{1}{r_{12}}|\Psi\rangle, \tag{1.9.}$$

众所周知, 行列式长这个样子:

$$\begin{vmatrix} \psi_1[q^1] & \psi_2[q^1] & \cdots & \psi_N[q^1] \\ \psi_1[q^2] & \psi_2[q^2] & \cdots & \psi_N[q^2] \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1[q^N] & \psi_2[q^N] & \cdots & \psi_N[q^N] \end{vmatrix} \tag{1.10.}$$

于是乎十分明显, 我们对前两行 Laplace 展开:

$$|\Psi\rangle = \sqrt{\frac{(N-2)!}{N!}} \sum_{i,j}^{N} (-1)^{1+2+i+j} |\Psi^{ij}\rangle (\psi_i[1]\psi_j[2] - \psi_j[1]\psi_i[2]), \tag{1.11.}$$

系数来源是归一化;
其中 $|\Psi^{ij}\rangle$ 对应了 2 阶行列式的余子式.

我们要的积分

$$I=\frac{(N-1)N}{2}\frac{1}{N(N-1)}\langle\sum_{i,j}^{N}\langle\Psi^{ij}|(\psi_i[1]\psi_j[2]-\psi_j[1]\psi_1[2])|\frac{1}{r_{12}}|\sum_{i,j}^{N}|\Psi^{ij}\rangle(\psi_i[1]\psi_j[2]-\psi_j[1]\psi_1[2])\rangle \tag{1.12.}$$

$$=\frac{1}{2}\sum_{i,j}\langle\psi_i[1]\psi_j[2]-\psi_j[1]\psi_i[2]|\frac{1}{r_{12}}|\psi_i[1]\psi_j[2]-\psi_j[1]\psi_i[2]\rangle\langle\Psi^{ij}|\Psi^{ij}\rangle \tag{1.13.}$$

$$=\frac{1}{2}\sum_{i,j}\langle\psi_i[1]\psi_j[2]-\psi_j[1]\psi_i[2]|\frac{1}{r_{12}}|\psi_i[1]\psi_j[2]-\psi_j[1]\psi_i[2]\rangle. \tag{1.14.}$$

3.

Hermitian 算符要求:

$$\langle A\psi|\psi\rangle=\langle\psi|A^\dagger\psi\rangle=\langle\psi|A\psi\rangle, \tag{1.15.}$$

对于 Hartree 算符 $\hat{f}$:
显然 $\hat{h}$ 事 Hermitian, 其就事单粒子能量;
对于库伦算符:

$$\langle\hat{J}_j[1]\psi_i[1]|\psi_i[1]\rangle=\int(\psi_j^*[2]\frac{1}{r_{12}}\psi_j[2]\psi_i[1])^*\psi_i[1]\,\mathrm{d}q^1\,\mathrm{d}q^2 \tag{1.16.}$$

$$=\int\psi_i^*[2]\psi_j^*[2]\frac{1}{r_{12}}\psi_j[2]\psi_i[1]\,\mathrm{d}q^1\,\mathrm{d}q^2 \tag{1.17.}$$

$$=\langle\psi_i[1]|\hat{J}_j[1]\psi_i[1]\rangle; \tag{1.18.}$$

对于交换算符:

$$\langle\hat{K}_j[1]\psi_i[1]|\psi_i[1]\rangle=\int(\psi_j^*[2]\frac{1}{r_{12}}\psi_i[2]\psi_j[1])^*\psi_i[1]\,\mathrm{d}q^1\,\mathrm{d}q^2 \tag{1.19.}$$

$$=\int\psi_i^*[2]\psi_j^*[1]\frac{1}{r_{12}}\psi_i[1]\psi_j[2]\,\mathrm{d}q^2\,\mathrm{d}q^1 \tag{1.20.}$$

$$=\int\psi_i^*[1]\psi_j^*[2]\frac{1}{r_{12}}\psi_i[2]\psi_j[1]\,\mathrm{d}q^1\,\mathrm{d}q^2 \tag{1.21.}$$

$$=\langle\psi_i[1]|\hat{K}_j[1]\psi_i[1]\rangle; \tag{1.22.}$$

这事线性空间的算符, 于是

$$\hat{f}=\hat{h}+\sum_j\hat{J}_j-\hat{K}_j \tag{1.23.}$$

事 Hermitian.

4.

这显然属于单粒子算符, 于是

$$\langle Q\rangle=\sum_i^n\langle\psi_i[1]|\hat{x}[1]|\psi_i[1]\rangle=\sum_i^n\langle\psi_i[1]|\hat{x}_1|\psi_i[1]\rangle. \tag{1.24.}$$

5.

考虑定义得到的完全展开式:

$$A = (a^\nu_\mu), \tag{1.25.}$$

$$\det[A] = n! a^1_{[\mu_1} a^2_{\mu_2} \cdots a^n_{\mu_n]}, \tag{1.26.}$$

其中 [ ] 为反对称化算符.

现对于

$$B = (b^\nu_\mu), \tag{1.27.}$$

$$AB = (a^\nu_\varrho b^\varrho_\mu), \tag{1.28.}$$

$$\begin{aligned} \det[AB] = \det[a^\nu_\varrho b^\varrho_\mu] = \det \begin{bmatrix} a^1_\varrho b^\varrho_\mu \\ a^2_\varrho b^\varrho_\mu \\ \vdots \\ a^n_\varrho b^\varrho_\mu \end{bmatrix} &\xlongequal{\text{Linearity}} a^1_{\mu_1} a^2_{\mu_2} \cdots a^n_{\mu_n} \det \begin{bmatrix} b^{\mu_1}_\mu \\ b^{\mu_2}_\mu \\ \vdots \\ b^{\mu_n}_\mu \end{bmatrix} \\ &= n! a^1_{[\mu_1} a^2_{\mu_2} \cdots a^n_{\mu_n]} \det \begin{bmatrix} b^{\mu_1}_\mu \\ b^{\mu_2}_\mu \\ \vdots \\ b^{\mu_n}_\mu \end{bmatrix} = \det A \det B. \end{aligned} \tag{1.29.}$$

其中利用了括号的传染性.

6.

$$\langle \Psi' | \hat{Q} | \Psi' \rangle = \langle \exp[\mathtt{i}\theta]\Psi | \hat{Q} | \exp[\mathtt{i}\theta]\Psi \rangle \tag{1.30.}$$

$$= \langle \Psi | \hat{Q} | \Psi \rangle \langle \exp[\mathtt{i}\theta] | \exp[\mathtt{i}\theta] \rangle \tag{1.31.}$$

$$= \langle \Psi | \hat{Q} | \Psi \rangle. \tag{1.32.}$$

7.

对于一般情况:

$$E_0 = \langle \Psi_0 | \hat{H}_{\mathrm{el}} | \Psi_0 \rangle \tag{1.33.}$$

$$= 2\sum_i \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{i,j} 2\langle \psi_i \psi_j | \frac{1}{r} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r} | \psi_j psi_i \rangle, \tag{1.34.}$$

对于限制性闭壳层:

$$E_0 = \langle \Psi_0 | \hat{H}_{\mathrm{el}} | \Psi_0 \rangle \tag{1.35.}$$

$$= 2\sum_i \langle \varphi_i | \hat{h} | \varphi_i \rangle + \sum_{i,j} 2\langle \varphi_i \varphi_j | \frac{1}{r} | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | \frac{1}{r} | \varphi_j \varphi_i \rangle, \tag{1.36.}$$

同时昆仑积分和交换积分具有对称性:

$$J_{12} = J_{21}, K_{12} = K_{21}, \tag{1.37.}$$

于是有

$$\begin{aligned}
&\text{(a)} & 2h_{11} + J_{11} = 2h_{11} + K_{11} \\
&\text{(b)} & h_{11} + h_{22} + J_{12} - K_{12} \\
&\text{(c)} & h_{11} + h_{22} + J_{12} \\
&\text{(d)} & 2h_{22} + J_{22} \\
&\text{(e)} & 2h_{11} + J_{11} + h_{22} + 2J_{12} - K_{12} \\
&\text{(f)} & 2h_{22} + J_{22} + h_{11} + 2J_{12} - K_{12} \\
&\text{(g)} & h_{11} + h_{22} + h_{33} + J_{12} - K_{12} + J_{23} - K23 + J_{31} - K_{31} \\
&\text{(h)} & 2h_{11} + J_{11} + 2h_{22} + J_{22} + 4J_{12} - 2K_{12} \\
&\text{(i)} & 2h_{11} + J_{11} + h_{22} + 2J_{12} - K_{12} + h_{33} + 2J_{13} - K_{13} + J_{23} - K_{23}
\end{aligned} \tag{1.38.}$$

8.

此时 $\mathrm{He} : (1\mathrm{s})^1(2\mathrm{s})^1$ 且自旋相同, 考虑两个自旋-轨道:

$$\varepsilon_1 = \langle\psi_1|\hat{h}|\psi_1\rangle + \langle\psi_1\psi_2|\psi_1\psi_2\rangle - \langle\psi_1\psi_2|\psi_2\psi_1\rangle = \varepsilon_1^0 + J_{1\mathrm{s}2\mathrm{s}} - K_{1\mathrm{s}2\mathrm{s}}, \tag{1.39.}$$

$$\varepsilon_2 = \varepsilon_2^0 + J_{1\mathrm{s}2\mathrm{s}} - K_{1\mathrm{s}2\mathrm{s}}, \tag{1.40.}$$

$$E = \varepsilon_1^0 + \varepsilon_2^0 + J_{1\mathrm{s}2\mathrm{s}} - K_{1\mathrm{s}2\mathrm{s}} = \varepsilon_1 + \varepsilon_2 - J_{1\mathrm{s}2\mathrm{s}} + K_{1\mathrm{s}2\mathrm{s}}. \tag{1.41.}$$

9.

对于 Hilbert 空间的线性算子, 有

$$\langle\alpha|\hat{f}\beta\rangle = (\langle\beta\hat{f}^\dagger|)^*(|\alpha\rangle)^* = \langle\beta\hat{f}^\dagger|\alpha\rangle^*, \tag{1.42.}$$

众所周知, Fock 算符是 Hermitian, i.e.

$$\langle\alpha|\hat{f}\beta\rangle = \langle\beta\hat{f}|\alpha\rangle^*. \tag{1.43.}$$

10.

利用 summation convention:

$$\varphi_i = c_i^\nu\chi_\nu, \tag{1.44.}$$

由库伦算符定义:

$$\langle\chi_\mu[1]|\hat{J}_j[1]|\chi_\nu[1]\rangle = \langle\chi_\mu[1]\varphi_j[2]|\frac{1}{r_{12}}|\varphi_j[2]\chi_\nu[1]\rangle, \tag{1.45.}$$

$$= \langle\chi_\mu[1]c_j^\lambda\chi_\lambda[2]|\frac{1}{r_{12}}|c_j^\sigma\chi_\sigma[2]\chi_\nu[1]\rangle \tag{1.46.}$$

$$= c_j^\sigma c_j^{\lambda *}(\mu\nu|\sigma\lambda). \tag{1.47.}$$

11.

闭壳层 RHF 的总能量:

$$E_0 = \sum_i^{N/2} 2\langle\varphi_i|\hat{h}|\varphi_i\rangle + \sum_{i,j}^{N/2} 2\langle\varphi_i\varphi_j|\frac{1}{r}|\varphi_i\varphi_j\rangle - \langle\varphi_i\varphi_j|\frac{1}{r}|\varphi_j\varphi_i\rangle, \tag{1.48.}$$

第一项:

$$\begin{aligned}
\sum_i^{N/2} 2\langle\varphi_i|\hat{h}|\varphi_i\rangle &= \sum_i 2\langle c_i^\mu\chi_\mu|\hat{h}|c_i^\nu\chi_\nu\rangle && \text{「1.49.」}\\
&= \sum_i 2\langle c_i^\mu| \otimes |c_i^\nu\rangle\langle\chi_\mu|\hat{h}|\chi_\nu\rangle && \text{「1.50.」}\\
&= 2\sum_i |c_i^\nu\rangle\langle c_i^\mu| h_{\mu\nu}^{\mathrm{core}} && \text{「1.51.」}\\
&= P^{\nu\mu} h_{\mu\nu}^{\mathrm{core}}, && \text{「1.52.」}
\end{aligned}$$

第二项:

$$\begin{aligned}
\sum_{i,j}^{N/2} 2\langle\varphi_i\varphi_j|\frac{1}{r}|\varphi_i\varphi_j\rangle &= \sum_{i,j} 2\langle c_i^\mu\chi_\mu[1]c_j^\lambda\chi_\lambda[2]|\frac{1}{r}|c_i^\nu\chi_\nu[1]c_j^\sigma\chi_\sigma[2]\rangle && \text{「1.53.」}\\
&= \frac{1}{2}P^{\nu\mu}P^{\sigma\lambda}(\mu\nu|\lambda\sigma), && \text{「1.54.」}
\end{aligned}$$

第三项:

$$\begin{aligned}
-\sum_{i,j}^{N/2}\langle\varphi_i\varphi_j|\frac{1}{r}|\varphi_j\varphi_i\rangle &= -\sum_{i,j}\langle c_i^\mu\chi_\mu[1]c_j^\lambda\chi_\lambda[2]|\frac{1}{r}|c_j^\sigma\chi_\sigma[1]c_i^\nu\chi_\nu[2]\rangle && \text{「1.55.」}\\
&= -\frac{1}{4}P^{\nu\mu}P^{\sigma\lambda}(\mu\sigma|\lambda\nu). && \text{「1.56.」}
\end{aligned}$$

12.

STO 基函数:

$$\chi_{nlm} = R_n[r,\zeta]Y_{lm}[\theta,\phi], \tag{1.57.}$$

$$R_n[r,\zeta] = N_{n\zeta}r^{n-1}\mathrm{e}^{-\zeta r} = \frac{(2\zeta)^{\frac{2n+1}{2}}}{\sqrt{(2n)!}}r^{n-1}\mathrm{e}^{-\zeta r}, \tag{1.58.}$$

基态氢原子:

$$\chi_{100} = \frac{(2\zeta)^{3/2}}{\sqrt{2}}\mathrm{e}^{-\zeta r}\frac{1}{2\sqrt{\pi}} = \frac{\zeta^{3/2}}{\sqrt{\pi}}\mathrm{e}^{-\zeta r}, \tag{1.59.}$$

$$\begin{aligned}
E[\zeta] = \langle\chi|\hat{H}|\chi\rangle &= \frac{\zeta^3}{\pi}\int \mathrm{e}^{-\zeta r}(-\frac{1}{2}\nabla^2 - \frac{1}{r})\mathrm{e}^{-\zeta r}\,\mathrm{d}\tau && \text{「1.60.」}\\
&= \frac{\zeta^3}{\pi}\int \mathrm{e}^{-\zeta r}(-\frac{1}{2}\zeta^2\mathrm{e}^{-\zeta r} + \frac{\zeta}{r}\mathrm{e}^{-\zeta r} - \frac{1}{r}\mathrm{e}^{-\zeta r})\,\mathrm{d}\tau && \text{「1.61.」}
\end{aligned}$$

$$= \frac{\zeta^3}{\pi}\int_0^\infty (-\frac{1}{2}\zeta^2 + \frac{\zeta-1}{r})\exp[-2\zeta r]4\pi r^2\,\mathrm{d}r = \frac{1}{2}\zeta^2 - \zeta, \tag{1.62.}$$

$$\partial_\zeta E = 0 \implies \tag{1.63.}$$

$$E = -\frac{1}{2}. \tag{1.64.}$$

GTO 基函数:

$$\chi_{i,j,k}[x,y,z;\alpha] = (\frac{2\alpha}{\pi})^{3/4}\sqrt{\frac{(8\alpha)^{i+j+k}i!j!k!}{(2i)!(2j)!(2k)!}}x^i y^j z^k \exp[-\alpha r^2], \tag{1.65.}$$

基态氢原子:

$$\chi_{0,0,0}[x,y,z;\alpha] = (\frac{2\alpha}{\pi})^{3/4}\exp[\alpha r^2], \tag{1.66.}$$

$$E[\alpha] = (\frac{2\alpha}{\pi})^{3/2}\int \exp[-\alpha r^2](-\frac{1}{2}\nabla^2 - \frac{1}{r})\exp[-\alpha r^2]\,\mathrm{d}\tau \tag{1.67.}$$

$$= \frac{3}{2}\alpha - 2^{3/2}\sqrt{\frac{\alpha}{\pi}}, \tag{1.68.}$$

$$\partial_\alpha E = 0 \implies \tag{1.69.}$$

$$E = -\frac{4}{3\pi}, \tag{1.70.}$$

真实能量:

$$E = -\frac{m_\mathrm{e}e^3}{8\varepsilon_0^2 h^2} = -\frac{1}{2}. \tag{1.71.}$$

14(b).

$$\langle g|g\rangle = N^2\int (r\sin\theta\cos\phi\exp[-\alpha r^2])^2 r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.72.}$$

$$= N^2\int_0^\infty r^4\exp[-2\alpha r^2]\,\mathrm{d}r\int_0^\pi \sin^3\theta\,\mathrm{d}\theta\int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi \tag{1.73.}$$

$$= N^2\frac{\pi^{3/2}}{8\sqrt{2}\alpha^{5/2}} = 1 \implies \tag{1.74.}$$

$$N = \left(\frac{\pi^{3/2}}{8\sqrt{2}\alpha^{5/2}}\right)^{-1/2}. \tag{1.75.}$$

16.

先注意到

$$N_{l+1,mn} = \left(\frac{(8\alpha)^{l+1+m+n}(l+1)!m!n!}{(2l+2)!(2m)!(2n)!}\right)^{1/2}\left(\frac{2\alpha}{\pi}\right)^{3/4} = \sqrt{\frac{8\alpha(l+1)}{(2l+2)(2l+1)}}N_{lmn} \tag{1.76.}$$

$$= \sqrt{\frac{4\alpha}{2l+1}}N_{lmn}, \tag{1.77.}$$

现在我们直接进行偏导:

$$\frac{\partial g_{lmn}}{\partial X_A} = N_{lmn} y_A z_A \frac{\partial x_A^l \exp[-\alpha(\vec{r}-\vec{R}_A)^2]}{\partial X_A} \tag{1.78.}$$

$$= N_{lmn} y_A z_A (-l x_A^{l-1} \exp[-\alpha(\vec{r}-\vec{R}_A)^2] + x_A^l(-\alpha)\exp[-\alpha(\vec{r}-\vec{R}_A)^2](-2x_A)) \tag{1.79.}$$

$$= -l\sqrt{\frac{4\alpha}{2l-1}} g_{l-1,mn} + 2\alpha\sqrt{\frac{2l+1}{4\alpha}} g_{l+1,mn} \tag{1.80.}$$

$$= \sqrt{(2l+1)\alpha} g_{l+1,mn} - 2l\sqrt{\frac{\alpha}{2l-1}} g_{l-1,mn}. \tag{1.81.}$$

17.

$$\mathrm{H} : 1\mathrm{s}(3\mathrm{G}) + 1\mathrm{s}'(1\mathrm{G}), \tag{1.82.}$$

$$\mathrm{C} : 1\mathrm{s}(6\mathrm{G}) + 2\mathrm{s}(3\mathrm{G}) + 3\times 2\mathrm{p}(3\mathrm{G}) + 2\mathrm{s}' + 3\times 2\mathrm{p}' + 6\times \mathrm{d}(1\mathrm{G}) \tag{1.83.}$$

$$\mathrm{base} : 4\times 2 + 1 + 4\times 2 + 6 = 23, \tag{1.84.}$$

$$\mathrm{Guassian} : 4\times 4 + 6 + 4\times 4 + 6 = 44. \tag{1.85.}$$

18.

(1)

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi^\alpha[1]\alpha[1] & \varphi^\alpha[2]\alpha[2] \\ \varphi^\beta[1]\beta[1] & \varphi^\beta[2]\beta[2] \end{vmatrix}, \tag{1.86.}$$

$$S^2 = \|S_x^1 + S_x^2, S_y^1 + S_y^2, S_z^2 + S_z^2\|^2 = S_1^2 + S_2^2 + 2(S_x^1 S_x^2 + S_y^2 S_y^2 + S_z^1 S_z^2), \tag{1.87.}$$

对于每一个电子, 有:

$$S_z^i \alpha[i] = \frac{\hbar}{2}\alpha, S_z^i \beta[i] = -\frac{\hbar}{2}\beta, \tag{1.88.}$$

$$S_i^2(\alpha[i], \beta[i]) = s_l(s_l+1)\hbar^2(\alpha[i], \beta[i]) = \frac{3}{4}\hbar^2(\alpha[i], \beta[i]), \tag{1.89.}$$

利用 Pauli 矩阵或者自旋的展开都可以得到

$$S_x(\alpha, \beta) = \frac{\hbar}{2}(\beta, \alpha), \tag{1.90.}$$

$$S_y(\alpha, \beta) = \frac{\hbar}{2}(\mathtt{i}\beta, -\mathtt{i}\alpha), \tag{1.91.}$$

此时有

$$S_1^2|\Psi\rangle = \frac{1}{\sqrt{2}} S_1^2(\varphi^\alpha[1]\alpha[1]\varphi^\beta[2]\beta[2] - \varphi^\alpha[2]\alpha[2]\varphi^\beta[1]\beta[1]) \tag{1.92.}$$

$$= \frac{1}{\sqrt{2}}(\varphi^\alpha[1]\frac{3}{4}\hbar^2\alpha[1]\varphi^\beta[2]\beta[2] - \varphi^\alpha[2]\alpha[2]\varphi^\beta[1]\frac{3}{4}\hbar^2\beta[1]) \tag{1.93.}$$

$$= \frac{3}{4}\hbar^2|\Psi\rangle, \tag{1.94.}$$

同理有

$$S_2^2|\Psi\rangle = \frac{3}{4}\hbar^2|\Psi\rangle, \tag{1.95.}$$

于是我们只需要关注交叉项:

$$S_x^1 S_x^2|\Psi\rangle = \frac{1}{\sqrt{2}} S_x^1(\varphi[1]\alpha[1]\varphi[2]\frac{\hbar}{2}\alpha[2] - \varphi[1]\beta[1]\varphi[2]\frac{\hbar}{2}\beta[2]) \tag{1.96.}$$

$$= \frac{1}{\sqrt{2}}(\varphi[1]\frac{\hbar}{2}\beta[1]\varphi[2]\frac{\hbar}{2}\alpha[2] - \varphi[1]\frac{\hbar}{2}\alpha[1]\varphi[2]\frac{\hbar}{2}\beta[2]), \tag{1.97.}$$

同理有 $S_y^1 S_y^2$ 也不是 $|\Psi\rangle$ 的本征函数, 这俩加起来也不是.
而可以验证 S_z 是, 于是线性组合得到 S^2 不是.
(2)

$$S^2|\Psi\rangle = \hbar^2\Psi + \frac{\hbar^2}{\sqrt{2}}(\varphi^\alpha[1]\beta[1]\varphi^\beta[2]\alpha[2] - \varphi^\alpha[2]\beta[2]\varphi^\beta[1]\alpha[1]), \tag{1.98.}$$

对于行列式波函数,

$$\langle\Psi|\Psi\rangle = 1 \implies \tag{1.99.}$$

$$\langle\Psi|S^2|\Psi\rangle = \hbar^2 + \frac{\hbar^2}{\sqrt{2}}\langle\Psi|\varphi^\alpha[1]\beta[1]\varphi^\beta[2]\alpha[2] - \varphi^\alpha[2]\beta[2]\varphi^\beta[1]\alpha[1]\rangle \tag{1.100.}$$

$$= \hbar^2 + \frac{\hbar^2}{2}\langle\varphi^\alpha[1]\alpha[1]\varphi^\beta[2]\beta[2] - \varphi^\alpha[2]\alpha[2]\varphi^\beta[1]\beta[1]|\varphi^\alpha[1]\beta[1]\varphi^\beta[2]\alpha[2] - \varphi^\alpha[2]\beta[2]\varphi^\beta[1]\alpha[1]\rangle \tag{1.101.}$$

$$= \hbar^2 + \frac{\hbar^2}{2}(-2(S^{\alpha\beta})^2) \tag{1.102.}$$

$$= 1 - |S^{\alpha\beta}|^2. \tag{1.103.}$$

19.

对于自旋-轨道 ψ 的库伦算符, 其作用于函数:

$$J_j[1]|f_k[1]\rangle = \int \psi_j[2]^* \frac{1}{r_{12}}\psi_j[2]f_k[1]\,\mathrm{d}q^2, \tag{1.104.}$$

同理的交换算符:

$$K_j[1]|f_k[1]\rangle = \int \psi_j[2]^* \frac{1}{r_{12}}\psi_j[1]f_k[2]\,\mathrm{d}q^2, \tag{1.105.}$$

于是

$$\langle a|\sum_j(J_j - K_j)|i\rangle = \sum_j\langle a[1]|j[2]|\frac{1}{r_{12}}|j[2]i[1]\rangle - \langle a[1]j[2]|\frac{1}{r_{12}}|j[1]i[2]\rangle \tag{1.106.}$$

$$= \sum_j\langle aj|ij\rangle - \langle aj|ji\rangle. \tag{1.107.}$$

20.

$$\mathrm{H}: 1\mathrm{s}(3\mathrm{G}), \tag{1.108.}$$

$$\mathrm{O}: 1\mathrm{s}(3\mathrm{G}), 2\mathrm{s}(3\mathrm{G}), 3\times 2\mathrm{p}(3\mathrm{G}), \tag{1.109.}$$

(1)$5+2=7$;

(2)$3\times 7=21$;

(3)$7\times 2=14$;

(4)$\mathit{\Omega}=\binom{14}{10}=1001$.

21.

$$\Delta E_Q \approx (1-C_0^2)(E_{\mathrm{CISD}}-E_{\mathrm{HF}}) = -9.722928\mathrm{e}-3. \tag{1.110.}$$

22.

$$\hat{H}' = \sum_{n<m}\frac{1}{r_{mn}} - \sum_j \hat{V}^{\mathrm{HF}}[j] = \hat{O}_2 - \hat{O}_1, \tag{1.111.}$$

$$|\mathit{\Psi}'\rangle = |\mathit{\Phi}_{ij}^{ab}\rangle, |\mathit{\Psi}\rangle = |\mathit{\Phi}_0\rangle, \tag{1.112.}$$

$$\langle\mathit{\Psi}'|\hat{H}'|\mathit{\Psi}\rangle = \langle\mathit{\Psi}'|\hat{O}_2|\mathit{\Psi}\rangle - \langle\mathit{\Psi}'|\hat{O}_1|\mathit{\Psi}\rangle \tag{1.113.}$$

$$= \langle ab|\frac{1}{r}|ij\rangle - \langle ab|\frac{1}{r}|ji\rangle - 0, \tag{1.114.}$$

$$\left|\langle\mathit{\Phi}_{ij}^{ab}|\hat{H}|\mathit{\Phi}_0\rangle\right| = \left|\langle ab|ij\rangle - \langle ab|ji\rangle\right|. \tag{1.115.}$$

23.

$$|z|^2 = z^* z \implies \tag{1.116.}$$

$$|\langle ab|ij\rangle - \langle ab|ji\rangle|^2 = (\langle ab|ij\rangle - \langle ab|ji\rangle)^*(\langle ab|ij\rangle - \langle ab|ji\rangle) \tag{1.117.}$$

$$= \langle ab|ij\rangle\langle ij|ab\rangle - \langle ab|ij\rangle\langle ji|ab\rangle - \langle ab|ji\rangle\langle ij|ab\rangle + \langle ab|ji\rangle\langle ji|ab\rangle \tag{1.118.}$$

$$= 2(\langle ab|ij\rangle\langle ij|ab\rangle - \langle ab|ij\rangle\langle ji|ab\rangle), \tag{1.119.}$$

其中最后一步是在求和意义下, i,j 是哑元.
而对于积分, q^1,q^2 也是哑元:

$$\langle j[1]i[2]|a[1]b[2]\rangle = \langle j[2]i[1]|a[2]b[1]\rangle = \langle ij|ba\rangle, \tag{1.120.}$$

故得证.

24.

$$T_{\mathrm{TF}}[\rho] = C_F \int \rho^{5/3}[\vec{r}]\,\mathrm{d}\vec{r}, \quad C_F = \frac{3}{10}(3\pi^2)^{2/3}, \tag{1.121.}$$

近似: 自由电子气, 即无相互作用; 低温极限, 化学势等于 Fermi 能.

25.

$$[\rho] = [\mathrm{length}]^{-3}, \tag{1.122.}$$

$$[x] = \frac{[\mathrm{length}]^{-1}[\mathrm{length}]^{-3}}{\mathrm{length}^{-4}} = 1. \tag{1.123.}$$

26.

由于

$$\rho_1[\vec{r},\vec{s}] = 3\rho[\vec{r}]\frac{\sin t - t\cos t}{t^3}, \tag{1.124.}$$

于是

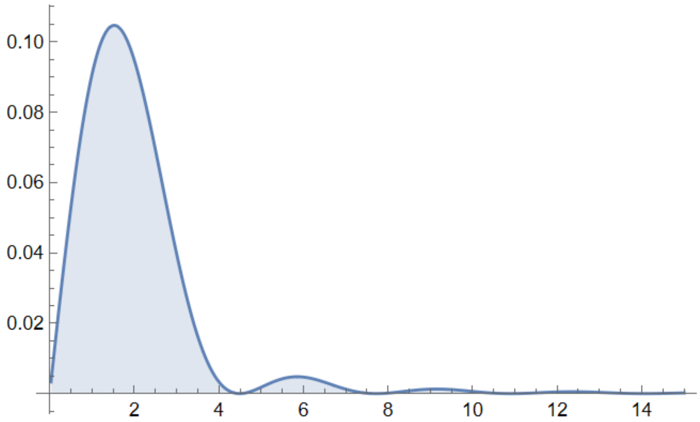
$$\begin{aligned}
K_D[\rho] &= \frac{1}{4}\int \frac{\rho_1^2[\vec{r},\vec{s}]}{s}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{s} && (1.125.)\\
&= \frac{1}{4}\int \frac{9}{s}\rho^2[\vec{r}](\frac{\sin t - t\cos t}{t^3})^2\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{s} && (1.126.)\\
&= 9\pi\int s\rho^2[\vec{r}](\frac{\sin t - t\cos t}{t^3})^2\,\mathrm{d}\vec{r}\,\mathrm{d}s && (1.127.)\\
&= 9\pi\int \frac{\rho^2[\vec{r}]}{k_F^2[\vec{r}]}\frac{(\sin t - t\cos t)^2}{t^5}\,\mathrm{d}\vec{r}\,\mathrm{d}t && (1.128.)\\
&= 9\pi\int \frac{\rho^2[\vec{r}]}{k_F^2[\vec{r}]}\,\mathrm{d}\vec{r}\int_0^\infty \frac{(\sin t - t\cos t)^2}{t^5}\,\mathrm{d}t. && (1.129.)
\end{aligned}$$

27.

由于某些原因 MATLAB 似了, 现在我只能用 Mathematica:

```
In[3]:= DiscretePlot[(Sin[t] - t Cos[t])^2/t^5, {t, 0, 15, 0.03}]
        Integrate[(Sin[t] - t Cos[t])^2/t^5, {t, 0, Infinity}]
```

Out[3]=



Out[4]= $\frac{1}{4}$

思考题 A1

基函数模长是归一的, 内积自然不大于 1.

思考题 A2

```
In[57]:= Simplify[Sin[1/2 ArcTan[2 a12/(-a11 + a22)]] (a11 Cos[1/2 ArcTan[2 a12/(-a11 + a22)]] - a12 Sin[1/2 ArcTan[2 a12/(-a11 + a22)]]) +
         Cos[1/2 ArcTan[2 a12/(-a11 + a22)]] (a12 Cos[1/2 ArcTan[2 a12/(-a11 + a22)]] - a22 Sin[1/2 ArcTan[2 a12/(-a11 + a22)]])]

Out[57]= 0
```

$$\lambda_1 = \frac{1}{2}a_{11}(1+\sec^2 2\theta) + \frac{1}{2}a_{22}(1-\sec^2 2\theta), \qquad \text{「1.130.」}$$

$$\lambda_2 = \frac{1}{2}a_{11}(1-\sec^2 2\theta) + \frac{1}{2}a_{22}(1+\sec^2 2\theta). \qquad \text{「1.131.」}$$