1.1.1节(三维矢量代数)习题解析

练习1.1 a. 由式(1.13),故 $\mathcal{O}\hat{e}_j=\sum_{k=1}^{3}\hat{e}_k O_{kj}$, $\therefore\ \hat{e}_i\cdot\mathcal{O}\hat{e}_j=\hat{e}_i\cdot\sum_{k=1}^{3}\hat{e}_k O_{kj}=\sum_{k=1}^{3}\delta_{ki}O_{kj}=O_{ij}$.

b. $\vec{b}=\sum_{i=1}^{3}b_i\hat{e}_i=\mathcal{O}\vec{a}=\mathcal{O}\sum_{j=1}^{3}a_j\hat{e}_j=\sum_{j=1}^{3}a_j\mathcal{O}\hat{e}_j=\sum_{j=1}^{3}a_j\sum_{i=1}^{3}\hat{e}_i O_{ji}=\sum_{i=1}^{3}\left(\sum_{j=1}^{3}O_{ji}a_j\right)\hat{e}_i$

由基线性表出的唯一性立得 $b_i=\sum_{j=1}^{3}O_{ji}a_j$.

练习1.2.

$$[A,B]=AB-BA=\begin{pmatrix}0&-2&4\\2&0&3\\-4&-3&0\end{pmatrix},\quad \{A,B\}=AB+BA=\begin{pmatrix}0&0&-2\\0&-2&3\\-2&3&-2\end{pmatrix}$$

1.1.2节(矩阵)习题解析

练习1.3　$(AB)^\dagger = B^\dagger A^\dagger \Longleftrightarrow [(AB)^\dagger](i;j) = [B^\dagger A^\dagger](i;j)$. 故验证后者成立即证得原命题成立。

$[(AB)^\dagger](i;j) = [(AB)^*](j;i) = \sum_{k=1}^{N} A_{jk}^* B_{ki}^* = \sum_{k=1}^{N} B_{ki}^* A_{jk}^* = \sum_{k=1}^{N} B_{ik}^\dagger A_{kj}^\dagger = (B^\dagger A^\dagger)(i;j)$.

练习1.4　a. $tr(AB) = \sum_{i=1}^{N}\sum_{k=1}^{N} a_{ik}b_{ki} = \sum_{k=1}^{N}\sum_{i=1}^{N} b_{ki}a_{ik} = tr(BA)$.

b. $AB(B^{-1}A^{-1}) = A(BB^{-1})A^{-1} = AA^{-1} = I$. 故 $B^{-1}A^{-1} = (AB)^{-1}$. 矩阵的逆的唯一性保证等式成立.

c. $\because B = U^\dagger A U$.　$\therefore A = (U^\dagger)^{-1} B U^{-1} = UBU^\dagger$

d. $\because C = AB$是Hermite矩阵　$\therefore C^* = B^*A^* = C = AB$.　$\because A, B$为Hermite矩阵　$\therefore B^*A^* = BA = AB$. 即$A, B$可交换

e. $\because (A^{-1})^\dagger A^\dagger = (AA^{-1})^\dagger = I^\dagger = I$.　$\therefore (A^\dagger)^{-1} = (A^{-1})^\dagger$　$\therefore (A^{-1})^\dagger = (A^\dagger)^{-1} = A^{-1}$　即A^{-1}是Hermite矩阵.

f. 若$a_{11}a_{22} - a_{12}a_{21} \neq 0$. 则验算得 $A\frac{1}{(a_{11}a_{22} - a_{12}a_{21})}\begin{pmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, 从而$A^{-1} = \frac{1}{a_{11}a_{22} - a_{12}a_{21}}\begin{pmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{pmatrix}$.

1.1.3节（行列式）习题解析.

练习1.5　改为对于n阶行列式证明性质(1)-(5).

(1) $|A|=\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_N)}a_{1i_1}a_{2i_2}\cdots a_{Ni_N}$. 由于有行/列中元素都是0. 则对于每一加数均为0. 则 $|A|=0$.

(2) $|A|=\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_N)}a_{1i_1}\delta_{1i_1}a_{2i_2}\delta_{2i_2}\cdots a_{Ni_N}\delta_{Ni_N}=a_{11}a_{22}\cdots a_{NN}$.

(3) $|A|=\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_i\cdots i_j\cdots i_N)}a_{1i_1}a_{2i_2}\cdots a_{ii}\cdots a_{ij}\cdots a_{Ni_N}=-\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_j\cdots i_i\cdots i_N)}a_{1j_1}a_{2i_2}\cdots a_{ij}\cdots a_{ii}\cdots a_{N}=-|A|$.

(4) $|A^{\dagger}|^{*}=\left(\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_N)}a^{*}_{i_1 1}a^{*}_{i_2 2}\cdots a^{*}_{i_N N}\right)^{*}=\sum_{i_1 i_2\cdots i_N}(-1)^{\tau(i_1 i_2\cdots i_N)}a_{1i_1}a_{2i_2}\cdots a_{Ni_N}=|A|$.

(5) 利用Laplace定理及分块矩阵运算. $\begin{vmatrix} A & 0 \\ -I & B \end{vmatrix}=\begin{vmatrix} -I & AB \\ & B \end{vmatrix}$　$\therefore |A||B|=(-1)^{n^2}(-1)^{n}|AB|=|AB|$.

练习1.6　(6). 由练习1.5性质(3). $\therefore |A|=-|A|$　$\therefore |A|=0$.

(7) 由 $AA^{-1}=I$. 由练习1.5性质(5)　$\therefore |A||A^{-1}|=1$.　$\therefore |A^{-1}|=|A|^{-1}$

(8) 由 $AA^{\dagger}=I$. 由练习1.5性质(5)　$\therefore |A||A|^{*}=1$.

(9) $\because U^{\dagger}U=I$.　$\therefore |U^{\dagger}||U|=1$.　由 $U^{\dagger}OU=\Omega$. 由练习1.5性质5. $\therefore |O|=|U^{\dagger}||O||U|=|U^{\dagger}OU|=|\Omega|$.

练习1.7　由Cramer法则立刻得到.

1.1.5节(基的更易)习题解析

练习1.8 $\operatorname{tr}(\Omega) = \operatorname{tr}[U^\dagger O U] = \operatorname{tr}[O U U^\dagger] = \operatorname{tr}(O)$.

1.1.6节(本征值问题)习题解析

练习1.9 $\mathcal{O}\mathbf{U}=\mathcal{O}(\mathbf{c}^1,\mathbf{c}^2,\cdots,\mathbf{c}^M)=(\mathcal{O}\mathbf{c}^1,\mathcal{O}\mathbf{c}^2,\cdots,\mathcal{O}\mathbf{c}^M)=(\omega_1\mathbf{c}^1,\omega_2\mathbf{c}^2,\cdots,\omega_N\mathbf{c}^M)=(\mathbf{c}^1,\mathbf{c}^2,\cdots,\mathbf{c}^M)\begin{pmatrix}\omega_1 & & & \\ & \omega_2 & & \\ & & \ddots & \\ & & & \omega_N\end{pmatrix}=\mathbf{U}\boldsymbol{\omega}.$

练习1.10 (略,似无处理内容)

练习1.11 (a).

$$|A-\lambda I|=\begin{vmatrix}3-\lambda & 1\\ 1 & 3-\lambda\end{vmatrix}=(4-\lambda)(2-\lambda)=0.\quad \therefore \lambda_1=4,\ \lambda_2=2.$$

$$A-\lambda_1 I=\begin{pmatrix}-1 & 1\\ 1 & -1\end{pmatrix}\to\begin{pmatrix}1 & -1\\ 0 & 0\end{pmatrix}$$ ∴属于本征值4的归一化本征向量为$\frac{1}{\sqrt{2}}(1,1)^T$.

$$A-\lambda_2 I=\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}\to\begin{pmatrix}1 & 1\\ 0 & 0\end{pmatrix}$$ ∴属于本征值2的归一化本征向量为$\frac{1}{\sqrt{2}}(1,-1)^T$.

用酉梅正交换法, $\frac{1}{2}(3-3)\sin 2\theta_0-1\cdot\cos 2\theta_0=0$. 取$\theta_0=\frac{\pi}{4}$. ∴$\lambda_1=4$, $\lambda_2=2$, $\mathbf{c}^1=\frac{1}{\sqrt{2}}(1,1)^T$, $\mathbf{c}^2=\frac{1}{\sqrt{2}}(1,-1)^T$.

(b) 同样,得 $\lambda_1=1.3820$, $\lambda_2=3.6180$. $\mathbf{c}^1=(0.5257,-0.8507)^T$, $\mathbf{c}^2=(0.8507,0.5257)^T$.

1.1.7节(矩阵函数)习题解析

练习1.12 a. $\det(A^n)=\det[(UaU^{\dagger})^n]=\det[Ua^nU^{\dagger}]=\det[a^n]=a_1^na_2^n\cdots a_N^n$.

b. $\operatorname{tr}(A^n)=\operatorname{tr}[(UaU^{\dagger})^n]=\operatorname{tr}[Ua^nU^{\dagger}]=\operatorname{tr}[a^nU^{\dagger}U]=\operatorname{tr}[a^n]=\sum_{\alpha=1}^{N}a_\alpha^n$.

c. $A=UaU^{\dagger}$, $\therefore \omega I-A=U(\omega I-a)U^{\dagger}$ $\therefore(\omega I-A)^{-1}=U(\omega I-a)^{-1}U^{\dagger}$ $\therefore G(\omega)=U(\omega I-a)^{-1}U^{\dagger}$

$$\therefore (G(\omega))_{ij}=\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\frac{U_{i\alpha}U_{j\beta}^*}{(\omega-a_\alpha)\delta_{\alpha\beta}}=\sum_{\alpha=1}^{N}\frac{U_{i\alpha}U_{j\alpha}^*}{\omega-a_\alpha}=\sum_{\alpha=1}^{N}\frac{\langle i|\alpha\rangle\langle\alpha|j\rangle}{\omega-a_\alpha}$$

练习1.13 $|A-\lambda I|=\begin{vmatrix}a-\lambda & b\\ b & a-\lambda\end{vmatrix}=(\lambda-a)^2-b^2=(\lambda-a-b)(\lambda-a+b)$ $\therefore \lambda_1=a+b$, $\lambda_2=a-b$.

$\therefore A-\lambda_1 I=\begin{pmatrix}-b & b\\ b & -b\end{pmatrix}\to\begin{pmatrix}1 & -1\\ 0 & 0\end{pmatrix}$, 属于本征值$\lambda_1=a+b$的归一化本征函数为$\frac{1}{\sqrt2}(1,1)^T$. 记为$C^1$

$A-\lambda_2 I=\begin{pmatrix}b & b\\ b & b\end{pmatrix}\to\begin{pmatrix}1 & 1\\ 0 & 0\end{pmatrix}$, 属于本征值$\lambda_2=a-b$的归一化本征函数为$\frac{1}{\sqrt2}(1,-1)^T$, 记为$C^2$.

$\therefore A(C^1,C^2)=(C^1,C^2)\begin{pmatrix}a+b & 0\\ 0 & a-b\end{pmatrix}\Leftrightarrow A=(C^1,C^2)\begin{pmatrix}a+b & 0\\ 0 & a-b\end{pmatrix}(C^1,C^2)^{-1}=UaU^{\dagger}$

$\therefore f(A)=Uf(a)U^{\dagger}=U\begin{pmatrix}f(a+b) & 0\\ 0 & f(a-b)\end{pmatrix}U^{\dagger}=\begin{pmatrix}\frac12[f(a+b)+f(a-b)] & \frac12[f(a+b)-f(a-b)]\\ \frac12[f(a+b)-f(a-b)] & \frac12[f(a+b)+f(a-b)]\end{pmatrix}$

1.2节（正交函数，本征函数及算符）习题解析

练习1.14　$\delta(x)$函数的筛选性质宜看作是其定义中的一部分，而无需证明。

练习1.15　$\mathcal{O}|i\rangle = \sum_j |j\rangle\langle j|\mathcal{O}|i\rangle = \sum_j |j\rangle O_{ji}$.　$O_{ji} = \langle j|\mathcal{O}|i\rangle$.

练习1.16　$\mathcal{O}\phi(x) = \mathcal{O}\sum_{j=1}^{+\infty} c_j \psi_j(x) = \sum_{j=1}^{+\infty} c_j \mathcal{O}\psi_j(x) = \omega\phi(x) = \omega\sum_{j=1}^{+\infty} c_j\psi_j(x)$.　两边同乘$\psi_i^*(x)$并对$x$测度积分，得

$\therefore \sum_{j=1}^{+\infty} O_{ij} c_j = \omega\sum_{j=1}^{+\infty} c_j \delta_{ij} = \omega c_i,\ i\in I_1^{\infty} \Leftrightarrow \mathbf{O}\mathbf{c} = \omega\mathbf{c}$. 用Dirac符号表示.

$\mathcal{O}|\phi\rangle = \mathcal{O}\sum_{j} c_j|\psi\rangle = \sum_j c_j \mathcal{O}|\psi_j\rangle = \omega|\phi\rangle = \omega\sum_j c_j|\psi_j\rangle$　$\therefore \sum_j O_{ij}c_j = \omega c_i,\ i\in I_1^{N} \Leftrightarrow \mathbf{O}\mathbf{c} = \omega\mathbf{c}$.

练习1.17.　a. $\int dx \langle i|x\rangle\langle x|j\rangle = \langle i|j\rangle = \delta_{ij}$，故若$\psi_i^*(x) = \langle i|x\rangle$, $\psi_j(x) = \langle x|j\rangle$.

b. $\langle x|x'\rangle = \sum_{i=1}^{+\infty}\langle x|i\rangle\langle i|x'\rangle = \delta(x-x')$　$\therefore \sum_i \psi_i^*(x')\psi_i(x) = \delta(x-x')$

c. $\int dx \langle x'|x\rangle\langle x|a\rangle = \langle x'|a\rangle \Leftrightarrow a(x') = \int dx\, \delta(x'-x)a(x)$

d. $b(x') = \langle x'|b\rangle = \overset{\langle x'|\mathcal{O}|a\rangle}{\cancel{\mathcal{O}a(x')}} = \int dx\, \overset{\langle x'|\mathcal{O}|x\rangle}{\cancel{\mathcal{O}a(x)}}\langle x|a\rangle = \int dx\, O(x',x)a(x)$.

e. $O(x,x') = \langle x|\mathcal{O}|x'\rangle = \langle x|\sum_i |i\rangle\langle i|\mathcal{O}|\sum_j |j\rangle\langle j|x'\rangle = \sum_i\sum_j \psi_i(x) O_{ij}\psi_j^*(x')$.

1.3.1节(变分原理)习题解析

练习1.18. 由波函数的归一化条件，得 $N^2=\sqrt{\frac{2\alpha}{\pi}}$.

$\therefore \langle\Phi|-\frac{1}{2}\frac{d^2}{dx^2}\pm\delta(x)|\Phi\rangle=\sqrt{\frac{2\alpha}{\pi}}\int_{-\infty}^{+\infty}e^{-\alpha x^2}\left(-\frac{1}{2}\frac{d^2}{dx^2}-\delta(x)\right)e^{-\alpha x^2}dx=\frac{\alpha}{2}-\sqrt{\frac{2\alpha}{\pi}}\quad\therefore E(\alpha)=\frac{\alpha}{2}-\sqrt{\frac{2\alpha}{\pi}}$

$\therefore \frac{dE}{da}=0\Rightarrow a_0=\frac{2}{\pi}\quad E(a_0)=-\frac{1}{\pi}$. 即用此试探函数得体系能量的上限值为 $-\frac{1}{\pi}$ Hartree.

练习1.19. 同练习1.18. $\langle\hat{\Phi}|\hat{\Phi}\rangle=N^2\int_0^{+\infty}r^2e^{-2\alpha r^2}dr\int_\Omega d\Omega=4\pi N^2\cdot\frac{\sqrt{\pi}}{8\sqrt{2}\,a^{3/2}}=1\quad\therefore N^2=\left(\frac{2\alpha}{\pi}\right)^{3/2}$

$\therefore E=\langle\hat{\Phi}|-\frac{1}{2}\nabla^2-\frac{1}{r}|\hat{\Phi}\rangle=N^2\int_0^{+\infty}(3\alpha r^2-2\alpha^2r^4-r)e^{-2\alpha r^2}dr\int_\Omega d\Omega=4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\left(\frac{3}{16}\sqrt{\frac{\pi}{2\alpha}}-\frac{1}{4\alpha}\right)=\frac{3}{2}\alpha-2\sqrt{\frac{2\alpha}{\pi}}$

$\therefore \frac{dE}{da}=0\Rightarrow a_0=\frac{8}{9\pi}\Rightarrow E(a_0)=-\frac{4}{3\pi}=-0.4244$ (Hartree).

练习1.20. $w(\theta)=C^{+}OC=O_{11}\cos^2\theta+2O_{12}\sin\theta\cos\theta+O_{22}\sin 2\theta\quad\therefore w'(\theta)=-O_{11}\sin 2\theta+2O_{12}\cos 2\theta+O_{22}\sin 2\theta=0.$

若 $O_{11}-O_{22}\neq0$. 则 $\theta_0=\frac{1}{2}\arctan\frac{2O_{12}}{O_{11}-O_{22}}$. 与用酉变换法所得相同. 该一法仅对求体系最小本征值有效.

1.3.2节(线性变分问题)习题解析

练习1.21 a. $\langle\tilde{\Phi}'|\mathcal{H}|\tilde{\Phi}'\rangle=\sum_\alpha\sum_\beta\langle\tilde{\Phi}'|\hat{\Phi}_\alpha\rangle\langle\hat{\Phi}_\alpha|\mathcal{H}|\hat{\Phi}_\beta\rangle\langle\hat{\Phi}_\beta|\tilde{\Phi}'\rangle=\sum_\alpha\mathcal{E}_\alpha|\langle\tilde{\Phi}'|\hat{\Phi}_\alpha\rangle|^2$

由于 $\mathcal{E}_0\le\mathcal{E}_1\le\mathcal{E}_2\le\cdots\le\mathcal{E}_{N-1}$，$\langle\tilde{\Phi}'|\hat{\Phi}_0\rangle=0$. $\therefore\langle\tilde{\Phi}'|\mathcal{H}|\tilde{\Phi}'\rangle=\sum_\alpha\mathcal{E}_\alpha|\langle\tilde{\Phi}'|\hat{\Phi}_\alpha\rangle|^2\ge\sum_\alpha\mathcal{E}_1|\langle\tilde{\Phi}'|\hat{\Phi}_\alpha\rangle|^2=\mathcal{E}_1$

b. $1=\langle\tilde{\Phi}'|\tilde{\Phi}'\rangle=(x^*\langle\hat{\Phi}_0|+y^*\langle\hat{\Phi}_1|)(x|\hat{\Phi}_0\rangle+y|\hat{\Phi}_1\rangle)=|x|^2+|y|^2+x^*y\langle\hat{\Phi}_0|\hat{\Phi}_1\rangle+xy^*\langle\hat{\Phi}_0|\hat{\Phi}_1\rangle=|x|^2+|y|^2$

c. $\langle\tilde{\Phi}'|\mathcal{H}|\tilde{\Phi}'\rangle=(x^*\langle\hat{\Phi}_0|+y^*\langle\hat{\Phi}_1|)\mathcal{H}(x|\hat{\Phi}_0\rangle+y|\hat{\Phi}_1\rangle)=|x|^2E_0+|y|^2E_1=(|x|^2+|y|^2)E_1-|x|^2E_1+|x|^2E_0$

$\therefore\langle\tilde{\Phi}'|\mathcal{H}|\tilde{\Phi}'\rangle=E_1-|x|^2(E_1-E_0)\ge E_0$

练习1.22 $\langle 1s|\mathcal{H}_0|1s\rangle=-\frac{1}{2}$. $\langle 1s|\mathcal{H}_0|2p_z\rangle=-\frac{1}{8}\langle 1s|2p_z\rangle=-\frac{1}{8}\int_0^{+\infty}r^3e^{-\frac{3}{2}r}dr\int_0^{\pi}\sin\theta\cos\theta d\theta\int_0^{2\pi}d\varphi\cdot\frac{1}{\sqrt{\pi}}\cdot\frac{1}{\sqrt{32\pi}}=0=\langle 2p_z|\mathcal{H}_0|1s\rangle$

$\langle 2p_z|\mathcal{H}_0|2p_z\rangle=-\frac{1}{8}\langle 2p_z|2p_z\rangle=-1/8$. 而

$\langle 1s|Fr\cos\theta|1s\rangle=\frac{1}{\pi}\int_0^{+\infty}Fr^3e^{-2r}dr\int_0^{\pi}\sin\theta\cos\theta d\theta\int_0^{2\pi}d\varphi=0.$

$\langle 1s|Fr\cos\theta|2p_z\rangle=\langle 2p_z|Fr\cos\theta|1s\rangle=\frac{1}{\sqrt{\pi}}\frac{1}{\sqrt{32\pi}}\int_0^{+\infty}Fr^4e^{-3r/2}dr\int_0^{\pi}\sin\theta\cos^2\theta d\theta\int_0^{2\pi}d\varphi=\frac{F}{4\sqrt{2}\pi}\cdot\frac{256}{81}\cdot\frac{2}{3}\cdot 2\pi=\frac{128\sqrt{2}}{243}F.$

$\langle 2p_z|Fr\cos\theta|2p_z\rangle=\frac{F}{32\pi}\int_0^{+\infty}r^5e^{-r}dr\int_0^{\pi}\sin\theta\cos^3\theta d\theta\int_0^{2\pi}d\varphi=0.$

$\therefore\langle 1s|\mathcal{H}(F)|1s\rangle=\langle 1s|\mathcal{H}_0+Fr\cos\theta|1s\rangle=\langle 1s|\mathcal{H}|1s\rangle+\langle 1s|Fr\cos\theta|1s\rangle=-1/2+0=-1/2$. 同理得

$\langle 1s|\mathcal{H}(F)|2p_z\rangle=\langle 2p_z|\mathcal{H}(F)|1s\rangle=\frac{128\sqrt{2}}{243}F$ $\quad\langle 2p_z|\mathcal{H}(F)|2p_z\rangle=-1/8$. 从而

$$|H-\lambda E|=\begin{vmatrix}-1/2-E & \frac{128\sqrt{2}}{243}F\\ \frac{128\sqrt{2}}{243}F & -1/8-E\end{vmatrix}=E^2+\frac{5}{8}E+\frac{1}{16}-\frac{128^2\cdot 2}{243^2}F^2=0.\quad\therefore E_{1,2}=-\frac{5}{16}\pm\frac{3}{16}\sqrt{1+\frac{128\cdot 256^2}{9\cdot 243^2}F^2}$$

由能量最小化原理，故取负号，并取二级幂级数近似，从而 $E=-\frac{1}{2}-\frac{1}{2}\cdot\frac{8\cdot 256^2}{3\cdot 243^2}F^2+o(F^4)$.

由Taylor级数的唯一性定理，从而 $\alpha=\frac{8\cdot 256^2}{3\cdot 243^2}\doteq 2.96.$