课堂练习

练习1：证明幺正算符的本征值$|\lambda|=1$

证明：根据幺正算符$\hat{U}$的定义，对任意态矢$|\lambda\rangle$，有$\langle\lambda|\hat{U}^\dagger\hat{U}|\lambda\rangle=\langle\lambda|\hat{I}\,|\lambda\rangle=\langle\lambda|\lambda\rangle$，而算符$\hat{U}$满足$\hat{U}|\lambda\rangle=\lambda|\lambda\rangle$，两边取厄米共轭，得$\langle\lambda|\hat{U}^\dagger=\langle\lambda|\lambda^*$，因此有$\langle\lambda|\hat{U}^\dagger\hat{U}|\lambda\rangle=|\lambda|^2\langle\lambda|\lambda\rangle$，从而$|\lambda|^2=1$，即$|\lambda|=1$（$|\lambda|$作为模长，必须满足$|\lambda|\geq 0$）

练习2：证明$\psi_k(x)$和$\psi_{k+K_m}(x)$，其中$K_m\equiv\frac{2\pi m}{a}$（m为任意整数），具有相同的平移对称性，即具有相同的平移算符本征值

证明：因为

$$\hat{D}(na)\psi_k(x)=\mathrm{e}^{\mathrm{i}kna}\psi_k(x)$$

$$\hat{D}(na)\psi_{k+K_m}(x)=\mathrm{e}^{\mathrm{i}(k+K_m)na}\psi_{k+K_m}(x)=\mathrm{e}^{\mathrm{i}kna}\cdot\mathrm{e}^{\mathrm{i}\cdot\frac{2\pi m}{a}\cdot na}\psi_{k+K_m}(x)=\mathrm{e}^{\mathrm{i}kna}\cdot\mathrm{e}^{2\pi\mathrm{i}mn}\psi_{k+K_m}(x)=\mathrm{e}^{\mathrm{i}kna}\psi_{k+K_m}(x)$$

所以$\psi_k(x)$和$\psi_{k+K_m}(x)$具有相同的平移算符本征值

第三章习题

3.1 已知$\hat{H}(\lambda)|\psi(\lambda)\rangle=E(\lambda)|\psi(\lambda)\rangle$，$\lambda$为一连续变化的（实）参数，设恒有$\langle\psi|\psi\rangle=1$，证明$\frac{\partial E}{\partial\lambda}=\langle\psi|\frac{\partial\hat{H}}{\partial\lambda}|\psi\rangle$，此结果称为费曼-海尔曼定理，在量子化学计算中有重要应用

证明：记态矢$|\psi(\lambda)\rangle$对λ的导数为$|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle$，对原式两边求导，得

$$\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\hat{H}(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle=\frac{\partial E(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+E(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle$$

两边左乘$\langle\psi(\lambda)|$，注意到哈密尔顿算符的厄米性，因此$E(\lambda)$为实数，从而

$$\begin{aligned}&\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\langle\psi(\lambda)|\hat{H}(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle=\langle\psi(\lambda)|\frac{\partial E(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\langle\psi(\lambda)|E(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle\\ \Rightarrow&\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+E(\lambda)\langle\psi(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle=\frac{\partial E(\lambda)}{\partial\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle+E(\lambda)\langle\psi(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle\\ \Rightarrow&\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle=\frac{\partial E(\lambda)}{\partial\lambda}\end{aligned}$$

另证：两边先左乘$\langle\psi(\lambda)|$，得$\langle\psi(\lambda)|\hat{H}(\lambda)|\psi(\lambda)\rangle=\langle\psi(\lambda)|E(\lambda)|\psi(\lambda)\rangle=E(\lambda)\langle\psi(\lambda)|\psi(\lambda)\rangle=E(\lambda)$，接下来对两边求导，结合哈密尔顿算符的厄米性，得

$$\begin{aligned}&\langle\frac{\partial\psi(\lambda)}{\partial\lambda}|\hat{H}(\lambda)|\psi(\lambda)\rangle+\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\langle\psi(\lambda)|\hat{H}(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle=\frac{\partial E(\lambda)}{\partial\lambda}\\ \Rightarrow&\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+E(\lambda)[\langle\frac{\partial\psi(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\langle\psi(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle]=\frac{\partial E(\lambda)}{\partial\lambda}\end{aligned}$$

而对归一化条件求导得$\langle\psi|\psi\rangle=1\Rightarrow\langle\frac{\partial\psi(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle+\langle\psi(\lambda)|\frac{\partial\psi(\lambda)}{\partial\lambda}\rangle=0$，代回上式，即有$\langle\psi(\lambda)|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle=\frac{\partial E(\lambda)}{\partial\lambda}$

3.2 可以用如下的势能体系作为化学键的最简单的模型

$$V(x)=\begin{cases}\infty & (x\le a_1)\\ -V_0 & (a_1<x<a_2)\\ 0 & (x\ge a_2)\end{cases}$$

其中$V_0>0$。请分别在$E>0$和$E<0$的情形下求解该体系，并联系化学键的性质进行讨论。体系能够有束缚态的条件是什么?

解：显然，当$x\le a_1$时，由于势函数为无穷大，因此体系的波函数只能为$\psi(x)=0$；当$x>a_1$时，薛定谔方程为$\begin{cases}-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=(E+V_0)\psi & (a_1<x<a_2)\\ -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=E\psi & (x\ge a_2)\end{cases}$，即$\begin{cases}\frac{d^2\psi}{dx^2}=-\frac{2m(E+V_0)}{\hbar^2}\psi & (a_1<x<a_2)\\ \frac{d^2\psi}{dx^2}=-\frac{2mE}{\hbar^2}\psi & (x\ge a_2)\end{cases}$。以下对$x>a_1$的部分进行讨论。

（1）$E>0$时，体系为非束缚态，此时令$k_1=\sqrt{\frac{2m(E+V_0)}{\hbar^2}}$，$k_2=\sqrt{\frac{2mE}{\hbar^2}}$，并设平面波$\mathrm{e}^{-\mathrm{i}k_2x}$从正无穷处入射，则波函数可写作$\psi(x)=\begin{cases}0 & (x\le a_1)\\ C\mathrm{e}^{-\mathrm{i}k_1x}+D\mathrm{e}^{\mathrm{i}k_1x} & (a_1<x<a_2)\\ \mathrm{e}^{-\mathrm{i}k_2x}+B\mathrm{e}^{\mathrm{i}k_2x} & (x\ge a_2)\end{cases}$，其导数为$\psi'(x)=\begin{cases}0 & (x\le a_1)\\ \mathrm{i}k_1(-C\mathrm{e}^{-\mathrm{i}k_1x}+D\mathrm{e}^{\mathrm{i}k_1x}) & (a_1<x<a_2)\\ \mathrm{i}k_2(-\mathrm{e}^{-\mathrm{i}k_2x}+B\mathrm{e}^{\mathrm{i}k_2x}) & (x\ge a_2)\end{cases}$，根据波函数连续性，以及在$x>a_1$处波函数导数的连续性，可得$\begin{cases}\psi(a_1^+)=\psi(a_1^-)\\ \psi(a_2^+)=\psi(a_2^-)\\ \psi'(a_2^+)=\psi'(a_2^-)\end{cases}$，代入得

$$\begin{cases}C\mathrm{e}^{-\mathrm{i}k_1a_1}+D\mathrm{e}^{\mathrm{i}k_1a_1}=0\\ \mathrm{e}^{-\mathrm{i}k_2a_2}+B\mathrm{e}^{\mathrm{i}k_2a_2}=C\mathrm{e}^{-\mathrm{i}k_1a_2}+D\mathrm{e}^{\mathrm{i}k_1a_2}\\ \mathrm{i}k_2(-\mathrm{e}^{-\mathrm{i}k_2a_2}+B\mathrm{e}^{\mathrm{i}k_2a_2})=\mathrm{i}k_1(-C\mathrm{e}^{-\mathrm{i}k_1a_2}+D\mathrm{e}^{\mathrm{i}k_1a_2})\end{cases}$$

由此解得$\begin{cases}B=\mathrm{e}^{-2\mathrm{i}k_2a_2}\frac{-(k_2-k_1)\mathrm{e}^{2\mathrm{i}k_1a_1}+(k_2+k_1)\mathrm{e}^{2\mathrm{i}k_1a_2}}{-(k_1+k_2)\mathrm{e}^{2\mathrm{i}k_1a_1}+(k_2-k_1)\mathrm{e}^{2\mathrm{i}k_1a_2}}\\ C=\frac{-2k_2\mathrm{e}^{\mathrm{i}[(k_1-k_2)a_2+2k_1a_1]}}{-(k_1+k_2)\mathrm{e}^{2\mathrm{i}k_1a_1}+(k_2-k_1)\mathrm{e}^{2\mathrm{i}k_1a_2}}\\ D=\frac{2k_2\mathrm{e}^{\mathrm{i}(k_1-k_2)a_2}}{-(k_1+k_2)\mathrm{e}^{2\mathrm{i}k_1a_1}+(k_2-k_1)\mathrm{e}^{2\mathrm{i}k_1a_2}}\end{cases}$

（2）

（3）

3.3 求解如下δ势阱的本征态，该势阱的势能函数满足$V(x)=-\gamma\delta(x)\ (\gamma>0)$

解：将势能函数代入薛定谔方程得$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}-\gamma\delta(x)\psi(x)=E\psi(x)$，即$\frac{d^2\psi(x)}{dx^2}=-\frac{2m}{\hbar^2}[E+\gamma\delta(x)]\psi(x)$，现在分$E>0$和$E<0$的情形进行讨论。

若$E>0$，体系为非束缚态，由于在$x=0$处δ函数发散，因此此处$\psi'(x)$不连续，在邻域$U(0,\varepsilon)$上对薛定谔方程积分，得$\psi'(\varepsilon)-\psi'(-\varepsilon)=-\frac{2mE}{\hbar^2}\cdot2\varepsilon-\frac{2m\gamma}{\hbar^2}\psi(0)$，取$\varepsilon\to0$，得$\psi'(0^+)-\psi'(0^-)=-\frac{2m\gamma}{\hbar^2}\psi(0)$，这是$x=0$处的跃变条件。设平面波$\mathrm{e}^{ikx}$从负无穷处入射，其中$k=\sqrt{\frac{2mE}{\hbar^2}}$，则在$x\neq0$处，波函数满足$\psi(x)=\begin{cases}\mathrm{e}^{ikx}+R\mathrm{e}^{-ikx} & (x<0)\\ S\mathrm{e}^{ikx} & (x>0)\end{cases}$，其导数满足$\psi'(x)=\begin{cases}\mathrm{i}k(\mathrm{e}^{ikx}-R\mathrm{e}^{-ikx}) & (x<0)\\ \mathrm{i}kS\mathrm{e}^{ikx} & (x>0)\end{cases}$，根据波函数的连续性，有$\psi(0^+)=\psi(0^-)$，联立这两个条件，并代入数据，得:

$$\begin{cases}1+R=S\\ \mathrm{i}k[S-(1-R)]=-\frac{2m\gamma}{\hbar^2}S\end{cases}\Rightarrow\begin{cases}R=-\frac{m\gamma}{\mathrm{i}k\hbar^2+m\gamma}\\ S=\frac{1}{1+\frac{m\gamma}{\mathrm{i}k\hbar^2}}=\frac{\mathrm{i}k\hbar^2}{\mathrm{i}k\hbar^2+m\gamma}\end{cases}$$

故相应的本征函数为$\psi(x)=\begin{cases}\mathrm{e}^{\mathrm{i}kx}-\frac{m\gamma}{\mathrm{i}k\hbar^2+m\gamma}\mathrm{e}^{-\mathrm{i}kx} & (x<0)\\ \frac{\mathrm{i}k\hbar^2}{\mathrm{i}k\hbar^2+m\gamma}\mathrm{e}^{\mathrm{i}kx} & (x>0)\end{cases}$

若$E<0$，因$x\neq 0$时，$\psi''(x)=-\frac{2mE}{\hbar^2}\psi(x)$，而$-\frac{2mE}{\hbar^2}>0$，因此$\psi(x)$为实函数，从而体系处于束缚态，又知$V(-x)=V(x)=0\ (x\neq 0)$，故$\psi(x)$必满足一定的宇称性。若$\psi(x)$为奇宇称，记$k'=\sqrt{-\frac{2mE}{\hbar^2}}$，则波函数可写为$\psi(x)=\begin{cases}A\mathrm{e}^{k'x} & (x<0)\\ -A\mathrm{e}^{-k'x} & (x>0)\end{cases}$（注意到波函数在$x\to\infty$时必须收敛至0，否则波函数无法归一化），根据波函数的连续性，有$\psi(0^+)=\psi(0^-)$，代入得$A=-A$，即$A=0$，此时$\psi(x)=0\ (x\neq 0)$，与束缚态相矛盾，故$\psi(x)$不可能为奇宇称。

若$\psi(x)$为偶宇称，则波函数可写为$\psi(x)=\begin{cases}A\mathrm{e}^{k'x} & (x<0)\\ A\mathrm{e}^{-k'x} & (x>0)\end{cases}$，此时$\psi(0^+)=\psi(0^-)=A$，满足波函数连续的条件，又波函数满足归一化条件，因此有

$$\begin{aligned}\int_{-\infty}^{+\infty}|\psi(x)|^2dx&=\int_0^{+\infty}|A\mathrm{e}^{-k'x}|^2dx+\int_{-\infty}^0|A\mathrm{e}^{k'x}|^2dx=|A|^2(\int_0^{+\infty}\mathrm{e}^{-2k'x}dx+\int_{-\infty}^0\mathrm{e}^{2k'x}dx)\\&=|A|^2[\int_0^{+\infty}\frac{\mathrm{e}^{-2k'x}}{-2k'}d(-2k'x)+\int_{-\infty}^0\frac{\mathrm{e}^{2k'x}}{2k'}d(2k'x)]\\&=|A|^2\{[\frac{\mathrm{e}^{-2k'x}}{-2k'}]_0^{+\infty}+[\frac{\mathrm{e}^{2k'x}}{2k'}]_{-\infty}^0\}=\frac{|A|^2}{k'}=1\end{aligned}$$

解得$|A|=\sqrt{k'}$，若A取正实数，则$A=\sqrt{k'}$，因此$\psi(x)=\begin{cases}\sqrt{k'}\mathrm{e}^{k'x} & (x<0)\\ \sqrt{k'}\mathrm{e}^{-k'x} & (x>0)\end{cases}$，相应的导数为$\psi'(x)=\begin{cases}k'^{\frac{3}{2}}\mathrm{e}^{k'x} & (x<0)\\ -k'^{\frac{3}{2}}\mathrm{e}^{-k'x} & (x>0)\end{cases}$，结合$x=0$处的跃变条件，我们有$(-k'^{\frac{3}{2}})-k'^{\frac{3}{2}}=-\frac{2m\gamma}{\hbar^2}k'^{\frac{1}{2}}$，解得$k'=\frac{m\gamma}{\hbar^2}=\sqrt{-\frac{2mE}{\hbar^2}}$，因此本征能量为$E=-\frac{m\gamma^2}{2\hbar^2}$，本征函数为$\psi(x)=\begin{cases}\sqrt{\frac{m\gamma}{\hbar^2}}\mathrm{e}^{\frac{m\gamma}{\hbar^2}x} & (x<0)\\ \sqrt{\frac{m\gamma}{\hbar^2}}\mathrm{e}^{-\frac{m\gamma}{\hbar^2}x} & (x>0)\end{cases}$

3.4 推导3.5节矩形势垒体系中，$E>V_0$时反射和投射系数

解：为讨论问题方便，设$k_1^2=\frac{2mE}{\hbar^2}$，$k_2^2=\frac{2m(E-V_0)}{\hbar^2}$，并假设平面波$\mathrm{e}^{\mathrm{i}k_1x}$从负无穷处向正方向传播，则对应的解为$\psi(x)=\begin{cases}\mathrm{e}^{\mathrm{i}k_1x}+B\mathrm{e}^{-\mathrm{i}k_1x}\ (x\leq-\frac{a}{2})\\ C\mathrm{e}^{\mathrm{i}k_2x}+D\mathrm{e}^{-\mathrm{i}k_2x}\ (|x|<\frac{a}{2})\\ S\mathrm{e}^{\mathrm{i}k_1x}\ (x\geq\frac{a}{2})\end{cases}$，其导函数为

$\psi'(x)=\begin{cases}\mathrm{i}k_1(\mathrm{e}^{\mathrm{i}k_1x}-B\mathrm{e}^{-\mathrm{i}k_1x})\ (x\leq-\frac{a}{2})\\ \mathrm{i}k_2(C\mathrm{e}^{\mathrm{i}k_2x}-D\mathrm{e}^{-\mathrm{i}k_2x})\ (|x|<\frac{a}{2})\\ \mathrm{i}k_1S\mathrm{e}^{\mathrm{i}k_1x}\ (x\geq\frac{a}{2})\end{cases}$

接下来，考虑到边界连续条件及波函数光滑条件，体系应满足$\begin{cases}\psi_{x\to(-\frac{a}{2})^-}=\psi_{x\to(-\frac{a}{2})^+}\\ \psi'_{x\to(-\frac{a}{2})^-}=\psi'_{x\to(-\frac{a}{2})^+}\\ \psi_{x\to(\frac{a}{2})^-}=\psi_{x\to(\frac{a}{2})^+}\\ \psi'_{x\to(\frac{a}{2})^-}=\psi'_{x\to(\frac{a}{2})^+}\end{cases}$，代入可得

$\begin{cases}\mathrm{e}^{-\frac{\mathrm{i}k_1a}{2}}+B\mathrm{e}^{\frac{\mathrm{i}k_1a}{2}}=C\mathrm{e}^{-\frac{\mathrm{i}k_2a}{2}}+D\mathrm{e}^{\frac{\mathrm{i}k_2a}{2}}\\ \mathrm{i}k_1(\mathrm{e}^{-\frac{\mathrm{i}k_1a}{2}}-B\mathrm{e}^{\frac{\mathrm{i}k_1a}{2}})=\mathrm{i}k_2(C\mathrm{e}^{-\frac{\mathrm{i}k_2a}{2}}-D\mathrm{e}^{\frac{\mathrm{i}k_2a}{2}})\\ C\mathrm{e}^{\frac{\mathrm{i}k_2a}{2}}+D\mathrm{e}^{-\frac{\mathrm{i}k_2a}{2}}=S\mathrm{e}^{\frac{\mathrm{i}k_1a}{2}}\\ \mathrm{i}k_2(C\mathrm{e}^{\frac{\mathrm{i}k_2a}{2}}-D\mathrm{e}^{-\frac{\mathrm{i}k_2a}{2}})=\mathrm{i}k_1S\mathrm{e}^{\frac{\mathrm{i}k_1a}{2}}\end{cases}$，经化简为

$$\begin{cases} Ce^{-\frac{ik_2a}{2}}+De^{\frac{ik_2a}{2}}=e^{-\frac{ik_1a}{2}}+Be^{\frac{ik_1a}{2}} & ① \\ Ce^{-\frac{ik_2a}{2}}-De^{\frac{ik_2a}{2}}=\frac{k_1}{k_2}(e^{-\frac{ik_1a}{2}}-Be^{\frac{ik_1a}{2}}) & ② \\ Ce^{\frac{ik_2a}{2}}+De^{-\frac{ik_2a}{2}}=Se^{\frac{ik_1a}{2}} & ③ \\ Ce^{\frac{ik_2a}{2}}-De^{-\frac{ik_2a}{2}}=\frac{k_1}{k_2}Se^{\frac{ik_1a}{2}} & ④ \end{cases}$$

$\frac{①+②}{2}\cdot e^{\frac{ik_2a}{2}}$，得$C=\frac{1}{2}e^{\frac{ik_2a}{2}}(\frac{k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}+\frac{-k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}})$，$\frac{③+④}{2}\cdot e^{-\frac{ik_2a}{2}}$，得 $C=\frac{1}{2}e^{-\frac{ik_2a}{2}}\cdot\frac{k_1+k_2}{k_2}Se^{\frac{ik_1a}{2}}=\frac{k_1+k_2}{2k_2}Se^{\frac{i(k_1-k_2)a}{2}}$，代入可得

$$\begin{aligned}&\frac{1}{2}e^{\frac{ik_2a}{2}}(\frac{k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}+\frac{-k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}})=\frac{k_1+k_2}{2k_2}Se^{\frac{i(k_1-k_2)a}{2}}\\ \Rightarrow&\frac{-k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}}=\frac{k_1+k_2}{k_2}Se^{\frac{i(k_1-2k_2)a}{2}}-\frac{k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}\quad ⑤\end{aligned}$$

$\frac{①-②}{2}\cdot e^{-\frac{ik_2a}{2}}$，得$D=\frac{1}{2}e^{-\frac{ik_2a}{2}}(\frac{-k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}+\frac{k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}})$；$\frac{③-④}{2}\cdot e^{\frac{ik_2a}{2}}$，得 $D=\frac{1}{2}e^{\frac{ik_2a}{2}}\cdot\frac{-k_1+k_2}{k_2}Se^{\frac{ik_1a}{2}}=\frac{-k_1+k_2}{2k_2}Se^{\frac{i(k_1+k_2)a}{2}}$，代入可得

$$\begin{aligned}&\frac{1}{2}e^{-\frac{ik_2a}{2}}(\frac{-k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}+\frac{k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}})=\frac{-k_1+k_2}{2k_2}Se^{\frac{i(k_1+k_2)a}{2}}\\ \Rightarrow&\frac{k_1+k_2}{k_2}Be^{\frac{ik_1a}{2}}=\frac{-k_1+k_2}{k_2}Se^{\frac{i(k_1+2k_2)a}{2}}-\frac{-k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}\quad ⑥\end{aligned}$$

故联立⑤与⑥得

$(-k_1+k_2)[(-k_1+k_2)Se^{\frac{i(k_1+2k_2)a}{2}}-(-k_1+k_2)e^{-\frac{ik_1a}{2}}]=(k_1+k_2)[(k_1+k_2)Se^{\frac{i(k_1-2k_2)a}{2}}-(k_1+k_2)e^{-\frac{ik_1a}{2}}]$

解得$S=\frac{4k_1k_2e^{-ik_1a}}{(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}}$，代入⑤式得

$$\begin{aligned}B&=\frac{\frac{k_1+k_2}{k_2}Se^{\frac{i(k_1-2k_2)a}{2}}-\frac{k_1+k_2}{k_2}e^{-\frac{ik_1a}{2}}}{\frac{-k_1+k_2}{k_2}e^{\frac{ik_1a}{2}}}=(k_1+k_2)[\frac{e^{-ik_2a}}{-k_1+k_2}S-\frac{e^{-ik_1a}}{-k_1+k_2}]\\ &=(k_1+k_2)[\frac{e^{-ik_2a}}{-k_1+k_2}\frac{4k_1k_2e^{-ik_1a}}{(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}}-\frac{e^{-ik_1a}}{-k_1+k_2}]\\ &=(k_1+k_2)\cdot\frac{4k_1k_2e^{i(k_1+k_2)a}-[(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}]e^{-ik_1a}}{(-k_1+k_2)[(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}]}\\ &=(k_1+k_2)\cdot\frac{-(-k_1+k_2)^2e^{-i(k_1+k_2)a}+(-k_1+k_2)^2e^{-i(k_1-k_2)a}}{(-k_1+k_2)[(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}]}\\ &=\frac{(k_1+k_2)(-k_1+k_2)[-e^{-i(k_1+k_2)a}+e^{-i(k_1-k_2)a}]}{(k_1+k_2)^2e^{-ik_2a}-(-k_1+k_2)^2e^{ik_2a}}\end{aligned}$$

3.5 计算谐振子势场中算符$\hat{x},\hat{p},\hat{x}^2,\hat{p}^2$在基态的期望值，并验证坐标和动量之间的测不准关系

解：由于湮灭和产生算符的定义为$\hat{a}=\sqrt{\frac{m\omega}{2\hbar}}(\hat{x}+\frac{i\hat{p}}{m\omega})$，$\hat{a}^\dagger=\sqrt{\frac{m\omega}{2\hbar}}(\hat{x}-\frac{i\hat{p}}{m\omega})$，因此有 $\hat{x}=\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)$，$\hat{p}=i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger-\hat{a})$，从而有

$$\begin{aligned}\hat{x}^2&=\frac{\hbar}{2m\omega}[\hat{a}^2+(\hat{a}^\dagger)^2+\hat{a}^\dagger\hat{a}+\hat{a}\hat{a}^\dagger]=\frac{\hbar}{2m\omega}[\hat{a}^2+(\hat{a}^\dagger)^2+(\hat{N}+\hat{N}+1)]=\frac{\hbar}{2m\omega}[\hat{a}^2+(\hat{a}^\dagger)^2+2\hat{N}+1)]\\ \hat{p}^2&=-\frac{m\hbar\omega}{2}[\hat{a}^2+(\hat{a}^\dagger)^2-\hat{a}^\dagger\hat{a}-\hat{a}\hat{a}^\dagger]=-\frac{m\hbar\omega}{2}[\hat{a}^2+(\hat{a}^\dagger)^2-\hat{N}-(\hat{N}+1)]=-\frac{m\hbar\omega}{2}[\hat{a}^2+(\hat{a}^\dagger)^2-2\hat{N}-1]\end{aligned}$$

因此

$$\langle 0|\hat{x}|0\rangle = \langle 0|\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\langle 0|\hat{a}|0\rangle + \langle 0|\hat{a}^\dagger|0\rangle) = \sqrt{\frac{\hbar}{2m\omega}}(\langle 0|\cdot\mathbf{0} + \langle 0|\cdot|1\rangle) = 0$$

$$\langle 0|\hat{p}|0\rangle = \langle 0|\mathrm{i}\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger-\hat{a})|0\rangle = \mathrm{i}\sqrt{\frac{m\hbar\omega}{2}}(\langle 0|\hat{a}^\dagger|0\rangle - \langle 0|\hat{a}|0\rangle) = \sqrt{\frac{\hbar}{2m\omega}}(\langle 0|\cdot|1\rangle - \langle 0|\cdot\mathbf{0}) = 0$$

$$\begin{aligned}\langle 0|\hat{x}^2|0\rangle &= \langle 0|\hat{x}|0\rangle = \langle 0|\frac{\hbar}{2m\omega}[\hat{a}^2+(\hat{a}^\dagger)^2+2\hat{N}+1)]|0\rangle = \frac{\hbar}{2m\omega}[\langle 0|\hat{a}^2|0\rangle + \langle 0|(\hat{a}^\dagger)^2|0\rangle + 2\langle 0|\hat{N}|0\rangle + \langle 0|0\rangle]\\ &= \frac{\hbar}{2m\omega}[(\langle 0|\hat{a})\cdot(\hat{a}|0\rangle) + (\langle 0|\hat{a}^\dagger)\cdot(\hat{a}^\dagger|0\rangle) + 2\langle 0|\cdot 0|0\rangle + 1] = \frac{\hbar}{2m\omega}[\langle 1|\cdot\mathbf{0} + \mathbf{0}\cdot|1\rangle + 1] = \frac{\hbar}{2m\omega}\\ \langle 0|\hat{p}^2|0\rangle &= \langle 0|-\frac{m\hbar\omega}{2}[\hat{a}^2+(\hat{a}^\dagger)^2-2\hat{N}-1]|0\rangle = -\frac{m\hbar\omega}{2}[\langle 0|\hat{a}^2|0\rangle + \langle 0|(\hat{a}^\dagger)^2|0\rangle - 2\langle 0|\hat{N}|0\rangle - \langle 0|0\rangle]\\ &= -\frac{m\hbar\omega}{2}[(\langle 0|\hat{a})\cdot(\hat{a}|0\rangle) + (\langle 0|\hat{a}^\dagger)\cdot(\hat{a}^\dagger|0\rangle) - 2\langle 0|\cdot 0|0\rangle - 1] = -\frac{m\hbar\omega}{2}[\langle 1|\cdot\mathbf{0} + \mathbf{0}\cdot|1\rangle - 1] = \frac{m\hbar\omega}{2}\end{aligned}$$

另一方面，设$\Delta\hat{x} = \hat{x} - \langle\hat{x}\rangle$，$\Delta\hat{p} = \hat{p} - \langle\hat{p}\rangle$，其中$\langle\hat{x}\rangle, \langle\hat{p}\rangle$为相应算符在态矢上的期望值，满足$\langle x\rangle = \langle n|\hat{x}|n\rangle$，$\langle p\rangle = \langle n|\hat{p}|n\rangle$，则对任意本征态矢，有

$$\begin{aligned}\langle(\Delta\hat{x})^2\rangle\langle(\Delta\hat{p})^2\rangle &= \langle n|(\hat{x}-\langle\hat{x}\rangle)^2|n\rangle\langle n|(\hat{p}-\langle\hat{p}\rangle)^2|n\rangle = \langle n|\hat{x}^2 - 2\langle\hat{x}\rangle\hat{x} + \langle\hat{x}\rangle^2|n\rangle\langle n|\hat{p}^2 - 2\langle\hat{p}\rangle\hat{p} + \langle\hat{p}\rangle^2|n\rangle \text{（此处用到期望值为实数的性质）}\\ &= (\langle x^2\rangle - 2\langle x\rangle^2 + \langle x\rangle^2)(\langle p^2\rangle - 2\langle p\rangle^2 + \langle p\rangle^2) = (\langle x^2\rangle - \langle x\rangle^2)((\langle p^2\rangle - \langle p\rangle^2))\\ &= (\frac{(2n+1)\hbar}{2m\omega} - 0)(\frac{(2n+1)m\hbar\omega}{2} - 0) = \frac{(2n+1)^2\hbar^2}{4}\end{aligned}$$

$$\frac{1}{4}|\langle[\hat{x},\hat{p}]\rangle|^2 = \frac{1}{4}|\langle n|[\hat{x},\hat{p}]|n\rangle|^2 = \frac{1}{4}|\mathrm{i}\hbar\langle n|n\rangle|^2 = \frac{\hbar^2}{4}$$

从而$\langle(\Delta\hat{x})^2\rangle\langle(\Delta\hat{p})^2\rangle = \frac{(2n+1)^2\hbar^2}{4} \ge \frac{(2\times 0+1)^2\hbar^2}{4} = \frac{\hbar^2}{4} = \frac{1}{4}|\langle[\hat{x},\hat{p}]\rangle|^2$，即谐振子体系满足不确定性原理

注：对任意状态（无论是基态还是激发态）验证$\hat{x}$和$\hat{p}$的对易关系，得

$$\begin{aligned}[\hat{x},\hat{p}]|n\rangle &= [\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger), \mathrm{i}\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger-\hat{a})]|n\rangle = \frac{\mathrm{i}\hbar}{2}[\hat{a}+\hat{a}^\dagger, \hat{a}^\dagger-\hat{a}]|n\rangle = \frac{\mathrm{i}\hbar}{2}([\hat{a}+\hat{a}^\dagger,\hat{a}^\dagger] - [\hat{a}+\hat{a}^\dagger,\hat{a}])|n\rangle\\ &= \frac{\mathrm{i}\hbar}{2}([\hat{a},\hat{a}^\dagger] + [\hat{a}^\dagger,\hat{a}^\dagger] - [\hat{a},\hat{a}] - [\hat{a}^\dagger,\hat{a}])|n\rangle = \frac{\mathrm{i}\hbar}{2}[1+0-0-(-1)]|n\rangle = \mathrm{i}\hbar|n\rangle\end{aligned}$$

因此$[\hat{x},\hat{p}] = \mathrm{i}\hbar$，满足对易关系

课堂练习（续）

练习3：升降算符满足如下的对易关系：（1）$[\hat{J}^2, \hat{J}_\pm] = 0$；（2）$[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z$；（3）$[\hat{J}_z, \hat{J}_\pm] = \pm\hat{J}_\pm$

证明：首先证明引理$[\hat{J}^2, \hat{J}_x] = [\hat{J}^2, \hat{J}_y] = [\hat{J}^2, \hat{J}_z] = 0$，显然

$$\begin{aligned}[\hat{J}^2,\hat{J}_x] &= [\hat{J}_x^2+\hat{J}_y^2+\hat{J}_z^2,\hat{J}_x] = [\hat{J}_x^2,\hat{J}_x] + [\hat{J}_y^2,\hat{J}_x] + [\hat{J}_z^2,\hat{J}_x] = 0 + \hat{J}_y[\hat{J}_y,\hat{J}_x] + [\hat{J}_y,\hat{J}_x]\hat{J}_y + \hat{J}_z[\hat{J}_z,\hat{J}_x] + [\hat{J}_z,\hat{J}_x]\hat{J}_z\\ &= \hat{J}_y\cdot(-\hat{J}_z) + (-\hat{J}_z)\cdot\hat{J}_y + \hat{J}_z\hat{J}_y + \hat{J}_y\hat{J}_z = 0\end{aligned}$$

$$\begin{aligned}[\hat{J}^2,\hat{J}_y] &= [\hat{J}_x^2+\hat{J}_y^2+\hat{J}_z^2,\hat{J}_y] = [\hat{J}_x^2,\hat{J}_y] + [\hat{J}_y^2,\hat{J}_y] + [\hat{J}_z^2,\hat{J}_y] = \hat{J}_x[\hat{J}_x,\hat{J}_y] + [\hat{J}_x,\hat{J}_y]\hat{J}_x + 0 + \hat{J}_z[\hat{J}_z,\hat{J}_y] + [\hat{J}_z,\hat{J}_y]\hat{J}_z\\ &= \hat{J}_x\hat{J}_z + \hat{J}_z\hat{J}_x + \hat{J}_z\cdot(-\hat{J}_x) + (-\hat{J}_x)\cdot\hat{J}_z = 0\end{aligned}$$

$$\begin{aligned}[\hat{J}^2,\hat{J}_z] &= [\hat{J}_x^2+\hat{J}_y^2+\hat{J}_z^2,\hat{J}_z] = [\hat{J}_x^2,\hat{J}_x] + [\hat{J}_y^2,\hat{J}_x] + [\hat{J}_z^2,\hat{J}_x] = 0 + \hat{J}_y[\hat{J}_y,\hat{J}_x] + [\hat{J}_y,\hat{J}_x]\hat{J}_y + \hat{J}_z[\hat{J}_z,\hat{J}_x] + [\hat{J}_z,\hat{J}_x]\hat{J}_z\\ &= \hat{J}_y\cdot(-\hat{J}_z) + (-\hat{J}_z)\cdot\hat{J}_y + \hat{J}_z\hat{J}_y + \hat{J}_y\hat{J}_z = 0\end{aligned}$$

（1）由于$\hat{J}_\pm = \hat{J}_x \pm \mathrm{i}\hat{J}_y$，因此$[\hat{J}^2, \hat{J}_\pm] = [\hat{J}^2, \hat{J}_x] \pm \mathrm{i}[\hat{J}^2, \hat{J}_y] = 0$

（2）易知

$$
\begin{aligned}
[\hat{J}_+, \hat{J}_-] &= \hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+ = (\hat{J}_x + \mathrm{i}\hat{J}_y)(\hat{J}_x - \mathrm{i}\hat{J}_y) - (\hat{J}_x - \mathrm{i}\hat{J}_y)(\hat{J}_x + \mathrm{i}\hat{J}_y) \\
&= (\hat{J}_x^2 - \hat{J}_y^2 - \mathrm{i}[\hat{J}_x, \hat{J}_y]) - (\hat{J}_x^2 - \hat{J}_y^2 + \mathrm{i}[\hat{J}_x, \hat{J}_y]) = -2\mathrm{i}[\hat{J}_x, \hat{J}_y] \\
&= -2\mathrm{i}\cdot \mathrm{i}\hbar\hat{J}_z = 2\hbar\hat{J}_z
\end{aligned}
$$

（3）易知

$$
[\hat{J}_z, \hat{J}_\pm] = [\hat{J}_z, \hat{J}_x \pm \mathrm{i}\hat{J}_y] = [\hat{J}_z, \hat{J}_x] \pm \mathrm{i}[\hat{J}_z, \hat{J}_y] = \mathrm{i}\hbar\hat{J}_y \pm \mathrm{i}(-\mathrm{i}\hbar\hat{J}_x) = \hbar(\mathrm{i}\hat{J}_y \pm \hat{J}_x) = \pm\hat{J}_\pm
$$

练习4：推导$\langle jm^{'}|\hat{J}_x|jm\rangle$的表达式

解：由于$\hat{J}_\pm = \hat{J}_x \pm \mathrm{i}\hat{J}_y$，即$\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$，因此

$$
\begin{aligned}
\langle jm^{'}|\hat{J}_x|jm\rangle &= \langle jm^{'}|\frac{1}{2}(\hat{J}_+ + \hat{J}_-)|jm\rangle = \frac{1}{2}(\langle jm^{'}|\hat{J}_+|jm\rangle + \langle jm^{'}|\hat{J}_-|jm\rangle) \\
&= \frac{1}{2}(\sqrt{j(j+1)-m(m+1)}\hbar\langle jm^{'}|j(m+1)\rangle + \sqrt{j(j+1)-m(m-1)}\hbar\langle jm^{'}|j(m-1)\rangle) \\
&= \frac{\hbar}{2}(\sqrt{(j+m+1)(j-m)}\delta_{m^{'},m+1} + \sqrt{(j-m+1)(j+m)}\delta_{m^{'},m-1})
\end{aligned}
$$