课堂练习

练习1：为什么采用玻恩-冯·卡门边界条件后，波矢必须表示成如下形式？

$$k = l\frac{2\pi}{L} = \frac{l}{N}\frac{2\pi}{a} \quad (l = 0, \pm1, \pm2, \pm3, \ldots)$$

解：玻恩-冯·卡门边界条件表明，$\phi_k(x+Na) = \phi_k(x)$，又平面波可表示为$\phi_k(x) = L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx}$，其中$L = Na$，代入得

$$L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}k(x+Na)} = L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx} \Rightarrow \mathrm{e}^{\mathrm{i}kNa} = 1 \Rightarrow kNa = 2\pi l \quad (l = 0, \pm1, \pm2, \pm3, \ldots)$$

由此可得$k = \frac{l}{N}\frac{2\pi}{a}(l = 0, \pm1, \pm2, \pm3, \ldots)$

练习2：对于矩阵元$V_{kk'} \equiv \langle\phi_k|\hat{V}|\phi_{k'}\rangle = L^{-1}\int_0^L V(x)\mathrm{e}^{-\mathrm{i}(k-k')x}dx$，求证只有当$k-k' = \frac{2\pi}{a}l$，其中$l$为任意整数时，矩阵元才不为零，并等于周期势函数$V(x)$对应于$q = \frac{2\pi}{a}l$的傅里叶积分

证明：注意到$V(x+na) = V(x)$，其中$n \in \mathbb{Z}$，利用傅里叶级数，我们有（设$V_l \equiv a^{-1}\int_0^a V(x)\mathrm{e}^{-\mathrm{i}\frac{2\pi l}{a}x}dx$）

$$V_{kk'} = L^{-1}\int_0^L V(x)\mathrm{e}^{-\mathrm{i}(k-k')x}dx = L^{-1}\int_0^L\Big[\sum_{l=-\infty}^{+\infty}V_l\mathrm{e}^{\mathrm{i}\frac{2\pi x}{a}l}\Big]\mathrm{e}^{-\mathrm{i}(k-k')x}dx = L^{-1}\int_0^L\Big[\sum_{l=-\infty}^{+\infty}V_l\mathrm{e}^{\mathrm{i}x(\frac{2\pi}{a}l-k+k')}\Big]dx$$

这样展开似乎找不出思路，我们改用如下方法：

$$\begin{aligned}
V_{kk'} &= L^{-1}\int_0^L V(x)\mathrm{e}^{-\mathrm{i}(k-k')x}dx = L^{-1}\sum_{n=0}^{N-1}\int_{na}^{(n+1)a}V(x)\mathrm{e}^{-\mathrm{i}(k-k')x}dx \\
&= L^{-1}\sum_{n=0}^{N-1}\int_0^a V(x'+na)\mathrm{e}^{-\mathrm{i}(k-k')(x'+na)}d(x'+na) \\
&= L^{-1}\sum_{n=0}^{N-1}\int_0^a V(x')\mathrm{e}^{-\mathrm{i}(k-k')x'}\cdot\mathrm{e}^{-\mathrm{i}(k-k')na}dx' \\
&= L^{-1}\int_0^a V(x')\mathrm{e}^{-\mathrm{i}(k-k')x'}dx'\cdot\sum_{n=0}^{N-1}\mathrm{e}^{-\mathrm{i}(k-k')na}
\end{aligned}$$

若$\mathrm{e}^{-\mathrm{i}(k-k')a} = \mathrm{e}^{-\mathrm{i}\frac{2\pi(l-l')}{L}a} \neq 1$，则$\sum_{n=0}^{N-1}\mathrm{e}^{-\mathrm{i}(k-k')na} = \frac{1-\mathrm{e}^{-\mathrm{i}(k-k')(N-1)a}}{1-\mathrm{e}^{-\mathrm{i}(k-k')a}} = \frac{1-\mathrm{e}^{-\mathrm{i}\frac{2\pi(l-l')}{L}(N-1)a}}{1-\mathrm{e}^{-\mathrm{i}\frac{2\pi(l-l')}{L}a}} = 0$，故为使级数不为零，必须使$\mathrm{e}^{-\mathrm{i}(k-k')a} = 1$，从而有$(k-k')a = 2\pi l\ (l \in \mathbb{Z})$，即$k-k' = \frac{2\pi}{a}l$，从而

$$V_{kk'} = L^{-1}\int_0^a V(x)\mathrm{e}^{-\mathrm{i}\frac{2\pi l}{a}x}\cdot Ndx = a^{-1}\int_0^a V(x)\mathrm{e}^{-\mathrm{i}\frac{2\pi l}{a}x}dx \equiv V_l$$

练习3：写出波函数的一阶修正$\delta\psi_k^{(1)}(x)$，证明考虑了一阶修正后的波函数$\psi_k(x) = \phi_k(x) + \delta\psi_k^{(1)}(x)$满足 Bloch定理

解：对于$k \neq k'$，波函数的一阶修正$\delta\psi_k^{(1)}(x) = \sum_{k'\neq k}\frac{V_{k'k}}{\varepsilon_k-\varepsilon_{k'}}\phi_k'(x)$，由于矩阵元$V_{kk'}$只有在$k-k' = \frac{2\pi}{a}l\ (l \in \mathbb{Z})$时才不为0，因此

$$
\begin{aligned}
\psi_k(x) &= \phi_k(x) + \delta\psi_k^{(1)}(x) = \phi_k(x) + \sum_{k^{'}\neq k}\frac{V_{k^{'}k}}{\varepsilon_k - \varepsilon_{k^{'}}}\phi_k^{'}(x) \\
&= L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx} + \sum_{l\neq 0}\frac{V_l^*}{\frac{\hbar^2}{2m}[k^2-(k-\frac{2\pi}{a}l)^2]}L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}(k-\frac{2\pi}{a}l)x} \\
&= L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx}\{1+\frac{2m}{\hbar^2}\sum_{l\neq 0}\frac{V_l^*}{[k^2-(k-\frac{2\pi}{a}l)^2]}\mathrm{e}^{-\mathrm{i}\frac{2\pi lx}{a}}\}
\end{aligned}
$$

因此

$$
\begin{aligned}
\psi_k(x+na) &= L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}k(x+na)}\{1+\frac{2m}{\hbar^2}\sum_{l\neq 0}\frac{V_l^*}{[k^2-(k-\frac{2\pi}{a}l)^2]}\mathrm{e}^{-\mathrm{i}\frac{2\pi l(x+na)}{a}}\} \\
&= \mathrm{e}^{\mathrm{i}kna}\cdot L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx}\{1+\frac{2m}{\hbar^2}\sum_{l\neq 0}\frac{V_l^*}{[k^2-(k-\frac{2\pi}{a}l)^2]}\mathrm{e}^{-\mathrm{i}\frac{2\pi lx}{a}}\mathrm{e}^{-2\pi\mathrm{i}nl}\} \\
&= \mathrm{e}^{\mathrm{i}kna}\cdot L^{-\frac{1}{2}}\mathrm{e}^{\mathrm{i}kx}\{1+\frac{2m}{\hbar^2}\sum_{l\neq 0}\frac{V_l^*}{[k^2-(k-\frac{2\pi}{a}l)^2]}\mathrm{e}^{-\mathrm{i}\frac{2\pi lx}{a}}\} = \mathrm{e}^{\mathrm{i}kna}\psi_k(x)
\end{aligned}
$$

从而$\psi_k(x)$满足Bloch原理，证毕

练习4：试应用简并态微扰理论，证明

$$
E_\pm = \frac{\varepsilon_k + \varepsilon_{k^{'}}}{2} + \sqrt{(\frac{\varepsilon_k - \varepsilon_{k^{'}}}{2})^2 + |V_l|^2}
$$

并推导当$\Delta \rightarrow 0$时，上式可简化为

$$
E_\pm \approx \varepsilon_l(1+\Delta^2) + (|V_l| + \frac{2\varepsilon_l^2\Delta^2}{|V_l|})
$$

其中$\varepsilon_l = \frac{\hbar^2}{2m}(\frac{l\pi}{a})^2$

证明：定义$k \equiv l\frac{\pi}{a}(1+\Delta)$，$k^{'} \equiv k - l\frac{2\pi}{a} = l\frac{\pi}{a}(-1+\Delta)$，则当$\Delta \ll 1$时为近简并态，必须采用简并态微扰理论。记哈密尔顿算符为$\hat{H} = \hat{H}_0 + \hat{H}^{'}$，其中$\hat{H}_0 = \frac{\hat{p}^2}{2m}$，$\hat{H}^{'} = \hat{V}$，则薛定谔方程可写作$(\hat{H}_0 + \hat{H}^{'})\psi_k = E\psi_k$，写成矩阵形式即为

$$
\begin{pmatrix} \varepsilon_k & 0 \\ 0 & \varepsilon_{k^{'}} \end{pmatrix} + \begin{pmatrix} 0 & V_{kk^{'}} \\ V_{k^{'}k} & 0 \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix} \Rightarrow \begin{pmatrix} \varepsilon_k - E & V_{kk^{'}} \\ V_{k^{'}k} & \varepsilon_{k^{'}} - E \end{pmatrix} = 0
$$

对应的久期方程为

$$
\begin{aligned}
\begin{vmatrix} \varepsilon_k - E & V_{kk^{'}} \\ V_{k^{'}k} & \varepsilon_{k^{'}} - E \end{vmatrix} = 0 &\Rightarrow (\varepsilon_k - E)(\varepsilon_{k^{'}} - E) - V_{kk^{'}}V_{k^{'}k} = 0 \\
&\Rightarrow E^2 - (\varepsilon_k + \varepsilon_{k^{'}})E + \varepsilon_k\varepsilon_{k^{'}} - |V_l|^2 = 0 \\
&\Rightarrow E_\pm = \frac{(\varepsilon_k + \varepsilon_{k^{'}}) + \sqrt{(\varepsilon_k + \varepsilon_{k^{'}})^2 - 4(\varepsilon_k\varepsilon_{k^{'}} - |V_l|^2)}}{2} \\
&\Rightarrow E_\pm = \frac{\varepsilon_k + \varepsilon_{k^{'}}}{2} + \sqrt{(\frac{\varepsilon_k - \varepsilon_{k^{'}}}{2})^2 + |V_l|^2}
\end{aligned}
$$

当$\Delta \rightarrow 0$时，由于$\varepsilon_k = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m}(\frac{l\pi}{a})^2(1+\Delta)^2$，$\varepsilon_{k^{'}} = \frac{\hbar^2k'^2}{2m} = \frac{\hbar^2}{2m}(\frac{l\pi}{a})^2(1-\Delta)^2$，因此代入得

$$
\begin{aligned}
E_{\pm} &= \frac{\hbar^2}{2m}(\frac{l\pi}{a})^2\frac{(1+\Delta)^2+(1-\Delta)^2}{2}+\sqrt{[\frac{\hbar^2}{2m}(\frac{l\pi}{a})^2\frac{(1+\Delta)^2-(1-\Delta)^2}{2}]^2+|V_l|^2} \\
&= \varepsilon_l(1+\Delta^2)+|V_l|\sqrt{(\frac{2\varepsilon_l\Delta}{|V_l|})^2+1}\approx\varepsilon_l(1+\Delta^2)+|V_l|[1+\frac{1}{2}(\frac{2\varepsilon_l\Delta}{|V_l|})^2] \\
&= \varepsilon_l(1+\Delta^2)+(|V_l|+\frac{2\varepsilon_l^2\Delta^2}{|V_l|})
\end{aligned}
$$

第六章习题

6.1 一维谐振子体系$V=\frac{1}{2}\mu\omega_0^2x^2$受到如下微扰（其中$\tau>0$）

$$
H^{'}=\begin{cases}0 & (t<0)\\ a_0x\mathrm{e}^{-\frac{t}{\tau}} & (t>0)\end{cases}
$$

用一级微扰理论计算当t足够大后从基态向各激发态的跃迁概率

解：由于一级微扰系数为

$$
\begin{aligned}
c_n^{(1)}(t) &= -\frac{\mathrm{i}}{\hbar}\int_0^t\langle n|\hat{H}_I^{'}(t_1)|i\rangle dt_1=-\frac{\mathrm{i}}{\hbar}\int_0^t\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_n-E_i)t_1}\langle n|\hat{H}^{'}(t_1)|i\rangle dt_1 \\
&= -\frac{\mathrm{i}}{\hbar}\int_0^t\mathrm{e}^{\mathrm{i}(n-i)\omega_0t_1}\langle n|a_0\hat{x}\mathrm{e}^{-\frac{t_1}{\tau}}|i\rangle dt_1=-\frac{\mathrm{i}a_0}{\hbar}\int_0^t\mathrm{e}^{[\mathrm{i}(n-i)\omega_0-\frac{1}{\tau}]t_1}\langle n|\hat{x}|i\rangle dt_1 \\
&= -\frac{\mathrm{i}a_0}{\hbar}\int_0^t\mathrm{e}^{[\mathrm{i}(n-i)\omega_0-\frac{1}{\tau}]t_1}\langle n|\sqrt{\frac{\hbar}{2\mu\omega_0}}(\sqrt{i+1}|i+1\rangle+\sqrt{i}|i-1\rangle)dt_1 \\
&= -\frac{\mathrm{i}a_0}{\hbar}\sqrt{\frac{\hbar}{2\mu\omega_0}}(\sqrt{i+1}\delta_{n,i+1}+\sqrt{i}\delta_{n,i-1})\int_0^t\mathrm{e}^{[\mathrm{i}(n-i)\omega_0-\frac{1}{\tau}]t_1}dt_1 \\
&= -\frac{\mathrm{i}a_0}{\hbar}\sqrt{\frac{\hbar}{2\mu\omega_0}}(\sqrt{i+1}\delta_{n,i+1}+\sqrt{i}\delta_{n,i-1})\frac{\mathrm{e}^{[\mathrm{i}(n-i)\omega_0-\frac{1}{\tau}]t}-1}{\mathrm{i}(n-i)\omega_0-\frac{1}{\tau}}
\end{aligned}
$$

而由题意，$i=0$，结合上式可知，当$n>1$时，有$c_n^{(1)}(t)=0$，从而$P_{n\leftarrow0}^{(1)}(t)=0$；当$n=1$时，有$c_1^{(1)}(t)=-\frac{\mathrm{i}a_0}{\hbar}\sqrt{\frac{\hbar}{2\mu\omega_0}}\frac{\mathrm{e}^{(\mathrm{i}\omega_0-\frac{1}{\tau})t}-1}{\mathrm{i}\omega_0-\frac{1}{\tau}}$，从而$t$足够大时，可得

$$
\lim_{t\to\infty}c_1^{(1)}(t)=\lim_{t\to\infty}-\frac{\mathrm{i}a_0}{\hbar}\sqrt{\frac{\hbar}{2\mu\omega_0}}\frac{\mathrm{e}^{(\mathrm{i}\omega_0-\frac{1}{\tau})t}-1}{\mathrm{i}\omega_0-\frac{1}{\tau}}=\frac{\mathrm{i}a_0}{\hbar}\sqrt{\frac{\hbar}{2\mu\omega_0}}\frac{1}{\mathrm{i}\omega_0-\frac{1}{\tau}}
$$

$$
\lim_{t\to\infty}P_{1\leftarrow0}^{(1)}(t)=\lim_{t\to\infty}|c_1^{(1)}(t)|^2=\lim_{t\to\infty}\frac{a_0}{2\mu\hbar\omega_0}\frac{\mathrm{e}^{-\frac{2}{\tau}t}-\mathrm{e}^{(\mathrm{i}\omega_0-\frac{1}{\tau})t}-\mathrm{e}^{-(\mathrm{i}\omega_0+\frac{1}{\tau})t}+1}{\frac{1}{\tau^2}+\omega_0^2}=\frac{a_0}{2\mu\hbar\omega_0}\frac{1}{\frac{1}{\tau^2}+\omega_0^2}
$$

6.2 精确求解一个带电为q的离子在谐振子势能面上同时受到均匀外电场ε的作用的问题，与§6.3节的结果比较。将极化率α定义为诱导偶极矩μ与外场强度ε之比，证明能量改变为$-\frac{\alpha\varepsilon^2}{2}$

解：体系的总哈密尔顿算符为$\hat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{m\omega_0^2\hat{x}^2}{2}-q\varepsilon\hat{x}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{m\omega_0^2}{2}(\hat{x}-\frac{q\varepsilon}{m\omega_0^2})^2-\frac{q^2\varepsilon^2}{2m\omega_0^2}$，故对应的薛定谔方程为

$$
\begin{aligned}
\hat{H}\psi(x)=E\psi(x) &\Rightarrow [-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{m\omega_0^2}{2}(\hat{x}-\frac{q\varepsilon}{m\omega_0^2})^2-\frac{q^2\varepsilon^2}{2m\omega_0^2}]\psi(x)=E\psi(x) \\
&\Rightarrow [-\frac{\hbar^2}{2m}\frac{d^2}{d(x-\frac{q\varepsilon}{m\omega_0^2})^2}+\frac{m\omega_0^2}{2}(\hat{x}-\frac{q\varepsilon}{m\omega_0^2})^2]\psi(x)=(E+\frac{q^2\varepsilon^2}{2m\omega_0^2})\psi(x)
\end{aligned}
$$

作代换$x^{'}=x-\frac{q\varepsilon}{m\omega_0^2}$（相应的算符为$\hat{x}^{'}=\hat{x}-\frac{q\varepsilon}{m\omega_0^2}$），$E_{tr}=E+\frac{q^2\varepsilon^2}{2m\omega_0^2}$，则$dx^{'}=dx$，再设$\hat{H}_{tr}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^{'2}}+\frac{m\omega_0^2\hat{x}^{'}}{2}$，则$\hat{H}_{tr}\psi(x^{'})=E_{tr}\psi(x^{'})$，与不加电场的谐振子体系方程形式上一致，从而有$\langle x^{'}\rangle=\langle x-\frac{q\varepsilon}{m\omega_0^2}\rangle=0$，即有$\langle x\rangle=\frac{q\varepsilon}{m\omega_0^2}$；$E=E_{tr}-\frac{q^2\varepsilon^2}{2m\omega_0^2}$，即有$\Delta E=E-E_{tr}=-\frac{q^2\varepsilon^2}{2m\omega_0^2}$

根据诱导偶极的定义，我们有$\mu=q\langle x\rangle=\frac{q^2\varepsilon}{m\omega_0^2}$，故极化率为$\alpha=\frac{\mu}{\varepsilon}=\frac{q^2}{m\omega_0^2}$，从而能量变化为$\Delta E=-\frac{q^2\varepsilon^2}{2m\omega_0^2}=-\frac{\alpha\varepsilon^2}{2}$，证毕

6.3 势能函数为如下形式的体系

$$V(x)=\begin{cases}\infty & (x\le 0,x\ge a)\\ 0 & (0<x<\frac{a}{3},\frac{2a}{3}<x<a)\\ \frac{\hbar^2\pi^2}{20ma^2} & (\frac{a}{3}\le x\le\frac{2a}{3})\end{cases}$$

(1)取$\hat{H}_0$的势能函数为$V_0(x)=\begin{cases}\infty & (x\le 0,x\ge a)\\ 0 & (0<x<a)\end{cases}$，求$\hat{H}$体系基态的一级微扰能量和展开到第5个能级的一级微扰波函数

(2)以$\psi(x)=\sin(\frac{\pi}{a}x)+\lambda\sin(\frac{3\pi}{a}x)$作为试探波函数，$\lambda$作为变分参数，求体系基态的能量

(3)以$\psi(x)=\sin(\frac{\pi}{a}x)+\lambda_1\sin(\frac{3\pi}{a}x)+\lambda_2\sin(\frac{5\pi}{a}x)$作为试探波函数，$\lambda_1,\lambda_2$作为变分参数，求体系基态的能量。对以上过程和结果进行讨论

解：(1)由题目可知，哈密尔顿算符的微扰项为$\hat{H}^{'}=\begin{cases}0 & (x<\frac{a}{3},x>\frac{2a}{3})\\ \frac{\hbar^2\pi^2}{20ma^2} & (\frac{a}{3}\le x\le\frac{2a}{3})\end{cases}$，因此基态能量的一级微扰为

$$\delta E_0^{(1)}=\langle\psi_0^{(0)}|\hat{H}^{'}|\psi_0^{(0)}\rangle=\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{\hbar^2\pi^2}{20ma^2}[\sqrt{\frac{2}{a}}\sin(\frac{\pi}{a}x)]^2dx=\frac{\hbar^2\pi^2}{20ma^2}\cdot\frac{2}{a}\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{1-\cos(\frac{2\pi}{a}x)}{2}dx=\frac{\hbar^2\pi^2}{10ma^2}(\frac{1}{6}-\frac{\sqrt{3}}{4\pi})$$

从而考虑一级微扰后的修正基态能量为

$$E_0^{(1)}=E_0^{(0)}+\delta E_0^{(1)}=\frac{\hbar^2\pi^2}{2ma^2}+\frac{\hbar^2\pi^2}{10ma^2}(\frac{1}{6}-\frac{\sqrt{3}}{4\pi})=\frac{\hbar^2\pi^2}{10ma^2}(\frac{31}{6}-\frac{\sqrt{3}}{4\pi})$$

若展开到第5个能级，则基态波函数的一级微扰为

$$\begin{aligned}|\delta\psi_0^{(1)}\rangle&=\sum_{i=1}^{4}\frac{H_{i0}^{'}}{E_0^{(0)}-E_i^{(0)}}|\psi_i^{(0)}\rangle=\sum_{i=1}^{4}\frac{\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{\hbar^2\pi^2}{20ma^2}(\sqrt{\frac{2}{a}})^2\sin[\frac{(i+1)\pi}{a}x]\sin(\frac{\pi}{a}x)dx}{\frac{\hbar^2\pi^2}{2ma^2}-\frac{(i+1)^2\hbar^2\pi^2}{2ma^2}}|\psi_i^{(0)}\rangle\\&=\sum_{i=1}^{4}\frac{\frac{\hbar^2\pi^2}{10ma^3}\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{1}{2}\{\cos(\frac{i\pi}{a}x)-\cos[\frac{(i+2)\pi}{a}x]\}dx}{-\frac{i(i+2)\hbar^2\pi^2}{2ma^2}}|\psi_i^{(0)}\rangle\\&=-\sum_{i=1}^{4}\frac{1}{10i(i+2)a}\cdot[\frac{\sin(\frac{i\pi}{a}x)}{\frac{i\pi}{a}}-\frac{\sin[\frac{(i+2)\pi}{a}x]}{\frac{(i+2)\pi}{a}}]_{\frac{a}{3}}^{\frac{2a}{3}}|\psi_i^{(0)}\rangle\\&=\frac{3\sqrt{3}}{320\pi}|\psi_2^{(0)}\rangle-\frac{\sqrt{3}}{960\pi}|\psi_4^{(0)}\rangle\end{aligned}$$

故考虑一级微扰后的基态波函数为

$$|\psi_0^{(1)}\rangle=|\psi_0^{(0)}\rangle+|\delta\psi_0^{(1)}\rangle=|\psi_0^{(0)}\rangle+\frac{3\sqrt{3}}{320\pi}|\psi_2^{(0)}\rangle-\frac{\sqrt{3}}{960\pi}|\psi_4^{(0)}\rangle$$

写成坐标形式即为

$$\psi_0^{(1)}(x)=\psi_0^{(0)}(x)+\frac{3\sqrt{3}}{320\pi}\psi_2^{(0)}(x)-\frac{\sqrt{3}}{960\pi}\psi_4^{(0)}(x)=\sin(\frac{\pi}{a}x)+\frac{3\sqrt{3}}{320\pi}\sin(\frac{3\pi}{a}x)-\frac{\sqrt{3}}{960\pi}\sin(\frac{5\pi}{a}x)$$

(2)由于总哈密尔顿算符为

$$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(\hat{x})=\begin{cases}\infty & (x\le 0, x\ge a)\\ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} & (0<x<\frac{a}{3},\frac{2a}{3}<x<a)\\ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{\hbar^2\pi^2}{20ma^2} & (\frac{a}{3}\le x\le\frac{2a}{3})\end{cases}$$

因此变分法得到的基态能量为

$$\begin{aligned}
\langle\widetilde{E}_0\rangle &=\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}=\frac{\int_0^a\psi(x)\cdot(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2})dx+\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}|\psi(x)|^2dx}{\int_0^a|\psi(x)|^2dx}\\
&=\frac{-\frac{\hbar^2}{2m}\int_0^a[\sin(\frac{\pi}{a}x)+\lambda\sin(\frac{3\pi}{a}x)]\cdot(-\frac{\pi^2}{a^2})[\sin(\frac{\pi}{a}x)+9\lambda\sin(\frac{3\pi}{a}x)]dx}{\int_0^a[\sin(\frac{\pi}{a}x)+\lambda\sin(\frac{3\pi}{a}x)]^2dx}\\
&\quad+\frac{\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}[\sin(\frac{\pi}{a}x)+\lambda\sin(\frac{3\pi}{a}x)]^2dx}{\int_0^a[\sin(\frac{\pi}{a}x)+\lambda\sin(\frac{3\pi}{a}x)]^2dx}\\
&=\frac{\frac{\hbar^2\pi^2}{2ma^2}\int_0^a[\sin(\frac{\pi}{a}x)^2+10\lambda\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)+9\lambda^2\sin^2(\frac{3\pi}{a}x)]dx}{\int_0^a[\sin^2(\frac{\pi}{a}x)+2\lambda\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)+\lambda^2\sin^2(\frac{3\pi}{a}x)]dx}\\
&\quad+\frac{\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}[\sin^2(\frac{\pi}{a}x)+2\lambda\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)+\lambda^2\sin^2(\frac{3\pi}{a}x)]dx}{\int_0^a[\sin^2(\frac{\pi}{a}x)+2\lambda\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)+\lambda^2\sin^2(\frac{3\pi}{a}x)]dx}\\
&=\frac{\frac{\hbar^2\pi^2}{2ma^2}\int_0^a\{\frac{1-\cos(\frac{2\pi}{a}x)}{2}+5\lambda[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]+9\lambda^2\frac{1-\cos(\frac{6\pi}{a}x)}{2}\}dx}{\int_0^a\{\frac{1-\cos(\frac{2\pi}{a}x)}{2}+\lambda[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]+\lambda^2\frac{1-\cos(\frac{6\pi}{a}x)}{2}\}dx}\\
&\quad+\frac{\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}\{\frac{1-\cos(\frac{2\pi}{a}x)}{2}+\lambda[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]+\lambda^2\frac{1-\cos(\frac{6\pi}{a}x)}{2}\}dx}{\int_0^a\{\frac{1-\cos(\frac{2\pi}{a}x)}{2}+\lambda[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]+\lambda^2\frac{1-\cos(\frac{6\pi}{a}x)}{2}\}dx}\\
&=\frac{\frac{\hbar^2\pi^2}{2ma^2}\cdot\frac{a}{2}(1+9\lambda^2)}{\frac{a}{2}(1+\lambda^2)}+\frac{\frac{\hbar^2\pi^2}{20ma^2}\cdot[(\frac{a}{6}+\frac{\sqrt{3}a}{4\pi})+\lambda\cdot(-\frac{3\sqrt{3}a}{4\pi})+\lambda^2\cdot\frac{a}{6}]}{\frac{a}{2}(1+\lambda^2)}\\
&=\frac{\hbar^2\pi^2}{2ma^2}[\frac{1+9\lambda^2}{1+\lambda^2}+\frac{1}{10}\frac{(\frac{1}{3}+\frac{\sqrt{3}}{2\pi})-\frac{3\sqrt{3}}{2\pi}\lambda+\frac{1}{3}\lambda^2}{1+\lambda^2}]\\
&=\frac{\hbar^2\pi^2}{2ma^2}\frac{(\frac{31}{30}+\frac{\sqrt{3}}{20\pi})-\frac{3\sqrt{3}}{20\pi}\lambda+\frac{271}{30}\lambda^2}{1+\lambda^2}
\end{aligned}$$

将$\langle\widetilde{E}_0\rangle$对$\lambda$求导，得

$$\begin{aligned}
\frac{d\langle\widetilde{E}_0\rangle}{d\lambda}&=\frac{\hbar^2\pi^2}{2ma^2}\frac{(-\frac{3\sqrt{3}}{20\pi}+\frac{271}{15}\lambda)(1+\lambda^2)-[(\frac{31}{30}+\frac{\sqrt{3}}{20\pi})-\frac{3\sqrt{3}}{20\pi}\lambda+\frac{271}{30}\lambda^2]\cdot 2\lambda}{(1+\lambda^2)^2}\\
&=\frac{\hbar^2\pi^2}{2ma^2}\frac{[-\frac{3\sqrt{3}}{20\pi}+\frac{271}{15}\lambda-\frac{3\sqrt{3}}{20\pi}\lambda^2+\frac{271}{15}\lambda^3]-[(\frac{31}{15}+\frac{\sqrt{3}}{10\pi})\lambda-\frac{3\sqrt{3}}{10\pi}\lambda^2+\frac{271}{15}\lambda^3]}{(1+\lambda^2)^2}\\
&=\frac{\hbar^2\pi^2}{2ma^2}\frac{-\frac{3\sqrt{3}}{20\pi}+(16-\frac{\sqrt{3}}{10\pi})\lambda+\frac{3\sqrt{3}}{20\pi}\lambda^2}{(1+\lambda^2)^2}
\end{aligned}$$

解得

$$\lambda=\frac{-(16-\frac{\sqrt{3}}{10\pi})\pm\sqrt{(16-\frac{\sqrt{3}}{10\pi})^2+4(\frac{3\sqrt{3}}{20\pi})^2}}{2\cdot\frac{3\sqrt{3}}{20\pi}}=\frac{\sqrt{3}-160\pi}{3\sqrt{3}}\pm\frac{10\pi}{3\sqrt{3}}\sqrt{256-\frac{16\sqrt{3}}{5\pi}+\frac{3}{10\pi^2}}$$

根据一阶导数的性质，我们取$\lambda=\frac{\sqrt{3}-160\pi}{3\sqrt{3}}+\frac{10\pi}{3\sqrt{3}}\sqrt{256-\frac{16\sqrt{3}}{5\pi}+\frac{3}{10\pi^2}}\approx 5.19\times10^{-3}$，代回能量的表达式，得$\langle\widetilde{E}_0\rangle\approx 0.530\frac{\hbar^2\pi^2}{ma^2}$

(3)假设基组正交归一，线性变分法要求解的方程为$\sum\limits_{j=1}^{N}(H_{ij}-E\delta_{ij})c_j=0$，对应的久期方程为

$$\begin{vmatrix} H_{11}-E & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22}-E & \dots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \dots & H_{NN}-E \end{vmatrix}=0$$

同理，假设基组正交，但不归一，且相同基组平方的积分为$S=\int|\psi_i(x)|^2dx$，则线性变分法要求解的方程为$\sum\limits_{j=1}^{N}(H_{ij}-ES\delta_{ij})c_j=0$，对应的久期方程为

$$\begin{vmatrix} H_{11}-ES & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22}-ES & \dots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \dots & H_{NN}-ES \end{vmatrix}=0$$

现在$N=3$，$c_1=1$，$c_2=\lambda_1$，$c_3=\lambda_2$，且该体系相同基组平方的积分为
$S=\int_0^a|\sin(\frac{i\pi}{a}x)|^2dx=\frac{a}{2}$，故接下来只需要知道$H_{ij}$的大小即可，而

$$\begin{aligned} H_{11}&=\int_0^a\sin(\frac{\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{\pi}{a}x)]}{dx^2}\}dx+\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{\hbar^2\pi^2}{20ma^2}\sin^2(\frac{\pi}{a}x)dx \\ &=\frac{\hbar^2\pi^2}{2ma^2}\int_0^a\sin^2(\frac{\pi}{a}x)dx+\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}\sin^2(\frac{\pi}{a}x)dx \\ &=\frac{\hbar^2\pi^2}{2ma^2}\int_0^a\frac{1-\cos(\frac{2\pi}{a}x)}{2}dx+\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{1-\cos(\frac{2\pi}{a}x)}{2}dx \\ &=\frac{\hbar^2\pi^2}{2ma^2}\cdot\frac{a}{2}+\frac{\hbar^2\pi^2}{20ma^2}\cdot(\frac{a}{6}+\frac{\sqrt{3}a}{4\pi})=\frac{\hbar^2\pi^2}{40ma}(\frac{31}{3}+\frac{\sqrt{3}}{2\pi}) \end{aligned}$$

$$\begin{aligned} H_{12}&=\int_0^a\sin(\frac{\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{3\pi}{a}x)]}{dx^2}\}dx+\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)dx \\ &=\frac{9\hbar^2\pi^2}{2ma^2}\int_0^a\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)dx+\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}\sin(\frac{\pi}{a}x)\sin(\frac{3\pi}{a}x)dx \\ &=\frac{9\hbar^2\pi^2}{2ma^2}\int_0^a\frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]dx+\frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}}\frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]dx \\ &=\frac{9\hbar^2\pi^2}{2ma^2}\cdot 0+\frac{\hbar^2\pi^2}{20ma^2}\cdot(-\frac{3\sqrt{3}a}{8\pi})=-\frac{3\sqrt{3}\hbar^2\pi}{160ma} \end{aligned}$$

$$
\begin{aligned}
H_{13} &= \int_0^a \sin(\frac{\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{5\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{\pi}{a}x)\sin(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \sin(\frac{\pi}{a}x)\sin(\frac{5\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin(\frac{\pi}{a}x)\sin(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1}{2}[\cos(\frac{4\pi}{a}x)-\cos(\frac{6\pi}{a}x)]dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1}{2}[\cos(\frac{4\pi}{a}x)-\cos(\frac{6\pi}{a}x)]dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\cdot 0 + \frac{\hbar^2\pi^2}{20ma^2}\cdot\frac{\sqrt{3}a}{8\pi} = \frac{\sqrt{3}\hbar^2\pi}{160ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{21} &= \int_0^a \sin(\frac{3\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{3\pi}{a}x)\sin(\frac{\pi}{a}x)dx \\
&= \frac{\hbar^2\pi^2}{2ma^2}\int_0^a \sin(\frac{3\pi}{a}x)\sin(\frac{\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin(\frac{3\pi}{a}x)\sin(\frac{\pi}{a}x)dx \\
&= \frac{\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{4\pi}{a}x)]dx \\
&= \frac{\hbar^2\pi^2}{2ma^2}\cdot 0 + \frac{\hbar^2\pi^2}{20ma^2}\cdot(-\frac{3\sqrt{3}a}{8\pi}) = -\frac{3\sqrt{3}\hbar^2\pi}{160ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{22} &= \int_0^a \sin(\frac{3\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{3\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin^2(\frac{3\pi}{a}x)dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\int_0^a \sin^2(\frac{3\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin^2(\frac{3\pi}{a}x)dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1-\cos(\frac{6\pi}{a}x)}{2}dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1-\cos(\frac{6\pi}{a}x)}{2}dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\cdot\frac{a}{2} + \frac{\hbar^2\pi^2}{20ma^2}\cdot\frac{a}{6} = \frac{271\hbar^2\pi^2}{120ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{23} &= \int_0^a \sin(\frac{3\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{5\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{3\pi}{a}x)\sin(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \sin(\frac{3\pi}{a}x)\sin(\frac{5\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin(\frac{3\pi}{a}x)\sin(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{8\pi}{a}x)]dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{8\pi}{a}x)]dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\cdot 0 + \frac{\hbar^2\pi^2}{20ma^2}\cdot(-\frac{3\sqrt{3}a}{16\pi}) = -\frac{3\sqrt{3}\hbar^2\pi}{320ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{31} &= \int_0^a \sin(\frac{5\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{5\pi}{a}x)\sin(\frac{\pi}{a}x)dx \\
&= \frac{\hbar^2\pi^2}{2ma^2}\int_0^a \sin(\frac{5\pi}{a}x)\sin(\frac{\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin(\frac{5\pi}{a}x)\sin(\frac{\pi}{a}x)dx \\
&= \frac{\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1}{2}[\cos(\frac{4\pi}{a}x)-\cos(\frac{6\pi}{a}x)]dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1}{2}[\cos(\frac{4\pi}{a}x)-\cos(\frac{6\pi}{a}x)]dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\cdot 0 + \frac{\hbar^2\pi^2}{20ma^2}\cdot\frac{\sqrt{3}a}{8\pi} = \frac{\sqrt{3}\hbar^2\pi}{160ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{32} &= \int_0^a \sin(\frac{5\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{3\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin(\frac{5\pi}{a}x)\sin(\frac{3\pi}{a}x)dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\int_0^a \sin(\frac{5\pi}{a}x)\sin(\frac{3\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin(\frac{5\pi}{a}x)\sin(\frac{3\pi}{a}x)dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{8\pi}{a}x)]dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1}{2}[\cos(\frac{2\pi}{a}x)-\cos(\frac{8\pi}{a}x)]dx \\
&= \frac{9\hbar^2\pi^2}{2ma^2}\cdot 0 + \frac{\hbar^2\pi^2}{20ma^2}\cdot(-\frac{3\sqrt{3}a}{16\pi}) = -\frac{3\sqrt{3}\hbar^2\pi}{320ma}
\end{aligned}
$$

$$
\begin{aligned}
H_{33} &= \int_0^a \sin(\frac{5\pi}{a}x)\cdot\{-\frac{\hbar^2}{2m}\frac{d^2[\sin(\frac{5\pi}{a}x)]}{dx^2}\}dx + \int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{\hbar^2\pi^2}{20ma^2}\sin^2(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \sin^2(\frac{5\pi}{a}x)dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \sin^2(\frac{5\pi}{a}x)dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\int_0^a \frac{1-\cos(\frac{10\pi}{a}x)}{2}dx + \frac{\hbar^2\pi^2}{20ma^2}\int_{\frac{a}{3}}^{\frac{2a}{3}} \frac{1-\cos(\frac{10\pi}{a}x)}{2}dx \\
&= \frac{25\hbar^2\pi^2}{2ma^2}\cdot\frac{a}{2} + \frac{\hbar^2\pi^2}{20ma^2}\cdot(\frac{a}{6}-\frac{\sqrt{3}a}{20\pi}) = \frac{\hbar^2\pi^2}{40ma}(\frac{751}{3}-\frac{\sqrt{3}}{10\pi})
\end{aligned}
$$

因此代回矩阵方程得

$$
\begin{bmatrix}
\frac{\hbar^2\pi^2}{40ma}(\frac{31}{3}+\frac{\sqrt{3}}{2\pi})-\frac{a}{2}E & -\frac{3\sqrt{3}\hbar^2\pi}{160ma} & \frac{\sqrt{3}\hbar^2\pi}{160ma} \\
-\frac{3\sqrt{3}\hbar^2\pi}{160ma} & \frac{271\hbar^2\pi^2}{120ma}-\frac{a}{2}E & -\frac{3\sqrt{3}\hbar^2\pi}{320ma} \\
\frac{\sqrt{3}\hbar^2\pi}{160ma} & -\frac{3\sqrt{3}\hbar^2\pi}{320ma} & \frac{\hbar^2\pi^2}{40ma}(\frac{751}{3}-\frac{\sqrt{3}}{10\pi})-\frac{a}{2}E
\end{bmatrix}
\begin{bmatrix} 1 \\ \lambda_1 \\ \lambda_2 \end{bmatrix} = 0
$$

该方程中符合条件的解为$\begin{cases} \lambda_1 \approx 5.18\times10^{-3} \\ \lambda_2 \approx -5.71\times10^{-4} \\ E \approx 0.530\frac{\hbar^2\pi^2}{ma^2} \end{cases}$，与（1）得出的结果相近

6.4 一维谐振子体系，势能为$V(x)=\frac{1}{2}m\omega^2x^2$，请用$\psi(x)=A\mathrm{e}^{-\frac{\lambda^2}{2}x^2}$作为试探波函数，用变分法获得最低能级的能量，其中$\lambda$为调节参数，并与精确解比较

解：一维谐振子体系的总哈密尔顿算符为$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2\hat{x}^2$，因此变分法得到最低能级的能量为

$$\langle \widetilde{E}_0\rangle = \frac{\langle\psi|\hat{H}_0|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\int_{-\infty}^{+\infty} A^* \mathrm{e}^{-\frac{\lambda^2}{2}x^2}\cdot(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2\hat{x}^2)(A\mathrm{e}^{-\frac{\lambda^2}{2}x^2})dx}{\int_{-\infty}^{+\infty}|A|^2\mathrm{e}^{-\lambda^2x^2}dx}$$
$$= \frac{\int_{-\infty}^{+\infty}|A|^2\cdot[-\frac{\hbar^2}{2m}\mathrm{e}^{-\frac{\lambda^2}{2}x^2}\frac{d^2(\mathrm{e}^{-\frac{\lambda^2}{2}x^2})}{dx^2}+\frac{1}{2}m\omega^2x^2\mathrm{e}^{-\lambda^2x^2}]dx}{\int_{-\infty}^{+\infty}|A|^2\mathrm{e}^{-\lambda^2x^2}dx}$$
$$= \frac{\int_{-\infty}^{+\infty}[-\frac{\hbar^2}{2m}\mathrm{e}^{-\frac{\lambda^2}{2}x^2}\frac{d(-\lambda^2x\mathrm{e}^{-\frac{\lambda^2}{2}x^2})}{dx}+\frac{1}{2}m\omega^2x^2\mathrm{e}^{-\lambda^2x^2}]dx}{\int_{-\infty}^{+\infty}\mathrm{e}^{-\lambda^2x^2}dx}$$
$$= \frac{\int_{-\infty}^{+\infty}[-\frac{\hbar^2}{2m}\mathrm{e}^{-\frac{\lambda^2}{2}x^2}(-\lambda^2\mathrm{e}^{-\frac{\lambda^2}{2}x^2}+\lambda^4x^2\mathrm{e}^{-\frac{\lambda^2}{2}x^2})+\frac{1}{2}m\omega^2x^2\mathrm{e}^{-\lambda^2x^2}]dx}{\int_{-\infty}^{+\infty}\mathrm{e}^{-\lambda^2x^2}dx}$$
$$= \frac{\frac{\hbar^2\lambda^2}{2m}\int_{-\infty}^{+\infty}\mathrm{e}^{-\lambda^2x^2}dx+(-\frac{\hbar^2\lambda^4}{2m}+\frac{m\omega^2}{2})\int_{-\infty}^{+\infty}x^2\mathrm{e}^{-\lambda^2x^2}dx}{\int_{-\infty}^{+\infty}\mathrm{e}^{-\lambda^2x^2}dx}$$
$$= \frac{\frac{\hbar^2\lambda^2}{2m}\frac{\sqrt{\pi}}{\lambda}+(-\frac{\hbar^2\lambda^4}{2m}+\frac{m\omega^2}{2})\frac{\sqrt{\pi}}{2\lambda^3}}{\frac{\sqrt{\pi}}{\lambda}} = \frac{\hbar^2\lambda^2}{2m}+(-\frac{\hbar^2\lambda^4}{2m}+\frac{m\omega^2}{2})\frac{1}{2\lambda^2}$$
$$= \frac{\hbar^2\lambda^2}{4m}+\frac{m\omega^2}{4\lambda^2}\geq 2\sqrt{\frac{\hbar^2\lambda^2}{4m}\cdot\frac{m\omega^2}{4\lambda^2}} = \frac{\hbar\omega}{2}$$

等号在$\frac{\hbar^2\lambda^2}{4m}=\frac{m\omega^2}{4\lambda^2}$，即$\lambda=\pm\sqrt{\frac{m\omega}{\hbar}}$成立，取$\lambda=\sqrt{\frac{m\omega}{\hbar}}$，则$\psi(x)=A\mathrm{e}^{-\frac{m\omega x^2}{2\hbar}}$，根据归一化条件，有

$$\langle\psi|\psi\rangle = \int_{-\infty}^{+\infty}|\psi(x)|^2dx = \int_{-\infty}^{+\infty}|A|^2\mathrm{e}^{-\lambda^2x^2}dx = |A|^2\cdot\frac{\sqrt{\pi}}{\lambda} = |A|^2\sqrt{\frac{\pi\hbar}{m\omega}} = 1$$

解得$|A|=(\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}$，若$A$取正实数，则$\psi(x)=(\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}\mathrm{e}^{-\frac{m\omega x^2}{2\hbar}}$，与精确解完全一致

课堂练习（续）

练习1：假定体系初态处于物理量算符$\hat{A}$的本征值为a_i的本征态$|a_i\rangle$，如果$\hat{A}$是个守恒量，证明体系将始终处于该算符的本征值为a_i的本征态

证明：由于$\hat{A}$为守恒量，因此$[\hat{A},\hat{H}]=0$，而时间演化算符$\hat{U}(t)=\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}$，因此有$[\hat{A},\hat{U}(t)]=0$，从而

$$\hat{A}|\psi(t)\rangle = \hat{A}\hat{U}(t)|a_i\rangle = \hat{U}(t)\hat{A}|a_i\rangle = \hat{U}(t)a_i|a_i\rangle = a_i|\psi(t)\rangle$$

练习2：证明宇称算符作用在动量本征态上满足$\hat{\pi}|\boldsymbol{p}\rangle=|-\boldsymbol{p}\rangle$，并且宇称算符和动量算符也反对易，满足$\hat{\boldsymbol{p}}\hat{\pi}=-\hat{\pi}\hat{\boldsymbol{p}}$，即动量算符和坐标算符一样，也是宇称奇算符

证明：我们知道宇称算符作用在坐标本征态的结果为$\hat{\pi}|\boldsymbol{x}\rangle=|-\boldsymbol{x}\rangle$，因此

$$\hat{\pi}|\boldsymbol{p}\rangle = \int\hat{\pi}|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\boldsymbol{p}\rangle d\boldsymbol{x} = \int|-\boldsymbol{x}\rangle\langle\boldsymbol{x}|\boldsymbol{p}\rangle d\boldsymbol{x} = \int(2\pi\hbar)^{-\frac{3}{2}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}}|-\boldsymbol{x}\rangle d\boldsymbol{x}$$
$$= \int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}dy\int_{-\infty}^{+\infty}dz(2\pi\hbar)^{-\frac{3}{2}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}}|-\boldsymbol{x}\rangle$$
$$= (-1)^3\int_{+\infty}^{-\infty}dx'\int_{+\infty}^{-\infty}dy'\int_{+\infty}^{-\infty}dz'\,(2\pi\hbar)^{-\frac{3}{2}}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}'}|\boldsymbol{x}'\rangle$$
$$= \int|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|-\boldsymbol{p}\rangle d\boldsymbol{x}' = |-\boldsymbol{p}\rangle$$

从而

$$\hat{\pi}\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \hat{\pi}\boldsymbol{p}|\boldsymbol{p}\rangle = \boldsymbol{p}\hat{\pi}|\boldsymbol{p}\rangle = \boldsymbol{p}|-\boldsymbol{p}\rangle \qquad \hat{\boldsymbol{p}}\hat{\pi}|\boldsymbol{p}\rangle = \hat{\boldsymbol{p}}|-\boldsymbol{p}\rangle = -\boldsymbol{p}|-\boldsymbol{p}\rangle$$

即有$\hat{\pi}\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle+\hat{\boldsymbol{p}}\hat{\pi}|\boldsymbol{p}\rangle=\boldsymbol{p}|-\boldsymbol{p}\rangle-\boldsymbol{p}|-\boldsymbol{p}\rangle=\boldsymbol{0}$，故$\hat{\boldsymbol{p}}\hat{\pi}=-\hat{\pi}\hat{\boldsymbol{p}}$，证毕

练习3：证明宇称偶算符的本征态总可以取为具有确定的宇称对称性

证明：若$[\hat{A},\hat{\pi}]=0$，$\hat{A}|a\rangle=a|a\rangle$，则可设$|\tilde{a}_{\pm}\rangle=\frac{1}{2}(1\pm\hat{\pi})|a\rangle$，此时有

$$
\begin{gathered}
\hat{\pi}|\tilde{a}_{\pm}\rangle=\hat{\pi}[\frac{1}{2}(1\pm\hat{\pi})|a\rangle]=\frac{1}{2}(\hat{\pi}\pm\hat{\pi}^2)|a\rangle=\frac{1}{2}(\hat{\pi}\pm1)|a\rangle=\pm|\tilde{a}_{\pm}\rangle \\
\hat{A}|\tilde{a}_{\pm}\rangle=\hat{A}[\frac{1}{2}(1\pm\hat{\pi})|a\rangle]=\frac{1}{2}(\hat{A}\pm\hat{A}\hat{\pi})|a\rangle=\frac{1}{2}(\hat{A}\pm\hat{\pi}\hat{A})|a\rangle=a\cdot\frac{1}{2}(1\pm\hat{\pi})|a\rangle=a_i|\tilde{a}_{\pm}\rangle
\end{gathered}
$$

故$|\tilde{a}_{\pm}\rangle$是算符$\hat{A}$的本征值为a的本征态，且具有确定的宇称对称性