

## 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？**

$$k = l \frac{2\pi}{L} = \frac{l}{N} \frac{2\pi}{a} \quad (l = 0, \pm 1, \pm 2, \pm 3, \dots)$$

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 $\phi_k(x) = L^{-\frac{1}{2}} e^{ikx}$ ，其中 $L = Na$ ，代入得

$$L^{-\frac{1}{2}} e^{ik(x+Na)} = L^{-\frac{1}{2}} e^{ikx} \Rightarrow e^{ikNa} = 1 \Rightarrow kNa = 2\pi l \quad (l = 0, \pm 1, \pm 2, \pm 3, \dots)$$

由此可得 $k = \frac{l}{N} \frac{2\pi}{a} (l = 0, \pm 1, \pm 2, \pm 3, \dots)$

**练习2：对于矩阵元 $V_{kk'} \equiv \langle \phi_k | \hat{V} | \phi_{k'} \rangle = L^{-1} \int_0^L V(x) e^{-i(k-k')x} dx$ ，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

$$V_l \equiv a^{-1} \int_0^a V(x) e^{-i \frac{2\pi l}{a} x} dx$$

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

这样展开似乎找不出思路，我们改用如下方法：

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

若 $e^{-i(k-k')a} = e^{-i \frac{2\pi(l-l')}{L} a} \neq 1$ ，则 $\sum_{n=0}^{N-1} e^{-i(k-k')na} = \frac{1 - e^{-i(k-k')(N-1)a}}{1 - e^{-i(k-k')a}} = \frac{1 - e^{-i \frac{2\pi(l-l')}{L} (N-1)a}}{1 - e^{-i \frac{2\pi(l-l')}{L} a}} = 0$ ，故为使级

数不为零，必须使 $e^{-i(k-k')a} = 1$ ，从而有 $(k - k')a = 2\pi l (l \in \mathbb{Z})$ ，即 $k - k' = \frac{2\pi}{a} l$ ，从而

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

**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

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

因此

$$\begin{aligned}
\psi_k(x + na) &= L^{-\frac{1}{2}} e^{ik(x+na)} \left\{ 1 + \frac{2m}{\hbar^2} \sum_{l \neq 0} \frac{V_l^*}{[k^2 - (k - \frac{2\pi}{a}l)^2]} e^{-i\frac{2\pi l(x+na)}{a}} \right\} \\
&= e^{ikna} \cdot L^{-\frac{1}{2}} e^{ikx} \left\{ 1 + \frac{2m}{\hbar^2} \sum_{l \neq 0} \frac{V_l^*}{[k^2 - (k - \frac{2\pi}{a}l)^2]} e^{-i\frac{2\pi lx}{a}} e^{-2\pi i n l} \right\} \\
&= e^{ikna} \cdot L^{-\frac{1}{2}} e^{ikx} \left\{ 1 + \frac{2m}{\hbar^2} \sum_{l \neq 0} \frac{V_l^*}{[k^2 - (k - \frac{2\pi}{a}l)^2]} e^{-i\frac{2\pi lx}{a}} \right\} = e^{ikna} \psi_k(x)
\end{aligned}$$

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

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

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

**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

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

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

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

## 第六章习题

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

$$H' = \begin{cases} 0 & (t < 0) \\ a_0 x e^{-\frac{t}{\tau}} & (t > 0) \end{cases}$$

**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

$$\begin{aligned}
c_n^{(1)}(t) &= -\frac{i}{\hbar} \int_0^t \langle n | \hat{H}'(t_1) | i \rangle dt_1 = -\frac{i}{\hbar} \int_0^t e^{\frac{i}{\hbar}(E_n - E_i)t_1} \langle n | \hat{H}'(t_1) | i \rangle dt_1 \\
&= -\frac{i}{\hbar} \int_0^t e^{i(n-i)\omega_0 t_1} \langle n | a_0 \hat{x} e^{-\frac{t_1}{\tau}} | i \rangle dt_1 = -\frac{ia_0}{\hbar} \int_0^t e^{[i(n-i)\omega_0 - \frac{1}{\tau}]t_1} \langle n | \hat{x} | i \rangle dt_1 \\
&= -\frac{ia_0}{\hbar} \int_0^t e^{[i(n-i)\omega_0 - \frac{1}{\tau}]t_1} \langle n | \sqrt{\frac{\hbar}{2\mu\omega_0}} (\sqrt{i+1}|i+1\rangle + \sqrt{i}|i-1\rangle) dt_1 \\
&= -\frac{ia_0}{\hbar} \sqrt{\frac{\hbar}{2\mu\omega_0}} (\sqrt{i+1}\delta_{n,i+1} + \sqrt{i}\delta_{n,i-1}) \int_0^t e^{[i(n-i)\omega_0 - \frac{1}{\tau}]t_1} dt_1 \\
&= -\frac{ia_0}{\hbar} \sqrt{\frac{\hbar}{2\mu\omega_0}} (\sqrt{i+1}\delta_{n,i+1} + \sqrt{i}\delta_{n,i-1}) \frac{e^{[i(n-i)\omega_0 - \frac{1}{\tau}]t} - 1}{i(n-i)\omega_0 - \frac{1}{\tau}}
\end{aligned}$$

而由题意,  $i = 0$ , 结合上式可知, 当  $n > 1$  时, 有  $c_n^{(1)}(t) = 0$ , 从而  $P_{n \leftarrow 0}^{(1)}(t) = 0$ ; 当  $n = 1$  时, 有

$$c_1^{(1)}(t) = -\frac{ia_0}{\hbar} \sqrt{\frac{\hbar}{2\mu\omega_0}} \frac{e^{(i\omega_0 - \frac{1}{\tau})t} - 1}{i\omega_0 - \frac{1}{\tau}}, \text{ 从而 } t \text{ 足够大时, 可得}$$

$$\begin{aligned}
\lim_{t \rightarrow \infty} c_1^{(1)}(t) &= \lim_{t \rightarrow \infty} -\frac{ia_0}{\hbar} \sqrt{\frac{\hbar}{2\mu\omega_0}} \frac{e^{(i\omega_0 - \frac{1}{\tau})t} - 1}{i\omega_0 - \frac{1}{\tau}} = \frac{ia_0}{\hbar} \sqrt{\frac{\hbar}{2\mu\omega_0}} \frac{1}{i\omega_0 - \frac{1}{\tau}} \\
\lim_{t \rightarrow \infty} P_{1 \leftarrow 0}^{(1)}(t) &= \lim_{t \rightarrow \infty} |c_1^{(1)}(t)|^2 = \lim_{t \rightarrow \infty} \frac{a_0^2}{2\mu\hbar\omega_0} \frac{e^{-\frac{2}{\tau}t} - e^{i(\omega_0 - \frac{1}{\tau})t} - e^{-i(\omega_0 + \frac{1}{\tau})t} + 1}{\frac{1}{\tau^2} + \omega_0^2} = \frac{a_0^2}{2\mu\hbar\omega_0} \frac{1}{\frac{1}{\tau^2} + \omega_0^2}
\end{aligned}$$

**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  $\varepsilon$  的作用的问题, 与 §6.3 节的结果比较。将极化率  $\alpha$  定义为诱导偶极矩  $\mu$  与外场强度  $\varepsilon$  之比, 证明能量改变为  $-\frac{\alpha\varepsilon^2}{2}$**

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

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

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  $\hat{H}_{tr} = -\frac{\hbar^2}{2m} \frac{d^2}{dx'^2} + \frac{m\omega_0^2 \hat{x}'^2}{2}$  , 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

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

(1)取  $\hat{H}_0$  的势能函数为  $V_0(x) = \begin{cases} \infty & (x \leq 0, x \geq a) \\ 0 & (0 < x < a) \end{cases}$  , 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  $\hat{H}' = \begin{cases} 0 & (x < \frac{a}{3}, x > \frac{2a}{3}) \\ \frac{\hbar^2\pi^2}{20ma^2} & (\frac{a}{3} \leq x \leq \frac{2a}{3}) \end{cases}$  , 因此基态能量的一级微扰为

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

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

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

因此变分法得到的基态能量为

$$\begin{aligned} \langle \tilde{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)|^2 dx}{\int_0^a |\psi(x)|^2 dx} \\ &= \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)]^2 dx} \\ &\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)]^2 dx}{\int_0^a [\sin(\frac{\pi}{a}x) + \lambda \sin(\frac{3\pi}{a}x)]^2 dx} \\ &= \frac{\frac{\hbar^2 \pi^2}{2ma^2} \int_0^a [\sin^2(\frac{\pi}{a}x) + 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 $\langle \tilde{E}_0 \rangle$ 对 $\lambda$ 求导, 得

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

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  $\lambda = \frac{\sqrt{3}-160\pi}{3\sqrt{3}} + \frac{10\pi}{3\sqrt{3}} \sqrt{256 - \frac{16\sqrt{3}}{5\pi} + \frac{3}{10\pi^2}} \approx 5.19 \times 10^{-3}$ ，代回能量的表达式，得  $\langle \tilde{E}_0 \rangle \approx 0.530 \frac{\hbar^2 \pi^2}{ma^2}$

(3)假设基组正交归一，线性变分法要求解的方程为  $\sum_{j=1}^N (H_{ij} - E\delta_{ij})c_j = 0$ ，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  $S = \int |\psi_i(x)|^2 dx$ ，则线性变分法要求解的方程为  $\sum_{j=1}^N (H_{ij} - ES\delta_{ij})c_j = 0$ ，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  $S = \int_0^a |\sin(\frac{i\pi}{a}x)|^2 dx = \frac{a}{2}$ ，故接下来只需要知道  $H_{ij}$  的大小即可，而

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

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

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

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

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

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

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

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

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

因此代回矩阵方程得

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

该方程中符合条件的解为  $\begin{cases} \lambda_1 \approx 5.18 \times 10^{-3} \\ \lambda_2 \approx -5.71 \times 10^{-4}, \text{ 与 (1) 得出的结果相近} \\ E \approx 0.530 \frac{\hbar^2 \pi^2}{ma^2} \end{cases}$

**6.4 一维谐振子体系，势能为  $V(x) = \frac{1}{2}m\omega^2 x^2$ ，请用  $\psi(x) = Ae^{-\frac{\lambda^2}{2}x^2}$  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



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

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  $\psi(x) = A e^{-\frac{m \omega x^2}{2\hbar}}$ , 根据归一化条件, 有

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

解得  $|A| = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}}$ , 若  $A$  取正实数, 则  $\psi(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} e^{-\frac{m \omega x^2}{2\hbar}}$ , 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  $\hat{U}(t) = e^{-\frac{i}{\hbar} \hat{H} t}$ , 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  $\hat{\pi} |p\rangle = |-p\rangle$ , 并且宇称算符和动量算符也反对易, 满足  $\hat{p} \hat{\pi} = -\hat{\pi} \hat{p}$ , 即动量算符和坐标算符一样, 也是宇称奇算符

**证明:**

**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:**