课堂练习

练习1：设有如下体系，其哈密尔顿算符$\hat{H}=\hat{H}_0+\hat{H}^{'}$，其中非扰动项$\hat{H}_0=E_1|1\rangle\langle 1|+E_2|2\rangle\langle 2|\ (E_1<E_2)$，扰动项$\hat{H}^{'}=V(|1\rangle\langle 2|+|2\rangle\langle 1|)\ (V\in\mathbb{R})$，求其能量的一阶修正和二阶修正

解：首先我们知道无扰动时，记此时的态矢为$|1^{(0)}\rangle$和$|2^{(0)}\rangle$，则基态能量为$E_1^{(0)}=\langle 1|\hat{H}_0|1\rangle=E_1$，$E_2^{(0)}=\langle 2|\hat{H}_0|2\rangle=E_2$，能量的一阶修正分别为$\delta E_1^{(1)}=\langle 1^{(0)}|\hat{H}^{'}|1^{(0)}\rangle=0$，$\delta E_2^{(1)}=\langle 2^{(0)}|\hat{H}^{'}|2^{(0)}\rangle=0$，而态矢的一阶修正为：

$$|\delta 1^{(1)}\rangle=(E_1^{(0)}-\hat{H}_0)^{-1}\hat{P}_1\hat{H}^{'}|1^{(0)}\rangle=\sum_{k\neq 1}|k^{(0)}\rangle\frac{H^{'}_{k,1}}{E_1^{(0)}-E_k^{(0)}}=\frac{\langle 2^{(0)}|\hat{H}^{'}|1^{(0)}\rangle}{E_1^{(0)}-E_2^{(0)}}|2^{(0)}\rangle=\frac{V}{E_1-E_2}|2^{(0)}\rangle$$

$$|\delta 2^{(1)}\rangle=(E_2^{(0)}-\hat{H}_0)^{-1}\hat{P}_2\hat{H}^{'}|2^{(0)}\rangle=\sum_{k\neq 2}|k^{(0)}\rangle\frac{H^{'}_{k,2}}{E_2^{(0)}-E_k^{(0)}}=\frac{\langle 1^{(0)}|\hat{H}^{'}|2^{(0)}\rangle}{E_2^{(0)}-E_1^{(0)}}|1^{(0)}\rangle=\frac{V}{E_2-E_1}|1^{(0)}\rangle$$

因此能量的二阶修正分别为$\delta E_1^{(2)}=\langle 1^{(0)}|\hat{H}^{'}|\delta 1^{(1)}\rangle=\frac{V}{E_1-E_2}H^{'}_{1,2}=\frac{V^2}{E_1-E_2}$，$\delta E_2^{(2)}=\langle 1^{(0)}|\hat{H}^{'}|\delta 2^{(1)}\rangle=\frac{V}{E_2-E_1}H^{'}_{2,1}=\frac{V^2}{E_2-E_1}$

练习2：设体系的哈密尔顿算符与练习1相同，但非扰动项中$E_1=E_2$，求其能量的一阶修正和二阶修正（注：与助教讨论后，发现不需要求二阶修正）

解：当非扰动项中$E_1=E_2$（可均设为E）时，整个体系变为简并态体系，此时考虑求解如下方程$(\boldsymbol{H}^{'}-\delta E^{(1)}\boldsymbol{I})\begin{bmatrix}a_1\\a_2\end{bmatrix}=\boldsymbol{0}$，其对应的久期方程为$|\boldsymbol{H}^{'}-\delta E^{(1)}\boldsymbol{I}|=0$，即：

$$\begin{vmatrix}H^{'}_{11}-\delta E^{(1)} & H^{'}_{12}\\ H^{'}_{21} & H^{'}_{22}-\delta E^{(1)}\end{vmatrix}=\begin{vmatrix}0-\delta E^{(1)} & V\\ V & 0-\delta E^{(1)}\end{vmatrix}=0$$

由以上可以得到$\delta E^{(1)}=\pm V$，相应的，代回原方程，可得$\frac{(a_1)_+}{(a_2)_+}=1$，$\frac{(a_1)_-}{(a_2)_-}=-1$，设原态矢组合后的态矢为$|\phi_+\rangle=(a_1)_+|1\rangle+(a_2)_+|2\rangle$，$|\phi_-\rangle=(a_1)_-|1\rangle+(a_2)_-|2\rangle$，则根据归一化性质$\begin{cases}\langle\phi_+|\phi_+\rangle=1\\ \langle\phi_-|\phi_-\rangle=1\end{cases}$，解得$\begin{cases}(a_1)_+=(a_2)_+=\frac{1}{\sqrt{2}}\\ (a_1)_-=-(a_2)_-=\frac{1}{\sqrt{2}}\end{cases}$，从而受微扰后，态矢变为$|\phi_+\rangle=\frac{1}{\sqrt{2}}(|1\rangle+|2\rangle)$，$|\phi_-\rangle=\frac{1}{\sqrt{2}}(|1\rangle-|2\rangle)$。

练习3：（1）用$(2n+1)$定理推导$E_n^{(3)}$；（2）根据微扰理论，直接求出考虑到三阶能量修正的结果，并与$(2n+1)$定理的结果做比较，看是否相同

解：（1）将受到微扰的态矢展开，得$|n\rangle\approx|n^{(p)}\rangle=|n^{(0)}\rangle+|\delta n^{(1)}\rangle+\cdots+|\delta n^{(p)}\rangle$，根据$(2n+1)$定理，考虑到$(2p+1)$阶能量修正的本征能量为$E_n^{(2p+1)}=\frac{\langle n^{(p)}|(\hat{H}_0+\hat{H}^{'})|n^{(p)}\rangle}{\langle n^{(p)}|n^{(p)}\rangle}$，因此当$p=1$时，代入得：

$$\begin{aligned}E_n^{(3)}&=\frac{\langle n^{(1)}|(\hat{H}_0+\hat{H}^{'})|n^{(1)}\rangle}{\langle n^{(1)}|n^{(1)}\rangle}=\frac{(\langle n^{(0)}|+\langle\delta n^{(1)}|)(\hat{H}_0+\hat{H}^{'})(|n^{(0)}\rangle+|\delta n^{(1)}\rangle)}{(\langle n^{(0)}|+\langle\delta n^{(1)}|)(|n^{(0)}\rangle+|\delta n^{(1)}\rangle)}\\&=\frac{\langle n^{(0)}|(\hat{H}_0+\hat{H}^{'})|n^{(0)}\rangle+\langle\delta n^{(1)}|(\hat{H}_0+\hat{H}^{'})|n^{(0)}\rangle+\langle n^{(0)}|(\hat{H}_0+\hat{H}^{'})|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|(\hat{H}_0+\hat{H}^{'})|\delta n^{(1)}\rangle}{\langle n^{(0)}|n^{(0)}\rangle+\langle\delta n^{(1)}|n^{(0)}\rangle+\langle n^{(0)}|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|\delta n^{(1)}\rangle}\\&=\frac{E_n^{(0)}+\delta E_n^{(1)}+2\delta E_n^{(2)}+\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|\hat{H}^{'}|\delta n^{(1)}\rangle}{1+\langle\delta n^{(1)}|\delta n^{(1)}\rangle}\ (\text{因}\ \delta E_n^{(2)}=\langle n^{(0)}|\hat{H}^{'}|\delta n^{(1)}\rangle\text{满足厄米性，从而为实数})\end{aligned}$$

对分母作泰勒展开，得：

$$\frac{1}{1+\langle\delta n^{(1)}|\delta n^{(1)}\rangle}=\sum_{i=0}^{\infty}\frac{d^i(\frac{1}{x})}{dx^i}\frac{\langle\delta n^{(1)}|\delta n^{(1)}\rangle^i}{i!}=1-\langle\delta n^{(1)}|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|\delta n^{(1)}\rangle^2-\langle\delta n^{(1)}|\delta n^{(1)}\rangle^3+\cdots\approx 1-\langle\delta n^{(1)}|\delta n^{(1)}\rangle$$

因此有：

$$\begin{aligned}E_n^{(3)}&\approx[E_n^{(0)}+\delta E_n^{(1)}+2\delta E_n^{(2)}+\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle](1-\langle\delta n^{(1)}|\delta n^{(1)}\rangle)\\&\approx E_n^{(0)}+\delta E_n^{(1)}+2\delta E_n^{(2)}+\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle+\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle-E_n^{(0)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle-\delta E_n^{(1)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle\\&=E_n^{(0)}+\delta E_n^{(1)}+(2\delta E_n^{(2)}+\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle-E_n^{(0)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle)+(\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle-\delta E_n^{(1)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle)\end{aligned}$$

又知道$|\delta n^{(1)}\rangle=\sum\limits_{k\neq n}|k^{(0)}\rangle\frac{H'_{kn}}{E_n^{(0)}-E_k^{(0)}}$，因此有：

$$\langle\delta n^{(1)}|\delta n^{(1)}\rangle=[\sum_{k_1\neq n}\langle k_1^{(0)}|(\frac{H'_{k_1n}}{E_n^{(0)}-E_{k_1}^{(0)}})^*](\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H'_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}})=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{\delta_{k_1k_2}H'_{nk_1}H'_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}=\sum_{k_1\neq n}\frac{|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}$$

此处利用到能量本征值为实数，且$\hat{H}'$为厄米算符的特点。而对$\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle$，有：

$$\begin{aligned}\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle&=[\sum_{k_1\neq n}\langle k_1^{(0)}|(\frac{H'_{k_1n}}{E_n^{(0)}-E_{k_1}^{(0)}})^*]\hat{H}_0(\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H'_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}})=[\sum_{k_1\neq n}\langle k_1^{(0)}|(\frac{H'_{k_1n}}{E_n^{(0)}-E_{k_1}^{(0)}})^*](\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{E_{k_2}^{(0)}H'_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}})\\&=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{\delta_{k_1k_2}E_{k_2}^{(0)}H'_{nk_1}H'_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}=\sum_{k_1\neq n}\frac{E_{k_1}^{(0)}|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}\end{aligned}$$

从而有：

$$\begin{aligned}&2\delta E_n^{(2)}+\langle\delta n^{(1)}|\hat{H}_0|\delta n^{(1)}\rangle-E_n^{(0)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle=2\delta E_n^{(2)}+\sum_{k_1\neq n}\frac{E_{k_1}^{(0)}|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}-E_n^{(0)}\sum_{k_1\neq n}\frac{|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}\\&=2\delta E_n^{(2)}-\sum_{k_1\neq n}\frac{(E_n^{(0)}-E_{k_1}^{(0)})|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}=2\delta E_n^{(2)}-\sum_{k_1\neq n}\frac{|H'_{k_1n}|^2}{E_n^{(0)}-E_{k_1}^{(0)}}=2\delta E_n^{(2)}-\delta E_n^{(2)}=\delta E_n^{(2)}\end{aligned}$$

对$\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle$，有：

$$\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle=[\sum_{k_1\neq n}\langle k_1^{(0)}|(\frac{H'_{k_1n}}{E_n^{(0)}-E_{k_1}^{(0)}})^*]\hat{H}'(\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H'_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}})=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{H'_{nk_1}H'_{k_1k_2}H'_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}$$

从而有：

$$\begin{aligned}&\langle\delta n^{(1)}|\hat{H}'|\delta n^{(1)}\rangle-\delta E_n^{(1)}\langle\delta n^{(1)}|\delta n^{(1)}\rangle=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{H'_{nk_1}H'_{k_1k_2}H'_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}-\delta E_n^{(1)}\sum_{k_1\neq n}\frac{|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}\\&=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{H'_{nk_1}H'_{k_1k_2}H'_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}-\sum_{k_1\neq n}\frac{H'_{nn}|H'_{k_1n}|^2}{(E_n^{(0)}-E_{k_1}^{(0)})^2}\equiv\delta E_n^{(3)}\end{aligned}$$

因此$E_n^{(3)}=E_n^{(0)}+\delta E_n^{(1)}+\delta E_n^{(2)}+\delta E_n^{(3)}$

（2）我们知道$\delta E_n^{(1)}=\langle n^{(0)}|\hat{H}'|n^{(0)}\rangle=H'_{nn}$，$|\delta n^{(1)}\rangle=\sum\limits_{k\neq n}|k^{(0)}\rangle\frac{H'_{kn}}{E_n^{(0)}-E_k^{(0)}}$，且

$\delta E_n^{(2)}=\sum\limits_{k\neq n}\frac{|H'_{kn}|^2}{E_n^{(0)}-E_k^{(0)}}$，因此态矢的二阶修正为：

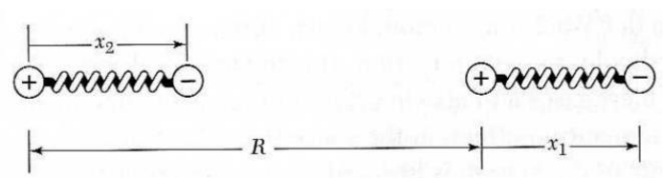
$$
\begin{aligned}
|\delta n^{(2)}\rangle &= (E_n^{(0)}-\hat{H}_0)^{-1}\hat{P}_n(\hat{H}^{'}-\delta E_n^{(1)})|\delta n^{(1)}\rangle = (E_n^{(0)}-\hat{H}_0)^{-1}\hat{P}_n\hat{H}^{'}|\delta n^{(1)}\rangle-(E_n^{(0)}-\hat{H}_0)^{-1}\hat{P}_n\delta E_n^{(1)}|\delta n^{(1)}\rangle \\
&= (E_n^{(0)}-\hat{H}_0)^{-1}(\sum_{k_1\neq n}|k_1^{(0)}\rangle\langle k_1^{(0)}|)\hat{H}^{'}\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H^{'}_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}}-(E_n^{(0)}-\hat{H}_0)^{-1}(\sum_{k_1\neq n}|k_1^{(0)}\rangle\langle k_1^{(0)}|)\delta E_n^{(1)}\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H^{'}_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}} \\
&= (E_n^{(0)}-\hat{H}_0)^{-1}\sum_{k_1\neq n}\sum_{k_2\neq n}|k_1^{(0)}\rangle\frac{H^{'}_{k_1k_2}H^{'}_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}}-(E_n^{(0)}-\hat{H}_0)^{-1}\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H^{'}_{nn}H^{'}_{k_2n}}{E_n^{(0)}-E_{k_2}^{(0)}} \\
&= \sum_{k_1\neq n}\sum_{k_2\neq n}|k_1^{(0)}\rangle\frac{H^{'}_{k_1k_2}H^{'}_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}-\sum_{k_2\neq n}|k_2^{(0)}\rangle\frac{H^{'}_{nn}H^{'}_{k_2n}}{(E_n^{(0)}-E_{k_2}^{(0)})^2}
\end{aligned}
$$

从而$\delta E_n^{(3)}=\langle n^{(0)}|\hat{H}^{'}|\delta n^{(2)}\rangle=\sum_{k_1\neq n}\sum_{k_2\neq n}\frac{H^{'}_{nk_1}H^{'}_{k_1k_2}H^{'}_{k_2n}}{(E_n^{(0)}-E_{k_1}^{(0)})(E_n^{(0)}-E_{k_2}^{(0)})}-\sum_{k_2\neq n}\frac{H^{'}_{nn}|H^{'}_{k_2n}|^2}{(E_n^{(0)}-E_{k_2}^{(0)})^2}$，故
$E_n^{(3)}=E_n^{(0)}+\delta E_n^{(1)}+\delta E_n^{(2)}+\delta E_n^{(3)}$

练习4：描述两个惰性气体原子之间的色散相互作用最简单的模型是用线性谐振子模型描述电子关于原子核的瞬时振荡。零阶的哈密顿算符对应于两个独立的谐振子哈密顿算符相加，而谐振子之间的静电相互作用对应于微扰项，采用微扰论方法推导出时原子之间的相互作用能表达式

解：如下图所示，设两个谐振子质量均为m，振动频率均为ω_0，谐振子内正电荷与负电荷电量均为e，且分别相距x_1,x_2，两个谐振子间正电荷相距$R(R\gg x_1,x_2)$，则该体系哈密尔顿算符可分为两部分，第一部分为不受相互作用时谐振子各自能量之和，即$\hat{H}_0=(\frac{\hat{p}_1^2}{2m}+\frac{m\omega_0^2\hat{x}_1^2}{2})+(\frac{\hat{p}_2^2}{2m}+\frac{m\omega_0^2\hat{x}_2^2}{2})$；第二部分则为因色散相互作用对体系能量的扰动，其具体的表达式为：

$$
\begin{aligned}
\hat{H}^{'} &= \frac{e^2}{4\pi\varepsilon_0}(\frac{1}{R}+\frac{1}{R+\hat{x}_1-\hat{x}_2}-\frac{1}{R-\hat{x}_2}-\frac{1}{R+\hat{x}_1})=\frac{e^2}{4\pi\varepsilon_0}[\frac{(R-\hat{x}_2)-R}{R(R-\hat{x}_2)}+\frac{(R+\hat{x}_1)-(R+\hat{x}_1-\hat{x}_2)}{(R+\hat{x}_1-\hat{x}_2)(R+\hat{x}_1)}] \\
&= \frac{e^2}{4\pi\varepsilon_0}[\frac{-\hat{x}_2}{R(R-\hat{x}_2)}+\frac{\hat{x}_2}{(R+\hat{x}_1-\hat{x}_2)(R+\hat{x}_1)}]=\frac{e^2\hat{x}_2}{4\pi\varepsilon_0}[\frac{-(R+\hat{x}_1-\hat{x}_2)(R+\hat{x}_1)+R(R-\hat{x}_2)}{R(R-\hat{x}_2)(R+\hat{x}_1-\hat{x}_2)(R+\hat{x}_1)}] \\
&= \frac{e^2\hat{x}_2}{4\pi\varepsilon_0}[\frac{(-2R-\hat{x}_1+\hat{x}_2)\hat{x}_1}{R(R-\hat{x}_2)(R+\hat{x}_1-\hat{x}_2)(R+\hat{x}_1)}]\approx-\frac{e^2\hat{x}_1\hat{x}_2}{2\pi\varepsilon_0R^3}
\end{aligned}
$$



利用分离变量法，得零级本征态波函数和能量为：

$$
\begin{cases}
\psi_{n_1n_2}^{(0)}(x_1,x_2)=\psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2) \\
E_{n_1n_2}^{(0)}=[(n_1+\frac{1}{2})+(n_2+\frac{1}{2})]\hbar\omega_0=(n_1+n_2+1)\hbar\omega_0
\end{cases}
$$

现在我们求考虑扰动对基态能量的影响，容易得到一阶能量修正为：

$$
\delta E_0^{(1)}=\langle\psi_{00}^{(0)}|\hat{H}^{'}|\psi_{00}^{(0)}\rangle=-\frac{e^2}{2\pi\varepsilon_0R^3}\iint x_1x_2|\psi_{00}^{(0)}(x_1,x_2)|^2dx_1dx_2=-\frac{e^2}{2\pi\varepsilon_0R^3}\int_{-\infty}^{+\infty}x_1|\psi_0^{(0)}(x_1)|^2dx_1\int_{-\infty}^{+\infty}x_2|\psi_0^{(0)}(x_2)|^2dx_2
$$

而$\psi_0^{(0)}(x_1)$和$\psi_0^{(0)}(x_2)$均具有$\psi(x)=\frac{1}{\pi^{\frac{1}{4}}\sqrt{x_0}}\mathrm{e}^{-\frac{x^2}{2x_0^2}}$ $(x_0=\sqrt{\frac{\hbar}{m\omega_0}})$的形式，因此这两个波函数均为偶函数（也是实函数），其平方的模也为偶函数（也是实函数），当它们乘上自变量后，$x_1|\psi_0^{(0)}(x_1)|^2$和$x_2|\psi_0^{(0)}(x_2)|^2$就变成奇函数，它们在实数轴上的积分为零，从而$\delta E_0^{(1)}=0$。
再考虑二阶能量修正，此时有：

$$\delta E_0^{(2)}=\sum_{n_1\neq 0}\sum_{n_2\neq 0}\frac{|\langle\psi_{n_1n_2}^{(0)}|\hat{H}'|\psi_{00}^{(0)}\rangle|^2}{E_{00}^{(0)}-E_{n_1n_2}^{(0)}}=\frac{e^4}{4\pi^2\varepsilon_0^2R^6}\sum_{n_1\neq 0}\sum_{n_2\neq 0}\frac{|\langle\psi_{n_1n_2}^{(0)}|\hat{x}_1\hat{x}_2|\psi_{00}^{(0)}\rangle|^2}{E_{00}^{(0)}-E_{n_1n_2}^{(0)}}=\frac{e^4}{4\pi^2\varepsilon_0^2R^6}\sum_{n_1\neq 0}\sum_{n_2\neq 0}\frac{|\langle\psi_{n_1}^{(0)}|\hat{x}_1|\psi_0^{(0)}\rangle\langle\psi_{n_2}^{(0)}|\hat{x}_2|\psi_0^{(0)}\rangle|^2}{-(n_1+n_2)\hbar\omega_0}$$
$$=\frac{e^4}{4\pi^2\varepsilon_0^2R^6}\sum_{n_1\neq 0}\sum_{n_2\neq 0}\frac{|\frac{\hbar}{2m\omega_0}\langle\psi_{n_1}^{(0)}|\psi_1^{(0)}\rangle\langle\psi_{n_2}^{(0)}|\psi_1^{(0)}\rangle|^2}{-(n_1+n_2)\hbar\omega_0}=\frac{e^4}{4\pi^2\varepsilon_0^2R^6}\cdot\frac{\hbar^2}{4m^2\omega_0^2}\cdot\frac{1}{-2\hbar\omega_0}=-\frac{e^4\hbar}{32\pi^2\varepsilon_0^2m^2\omega_0^3}\frac{1}{R^6}\propto\frac{1}{R^6}$$

练习5：通过线性变分得到的激发态能量是否满足变分原理（即$\lambda_k>E_k$）？为什么？

解：通过线性变分得到的激发态能量可以满足变分原理，但其应用条件较为严苛。将第k个激发态的试探态矢$|\tilde{k}\rangle$用试探基组$\{|\chi_i\rangle\}$展开，即$|\tilde{k}\rangle=\sum\limits_i|\chi_i\rangle\langle\chi_i|\tilde{k}\rangle$，若已知基态和激发态真实态矢$|0\rangle,|1\rangle,\ldots,|k-1\rangle$，且这些态矢均与$|\tilde{k}\rangle$正交，即$\langle 0|\tilde{k}\rangle=\langle 1|\tilde{k}\rangle=\cdots=\langle k-1|\tilde{k}\rangle=0$，则$|\tilde{k}\rangle=\sum\limits_{i'=0}|i'\rangle\langle i'|\tilde{k}\rangle=\sum\limits_{i'=k}|i'\rangle\langle i'|\tilde{k}\rangle$，用该试探态矢$|\tilde{k}\rangle$作线性变分，则有：

$$\langle\tilde{E}_k\rangle=\frac{\langle\tilde{k}|\hat{H}|\tilde{k}\rangle}{\langle\tilde{k}|\tilde{k}\rangle}=\frac{(\sum\limits_{i'=k}\langle\tilde{k}|i'\rangle\langle i'|)\hat{H}(\sum\limits_{j'=k}|j'\rangle\langle j'|\tilde{k}\rangle)}{(\sum\limits_{i'=k}\langle\tilde{k}|i'\rangle\langle i'|)(\sum\limits_{j'=k}|j'\rangle\langle j'|\tilde{k}\rangle)}=\frac{\sum\limits_{i'=k}|\langle i'|\tilde{k}\rangle|^2E_{i'}}{\sum\limits_{i'=k}|\langle i'|\tilde{k}\rangle|^2}=\frac{\sum\limits_{i'=k}|\langle i'|\tilde{k}\rangle|^2(E_{i'}-E_k)}{\sum\limits_{i'=k}|\langle i'|\tilde{k}\rangle|^2}+E_k\geq E_k$$

因此通过线性变分得到的激发态能量可以满足变分原理。
但是，如何把“可以”变为“一定”呢？毕竟我们仍无法确定，经线性变分得到的态矢$|\tilde{k}\rangle$，均能保证与基态和激发态真实态矢$|0\rangle,|1\rangle,\ldots,|k-1\rangle$正交。以下我们有简短的说明：
首先我们知道，若采用$|\tilde{0}\rangle,|\tilde{1}\rangle,\ldots,|\tilde{k}\rangle$作为近似基矢，其中$\langle\tilde{i}|\tilde{j}\rangle=\delta_{ij},\langle\tilde{i}|\hat{H}|\tilde{j}\rangle=\tilde{E}_i\delta_{ij}$，则对于任意$|\tilde{f}\rangle\in\{|\tilde{k}\rangle\}$，有：

$$\frac{\langle\tilde{f}|\hat{H}|\tilde{f}\rangle}{\langle\tilde{f}|\tilde{f}\rangle}=\frac{(\sum\limits_{i=0}^{k}\langle\tilde{f}|\tilde{i}\rangle\langle\tilde{i}|)\hat{H}(\sum\limits_{j'=0}^{k}|\tilde{j}\rangle\langle\tilde{j}|\tilde{f}\rangle)}{(\sum\limits_{i=0}^{k}\langle\tilde{f}|\tilde{i}\rangle\langle\tilde{i}|)(\sum\limits_{j'=0}^{k}|\tilde{j}\rangle\langle\tilde{j}|\tilde{f}\rangle)}=\frac{\sum\limits_{i=0}^{k}|\langle\tilde{i}|\tilde{f}\rangle|^2\tilde{E}_i}{\sum\limits_{i=0}^{k}|\langle\tilde{i}|\tilde{f}\rangle|^2}\leq\frac{\sum\limits_{i=0}^{k}|\langle\tilde{i}|\tilde{f}\rangle|^2\tilde{E}_k}{\sum\limits_{i=0}^{k}|\langle\tilde{i}|\tilde{f}\rangle|^2}=\tilde{E}_k$$

接下来，我们要证明，由能量小于等于$\tilde{E}_n$的实际态矢构成的线性空间$\{|n\rangle\}$，其维度应不小于$\tilde{E}_n$对应的试探态矢空间$\{|\tilde{n}\rangle\}$。
设投影算符$\hat{P}=\sum\limits_{E_j\leq\tilde{E}_n}|j\rangle\langle j|$，则$\hat{P}|\tilde{k}\rangle=\sum\limits_{E_j\leq\tilde{E}_n}|j\rangle\langle j|\tilde{k}\rangle\in\{|n\rangle\}$。现在我们证明$\hat{P}|\tilde{0}\rangle,\hat{P}|\tilde{1}\rangle,\ldots,\hat{P}|\tilde{n}\rangle$线性无关，若不然，存在不全为零的系数$a_0,a_1,\ldots,a_n$，使$\sum\limits_{i=0}^{n}a_i(\hat{P}|\tilde{i}\rangle)=0$，则$\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle=\sum\limits_{i=0}^{n}a_i(\hat{I}|\tilde{i}\rangle)=\sum\limits_{i=0}^{n}a_i[(\hat{I}-\hat{P})|\tilde{i}\rangle]=(\hat{I}-\hat{P})\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle$，另一方面，对$\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle$求能量（哈密尔顿量）平均值，得：

$$(\sum_{i=0}^{n}a_i^*\langle\tilde{i}|)\hat{H}(\sum_{i=0}^{n}a_i|\tilde{i}\rangle)=[(\hat{I}-\hat{P})\sum_{i=0}^{n}a_i^*\langle\tilde{i}|]\hat{H}[(\hat{I}-\hat{P})\sum_{i=0}^{n}a_i|\tilde{i}\rangle]=[\sum_{i=0}^{n}a_i^*\sum_{E_j>\tilde{E}_n}\langle\tilde{i}|j\rangle\langle j|]\hat{H}[\sum_{i=0}^{n}a_i\sum_{E_j>\tilde{E}_n}|j\rangle\langle j|\tilde{i}\rangle]$$
$$=\sum_{i=0}^{n}\sum_{E_j>\tilde{E}_n}|a_i|^2|\langle\tilde{i}|j\rangle|^2E_j>\sum_{i=0}^{n}\sum_{E_j>\tilde{E}_n}|a_i|^2|\langle\tilde{i}|j\rangle|^2\tilde{E}_n=\tilde{E}_n|(\hat{I}-\hat{P})\sum_{i=0}^{n}a_i|\tilde{i}\rangle|^2=\tilde{E}_n(\sum_{i=0}^{n}a_i^*\langle\tilde{i}|)(\sum_{i=0}^{n}a_i|\tilde{i}\rangle)$$

即$\frac{(\sum\limits_{i=0}^{n}a_i^*\langle\tilde{i}|)\hat{H}(\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle)}{(\sum\limits_{i=0}^{n}a_i^*\langle\tilde{i}|)(\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle)}>\tilde{E}_n$，这与上式中$\frac{\langle\tilde{f}|\hat{H}|\tilde{f}\rangle}{\langle\tilde{f}|\tilde{f}\rangle}\leq\tilde{E}_n$相矛盾（这是因为$\sum\limits_{i=0}^{n}a_i|\tilde{i}\rangle\in\{|\tilde{n}\rangle\}$），因此$\hat{P}|\tilde{0}\rangle,\hat{P}|\tilde{1}\rangle,\ldots,\hat{P}|\tilde{n}\rangle$线性无关，从而实际态矢构成的线性空间$\{|n\rangle\}$，其维度应不小于试探态矢$\{|\tilde{k}\rangle\}$，这等价于能量小于$\tilde{E}_n$的实际态矢有$(n+1)$个（此处从$|0\rangle$一直统计到$|n\rangle$），从而$E_n\leq\tilde{E}_n$。