Part I

作业

1 10.1

零级方程

$$(\hat{H}_0 - E_n^{(0)})\,|n\rangle = 0. \tag{1.1}$$

由谐振子结论，$E_n^{(0)} = (n+1/2)\,\hbar\omega$

$$\langle x|n\rangle = \psi_n^{(0)}(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}} H_n(\alpha x)\,\mathrm{e}^{-\alpha^2 x^2/2}, \quad \alpha = \sqrt{\frac{\mu\omega}{\hbar}}. \tag{1.2}$$

由 Hermite 多项式的结论

$$2zH_n(z) = 2nH_{n-1}(z) + H_{n+1}(z) \tag{1.3}$$

故

$$x\,|n\rangle = \frac{1}{\sqrt{2}\alpha}\left(\sqrt{n}\,|n-1\rangle + \sqrt{n+1}\,|n+1\rangle\right); \tag{1.4}$$

$$x^2\,|n\rangle = \frac{1}{2\alpha^2}\left[\sqrt{n(n-1)}\,|n-2\rangle + (2n+1)\,|n\rangle + \sqrt{(n+1)(n+2)}\,|n+2\rangle\right]; \tag{1.5}$$

$$\begin{aligned} x^3\,|n\rangle = \frac{1}{2\sqrt{2}\alpha^3}\Big[&\sqrt{n(n-1)(n-2)}\,|n-3\rangle + 3n\sqrt{n}\,|n-1\rangle + \\ &3(n+1)\sqrt{n+1}\,|n+1\rangle + \sqrt{(n+1)(n+2)(n+3)}\,|n+3\rangle\Big]. \end{aligned} \tag{1.6}$$

因此

$$\begin{aligned} H'_{nk} &= \langle n|\,\hat{H}'\,|k\rangle = \beta\,\langle n|\,x^3\,|k\rangle \\ &= \beta\left(\frac{\hbar}{2\mu\omega}\right)^{3/2}\left[\sqrt{n(n-1)(n-2)}\,\delta_{n,k-3} + \cdots\right]. \end{aligned} \tag{1.7}$$

一级微扰能 $E_n^{(1)} = H'_{nn} = 0$，二级微扰能

$$E_n^{(2)} = \sum_{m\neq n}\frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} = \sum_{m=\cdots}\frac{|H'_{mn}|^2}{(n-m)\hbar\omega} \tag{1.8}$$

由式 (1.7) 知，$m = n\pm 1, n\pm 3$，代入有

$$E_n^{(2)} = \frac{\beta^2}{\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^3\left[\frac{n(n-1)(n-2)}{3} + 9n^3 - 9(n+1)^3 - \frac{(n+1)(n+2)(n+3)}{3}\right]$$

$$= -(30n^2+30n+11)\frac{\beta^2\hbar^2}{8\mu^3\omega^4}. \tag{1.9}$$

故能量本征值

$$E_n = (2n+1)\frac{\hbar\omega}{2} - (30n^2+30n+11)\frac{\beta^2\hbar^2}{8\mu^3\omega^4}. \tag{1.10}$$

一阶微扰波函数

$$\psi_n^{(1)} = \sum_{m\neq n}\frac{H'_{mn}}{E_m^{(0)}-E_n^{(0)}}\psi_m^{(0)} \tag{1.11}$$

$$= \frac{\beta}{\hbar\omega}\left(\frac{\hbar}{2\mu\omega}\right)^{3/2}\left[\frac{\sqrt{n(n-1)(n-2)}}{3}\psi_{n-3}^{(0)} + 3n\sqrt{n}\psi_{n-1}^{(0)}\right.$$
$$\left. -3(n-1)\sqrt{n-1}\psi_{n+1}^{(0)} - \frac{\sqrt{(n+1)(n+2)(n+3)}}{3}\psi_{n+3}^{(0)}\right]. \tag{1.12}$$

波函数

$$\psi_n(x) = \psi_n^{(0)}(x) + \psi_n^{(1)}(x). \tag{1.13}$$

2 10.2

(a)

分离 $\Psi(x_1,x_2)=\psi_1(x_1)\psi_2(x_2)$

$$H_0 = \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x_1^2} + \frac{1}{2}\mu\omega^2x_1^2\right) + \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x_2^2} + \frac{1}{2}\mu\omega^2x_2^2\right). \tag{2.1}$$

易知，ψ_1,ψ_2 分别满足谐振子．故能量本征值

$$E_N^{(0)} = (n_1+n_2+1)\hbar\omega =: (N+1)\hbar\omega. \tag{2.2}$$

能级简并度 $f=N+1$.

(b)

第一激发态 $N=1$，有

$$\Psi_{11}^{(0)} = \psi_1(x_1)\psi_0(x_2), \quad \Psi_{12}^{(0)} = \psi_0(x_1)\psi_1(x_2). \tag{2.3}$$

则

$$H'_{11} = \left\langle \Psi_{11}^{(0)}, \hat{H}'\Psi_{11}^{(0)}\right\rangle = -\lambda\left\langle 1\right| x_1 \left|1\right\rangle \left\langle 0\right| x_2\left|0\right\rangle = 0, \tag{2.4}$$

$$H'_{12} = H'_{21} = \left\langle \Psi_{11}^{(0)}, \hat{H}' \Psi_{12}^{(0)} \right\rangle = -\lambda \left\langle 1 \right| x_1 \left| 0 \right\rangle \left\langle 0 \right| x_2 \left| 1 \right\rangle = -\frac{\lambda}{2\alpha^2}, \tag{2.5}$$

$$H'_{22} = \left\langle \Psi_{12}^{(0)}, \hat{H}' \Psi_{12}^{(0)} \right\rangle = -\lambda \left\langle 0 \right| x_1 \left| 0 \right\rangle \left\langle 1 \right| x_2 \left| 1 \right\rangle = 0, \tag{2.6}$$

久期方程

$$\begin{vmatrix} H'_{11} - E_1^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_1^{(1)} \end{vmatrix} = 0 \quad \Rightarrow \quad E_1^{(1)} = \pm \frac{\lambda}{2\alpha^2}. \tag{2.7}$$

故一级近似

$$E_1 = 2\hbar\omega \pm \frac{\lambda\hbar}{2\mu\omega}. \tag{2.8}$$

(c)

作坐标变换

$$\begin{cases} x_1 = \dfrac{1}{\sqrt{2}}(\xi + \eta) \\ x_2 = \dfrac{1}{\sqrt{2}}(\xi - \eta) \end{cases} \quad \Leftrightarrow \quad \begin{cases} \xi = \dfrac{1}{\sqrt{2}}(x_1 + x_2) \\ \eta = \dfrac{1}{\sqrt{2}}(x_1 - x_2) \end{cases} \tag{2.9}$$

则

$$\frac{\partial}{\partial x_1} = \frac{\partial \xi}{\partial x_1}\frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial x_1}\frac{\partial}{\partial \eta} = \frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta}\right); \tag{2.10}$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{1}{2}\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial}{\partial \xi}\frac{\partial}{\partial \eta} + \frac{\partial^2}{\partial \eta^2}\right). \tag{2.11}$$

故

$$\begin{aligned} H_0 &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) + \frac{1}{2}\mu\omega^2\left(x_1^2 + x_2^2\right) \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}\right) + \frac{1}{2}\mu\omega^2(\xi^2 + \eta^2); \end{aligned} \tag{2.12}$$

$$H' = -\lambda x_1 x_2 = -\frac{\lambda}{2}(\xi^2 - \eta^2). \tag{2.13}$$

故

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}\right) + \frac{1}{2}\mu\omega^2(\xi^2 + \eta^2) - \frac{\lambda}{2}(\xi^2 - \eta^2) \\ &= \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \xi^2} + \frac{1}{2}(\mu\omega^2 - \lambda)\xi^2\right] + \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \eta^2} + \frac{1}{2}(\mu\omega^2 + \lambda)\eta^2\right]. \end{aligned} \tag{2.14}$$

可得能量本征值

$$E_{n_\xi,n_\eta} = \left(n_\xi + \frac{1}{2}\right)\hbar\sqrt{\omega^2 - \frac{\lambda}{\mu}} + \left(n_\eta + \frac{1}{2}\right)\hbar\sqrt{\omega^2 + \frac{\lambda}{\mu}}. \tag{2.15}$$

取 $n_\xi = 1, n_\eta = 0$，则

$$E_{1,0} = \frac{\hbar\omega}{2}\left(3\sqrt{1 - \frac{\lambda}{\mu\omega^2}} + \sqrt{1 + \frac{\lambda}{\mu\omega^2}}\right) \tag{2.16}$$

与式 (2.8) 比较，当 $\lambda \ll \mu\omega^2$ 时，有

$$E_{1,0} \doteq \frac{\hbar\omega}{2}\left[3\left(1 - \frac{\lambda}{2\mu\omega^2}\right) + \left(1 + \frac{\lambda}{2\mu\omega^2}\right)\right] = 2\hbar\omega - \frac{\lambda\hbar}{2\mu\omega}. \tag{2.17}$$

而取 $n_\xi = 0, n_\eta = 1$ 对应式 (2.8) 取 $+$. 微扰项需 $\lambda \ll \mu\omega^2$.

3 10.8

(a)

设转子能量本征函数为 $\psi(\varphi)$，

$$H\psi = -\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\varphi^2} = E\psi, \tag{3.1}$$

解得

$$\psi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}m\varphi}, \quad m = 0, \pm 1, \pm 2, \dots \tag{3.2}$$

能量本征值

$$E_m = \frac{m^2\hbar^2}{2I}. \tag{3.3}$$

(b)

由于一个 E_m 对应 $\pm m$，故简并度 $f = 2$.

$$H'_{++} = \left\langle \psi_m, \hat{H}'\psi_m \right\rangle = -\frac{D\mathscr{E}}{2\pi}\int_0^{2\pi}\cos\varphi\,\mathrm{d}\varphi = 0; \tag{3.4}$$

$$H'_{+-} = \left\langle \psi_m, \hat{H}'\psi_{-m} \right\rangle = -\frac{D\mathscr{E}}{2\pi}\int_0^{2\pi}\cos\varphi\,\mathrm{e}^{-2\mathrm{i}m\varphi}\,\mathrm{d}\varphi = 0; \tag{3.5}$$

$$H'_{--} = \left\langle \psi_{-m}, \hat{H}'\psi_{-m} \right\rangle = -\frac{D\mathscr{E}}{2\pi}\int_0^{2\pi}\cos\varphi\,\mathrm{d}\varphi = 0. \tag{3.6}$$

一级微扰能 $E_m^{(1)}=0$，故能级仍为 E_m.

设

$$\psi_m^{(1)}=\sum_n c_{mn}\psi_n^{(0)} \tag{3.7}$$

代入一级微扰方程 $(\hat{H}_0-E_m^{(0)})\psi_m^{(1)}=-(\hat{H}'-E_m^{(1)})\psi_m^{(0)}$

$$\sum_n c_{mn}(E_n-E_m)\psi_n^{(0)}=-\hat{H}'\psi_m^{(0)} \tag{3.8}$$

与 $\psi_k^{(0)}$ 内积

$$\begin{aligned}(E_k-E_m)c_{mk}&=-\left\langle\psi_k^{(0)},\hat{H}'\psi_m^{(0)}\right\rangle\\ \frac{\hbar^2}{2I}(k^2-m^2)c_{mk}&=\frac{D\mathscr{E}}{2\pi}\int_0^{2\pi}\cos\varphi\,\mathrm{e}^{\mathrm{i}(m-k)\varphi}\,\mathrm{d}\varphi\end{aligned} \tag{3.9}$$

积分只有在 $m-k=\pm1$ 时不为 0，此时

$$c_{m,m-1}=\frac{ID\mathscr{E}}{(-2m+1)\hbar^2},\quad c_{m,m+1}=\frac{ID\mathscr{E}}{(2m+1)\hbar^2} \tag{3.10}$$

故

$$\psi_m^{(1)}=\frac{ID\mathscr{E}}{\hbar^2}\left[\frac{1}{2m+1}\psi_{m+1}^{(0)}-\frac{1}{2m-1}\psi_{m-1}^{(0)}\right]. \tag{3.11}$$

(c)

Schrödinger 方程变为

$$\begin{aligned}-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\varphi^2}-D\mathscr{E}\left(1-\frac{\varphi^2}{2}\right)\psi=E\psi.\\ -\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{1}{2}D\mathscr{E}\varphi^2\psi=(E+D\mathscr{E})\psi.\end{aligned} \tag{3.12}$$

是谐振子的形式，故振动能级

$$E_n=\left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{D\mathscr{E}}{I}}-D\mathscr{E},\quad n=0,1,2,\dots \tag{3.13}$$

本征函数

$$\psi_n(\varphi)=\sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}}H_n(\alpha\varphi)\,\mathrm{e}^{-\alpha^2\varphi^2/2},\quad \alpha=\sqrt[4]{\frac{ID\mathscr{E}}{\hbar^2}}. \tag{3.14}$$

4 补充题

(1)

氢原子 1s 基态归一化波函数

$$\psi_{100}(r,\theta,\phi)=\frac{1}{\sqrt{\pi a_0^3}}\,\mathrm{e}^{-r/a_0}. \tag{4.1}$$

故，只需将 Bohr 半径换为

$$a=\frac{\hbar^2}{\mu e^2}=\frac{2\hbar^2}{m_\mathrm{e}e^2}=2a_0. \tag{4.2}$$

即得电子偶素的波函数

$$\psi_{100}(r)=\frac{1}{2\sqrt{2\pi a_0^3}}\,\mathrm{e}^{-r/2a_0}. \tag{4.3}$$

(2)

取 $a_0=1$，则

$$\overline{r^2}=4\pi\int_0^{+\infty}r^2\left|\psi_{100}\right|^2r^2\,\mathrm{d}r=\frac{1}{2}\int_0^{+\infty}\mathrm{e}^{-r}r^4\,\mathrm{d}r=12. \tag{4.4}$$

故均方根值

$$\sqrt{\overline{r^2}}=2\sqrt{3}. \tag{4.5}$$

这应该是电子偶素半径或直径的物理估计.

(3)

超精细相互作用

$$\hat{H}'=-\frac{8\pi}{3}\hat{\boldsymbol{\mu}}_\mathbf{p}\cdot\hat{\boldsymbol{\mu}}_\mathbf{e}\,\delta(\boldsymbol{r})=-\frac{8\pi}{3}\left(\frac{e}{m_\mathrm{e}c}\right)^2\hat{S}_\mathrm{p}\cdot\hat{S}_\mathrm{e}\,\delta(\boldsymbol{r}). \tag{4.6}$$

总角动量 $\hat{J}=\hat{S}_\mathrm{p}+\hat{S}_\mathrm{e}$，则

$$\hat{H}'=-\frac{4\pi}{3}\left(\frac{e}{m_\mathrm{e}c}\right)^2\left(\hat{J}^2-\hat{S}_\mathrm{p}^2-\hat{S}_\mathrm{e}^2\right)\delta(\boldsymbol{r}). \tag{4.7}$$

1s 态中，$S_\mathrm{p}=S_\mathrm{e}=1/2$，单态 χ_{00} 下，

$$\left\langle\psi_{100}\chi_{00},\hat{H}'\psi_{100}\chi_{00}\right\rangle=-\frac{1}{8\pi a_0^3}\frac{4\pi}{3}\left(\frac{e}{m_\mathrm{e}c}\right)^2\left(0-\frac{3}{4}-\frac{3}{4}\right)\hbar^2 \tag{4.8}$$

三重态 χ_1 下，

$$\left\langle \psi_{100}\chi_1, \hat{H}'\psi_{100}\chi_1 \right\rangle = -\frac{1}{8\pi a_0^3}\frac{4\pi}{3}\left(\frac{e}{m_\mathrm{e}c}\right)^2\left(2-\frac{3}{4}-\frac{3}{4}\right)\hbar^2. \tag{4.9}$$

故单态能级最低，能级差

$$\Delta E = \frac{1}{3a_0^3}\left(\frac{e\hbar}{m_\mathrm{e}c}\right)^2. \tag{4.10}$$

能移

$$\Delta\nu = \frac{\Delta E}{h} = 1.16\,\mathrm{GHz}. \tag{4.11}$$

Part II 笔记

5 微扰理论

可以精确求解的量子力学问题很少，在处理各种实际问题时，除了采用适当的模型以简化问题外，往往还需要采用合适的近似解法.

5.1 非简并定态微扰理论

当 $\hat{H}$ 比较复杂时，定态 Schrödinger 方程不能精确求解，若 $\hat{H}$ 具有以下形式

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

其中 $\hat{H}_0$ 是可解的，$\hat{H}' \ll \hat{H}_0$ 是小的修正，可令

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$
$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \cdots$$

其中 $E_n^{(k)}$ 和 $\psi_n^{(k)}$ 与 $\hat{H}'$ 的 k 次方成正比．代入原方程有

$$(\hat{H}_0 + \hat{H}')(\psi_n^{(0)} + \psi_n^{(1)} + \cdots) = (E_n^{(0)} + E_n^{(1)} + \cdots)(\psi_n^{(0)} + \psi_n^{(1)} + \cdots)$$

逐阶比较得到

零级方程： $$(\hat{H}_0 - E_n^{(0)})\psi_n^{(0)} = 0; \tag{5.1}$$

一级方程： $$(\hat{H}_0 - E_n^{(0)})\psi_n^{(1)} = -(\hat{H}' - E_n^{(1)})\psi_n^{(0)}; \tag{5.2}$$

二级方程： $$(\hat{H}_0 - E_n^{(0)})\psi_n^{(2)} = -(\hat{H}' - E_n^{(1)})\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}; \tag{5.3}$$

……

一般说来，越高次的项越小，所以可以只保留最低的几阶，便有足够的精度.

以下约定：波函数的各级高级近似解与零级近似解都正交，即

$$\left\langle \psi_n^{(0)}, \psi_n^{(k)} \right\rangle = 0.$$

对于非简并情形，即 $\hat{H}_0$ 属于 $E_n^{(0)}$ 的本征态只有一个

$$\psi_n^{(1)} = \sum_m a_{nm}^{(1)} \psi_m^{(0)}$$

代入一级方程有

$$\sum_m a_{nm}^{(1)}(\hat{H}_0 - E_n^{(0)})\psi_m^{(0)} = -(\hat{H}' - E_n^{(1)})\psi_n^{(0)}$$

等式的两端与 $\psi_k^{(0)}$ 内积

$$a_{nk}^{(1)}(E_k^{(0)} - E_n^{(0)}) = -\left\langle \psi_k^{(0)}, \hat{H}'\psi_n^{(0)} \right\rangle + E_n^{(1)}\,\delta_{kn}$$

取 $k = n$ 得到一级微扰能

$$E_n^{(1)} = \left\langle \psi_n^{(0)}, \hat{H}'\psi_n^{(0)} \right\rangle =: H'_{nn} \tag{5.4}$$

若取 $k \neq n$，得到

$$a_{nk}^{(1)} = \frac{H'_{kn}}{E_k^{(0)} - E_n^{(0)}}, \quad H'_{kn} := \left\langle \psi_k^{(0)}, \hat{H}'\psi_n^{(0)} \right\rangle. \tag{5.5}$$

故一阶微扰波函数

$$\psi_n^{(1)} = \sum_{m\neq n} \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}}\psi_m^{(0)} \tag{5.6}$$

微扰适用条件为

$$\left| \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}} \right| \ll 1. \tag{5.7}$$

二阶微扰能　二级微扰方程

$$(\hat{H}_0 - E_n^{(0)})\psi_n^{(2)} = -(\hat{H}' - E_n^{(1)})\sum_{m\neq n} \frac{H'_{kn}}{E_k^{(0)} - E_n^{(0)}}\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)}$$

两端与 $\psi_n^{(0)}$ 内积，得到

$$\begin{aligned} 0 = -\sum_{m\neq n} \frac{H'_{mn}}{E_k^{(0)} - E_n^{(0)}} \left\langle \psi_n^{(0)}, \hat{H}'\psi_m^{(0)} \right\rangle + 0 + E_n^{(2)}, \\ \Rightarrow \quad E_n^{(2)} = \sum_{m\neq n} \frac{\left|H'_{mn}\right|^2}{E_n^{(0)} - E_m^{(0)}}. \end{aligned} \tag{5.8}$$

准确到二级近似下，能量的本征值为

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{m\neq n} \frac{\left|H'_{mn}\right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{5.9}$$

上述理论成立需要 $\hat{H}_0$ 为分离谱，无简并.

例 5.1.1: 电介质的极化率

各向同性的非极性分子电介质在外电场作用下极化，求感生电偶极矩.

考虑正离子运动，无外场时为简谐运动

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}\mu\omega^2 x^2,$$

$$\hat{H}_n |n\rangle = E_n^{(0)} |n\rangle, \quad E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega.$$

沿 x 向加恒定电场相当于施加微扰 $\hat{H}' = -q\varepsilon x$

$$\begin{aligned} H'_{nk} &= \langle n| \hat{H}' |k\rangle = -q\varepsilon \langle n| x |k\rangle \\ &= -q\varepsilon\sqrt{\frac{\hbar}{\mu\omega}}\left(\sqrt{\frac{k+1}{2}}\,\delta_{n,k+1} + \sqrt{\frac{k}{2}}\,\delta_{n,k-1}\right) \end{aligned}$$

一级能量修正 $H'_{kk} = 0$，二阶近似能量

$$E_k = E_k^{(0)} + 0 + \sum_{n\neq k}\frac{|H'_{nk}|^2}{E_k^{(0)} - E_n^{(0)}} = E_k^{(0)} - \frac{q^2\varepsilon^2}{2\mu\omega^2}.$$

实际上，能量是有精确解的

$$V = \frac{1}{2}\mu\omega^2 x^2 - q\varepsilon x = \frac{1}{2}\mu\omega^2\left(x - \frac{q\varepsilon}{\mu\omega^2}\right)^2 - \frac{q^2\varepsilon^2}{2\mu\omega^2}.$$

它的第一项只不过是把原来的谐振子势能平移了一段距离，这个移动不会影响谐振子的能级，而它的第二项正是前面求出的常数项.

一级近似态

$$\begin{aligned} |\psi_k\rangle &= |k\rangle + \sum_{n\neq k}\frac{H'_{nk}}{E_k^{(0)} - E_n^{(0)}}|n\rangle \\ &= |k\rangle + \frac{q\varepsilon}{\sqrt{\hbar\mu\omega^3}}\left(\sqrt{\frac{k+1}{2}}\,|k+1\rangle - \sqrt{\frac{k}{2}}\,|k-1\rangle\right), \end{aligned}$$

无外加场时，非极性分子正 (负) 离子的位置平均值 $\langle k| x |k\rangle = 0$，即固有电偶极矩为零，而加外电场后正离子位移

$$\langle \psi_k| x |\psi_k\rangle = \frac{2q\varepsilon}{\sqrt{\hbar\mu\omega^3}}\left(\sqrt{\frac{k+1}{2}}\,\langle k|k+1\rangle - \sqrt{\frac{k}{2}}\,\langle k|k-1\rangle\right) = \frac{q\varepsilon}{\mu\omega^2}.$$

故感生电偶极矩 D 和极化率 κ

$$D = |q|\,\frac{2\,|q|\,\varepsilon}{\mu\omega^2} = \frac{2q^2\varepsilon}{\mu\omega^2}, \quad \kappa = \frac{D}{\varepsilon} = \frac{2q^2}{\mu\omega^2}.$$

例 5.1.2: 氦原子

氦原子在原子核外有两个电子，Hamilton 量包括两个电子在原子核的 Column 引力场中的运动

$$\hat{H}_0 = \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right) + \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_2}\right);$$

以及两个电子之间的 Column 排斥能 (微扰项)

$$\hat{H}' = \frac{1}{r_{12}}.$$

它对于两个电子空间坐标的交换是对称的．由于电子是 Fermi 子，两个电子相应的自旋态只能反对称的自旋单态 χ_{00}

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2)\chi_{00}(s_{1z}, s_{2z}).$$

相应的本征值 $E_1^0 = -Z^2$，一级修正

$$\left\langle \frac{1}{r_{12}} \right\rangle = \int \frac{|\psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2)|^2}{r_{12}} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2.$$

由

$$\psi_{100}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{\pi}} \mathrm{e}^{-Zr}; \qquad \int \frac{\mathrm{e}^{-Z(r_1+r_2)}}{r_{12}} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 = \frac{5\pi^2}{8Z^5}.$$

得

$$E = -Z^2 + \frac{5}{8}Z.$$

5.2　简并定态微扰理论

实际问题中，特别是处理体系的激发态时，常常碰到简并态或近似简并态．此时，非简并态微扰论是不适用的．

这里首先碰到的困难是：零级能量给定后，对应的零级波函数并未确定，这是简并态微扰论首先要解决的问题．

体系能级的简并性与体系的对称性密切相关．当考虑微扰之后，如体系的某种对称性受到破坏，则能级可能分裂，简并将部分或全部解除．因而在简并态微扰中，充分考虑体系的对称性及其破缺是至关重要的．

一级微扰能和零级波函数　$E_n^{(0)}$ 简并时，

$$\hat{H}^{(0)}\psi_{ni}^{(0)} = E_n^{(0)}\psi_{ni}^{(0)}, \quad (i = 1, 2, \ldots, k).$$

简并度 $f_n = k$，引入微扰后假设

$$\psi_n^{(0)} = \sum_{i=1}^{k} c_i^{(0)}\psi_{ni}^{(0)}.$$

代入一级微扰方程

$$(\hat{H}_0 - E_n^{(0)})\psi_n^{(1)} = -(\hat{H}' - E_n^{(1)})\sum_{i=1}^{k} c_i^{(0)}\psi_{ni}^{(0)}.$$

两端与 $\psi_{nj}^{(0)}$ 内积

$$0 = -\sum_{k=1}^{n} c_i^{(0)}\left[\left\langle \psi_{nj}^{(0)}, \hat{H}'\psi_{ni}^{(0)}\right\rangle - E_n^{(1)}\,\delta_{ij}\right].$$

记

$$H'_{ji} := \left\langle \psi_{nj}^{(0)}, \hat{H}'\psi_{ni}^{(0)}\right\rangle \tag{5.10}$$

得到久期 (secular) 方程

$$\det(H' - E_n^{(1)}I) = \begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \cdots & H'_{1k} \\ H'_{21} & H'_{22} - E_n^{(1)} & \cdots & H'_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{k1} & H'_{k2} & \cdots & H'_{kk} - E_n^{(1)} \end{vmatrix} = 0. \tag{5.11}$$

从中可以解出 $E_n^{(1)}$ 以及它们对应的 $c_i^{(0)}$，这就决定了一级微扰能和零级波函数.

Stark 效应　Stark 效应就是原子或分子在外电场作用下能级和光谱发生分裂的现象.