第五章 微扰理论

§5.1 非简并定态微扰理论

（1）微扰体系的方程

（2）态矢量和能量的一级修正

（3）能量的二级修正

（4）微扰理论的适用条件

（5）讨论

（6）例题

（1）微扰体系的方程

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \qquad \hat{H}^{(0)} | \psi_n^{(0)} >= E_n^{(0)} | \psi_n^{(0)} >$$

$$\hat{H} | \psi_n >= E_n | \psi_n >$$

$H' = 0$ ， $|\psi_n\rangle = |\psi_n^{(0)}\rangle$ ， $E_n = E_n^{(0)}$

$H' \neq 0$ ， $E_n^{(0)} \to E_n$ ， $|\psi_n^{(0)}\rangle \to |\psi_n\rangle$

为明显表示微小程度，微扰项写成如下形式：

$$\hat{H}' = \lambda \hat{H}^{(1)}$$

λ 是一个很小的实参数，**En**和 ψ n都和微扰有关，可以把它们看做是 λ 的函数，可以将它们展开为的幂级数

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \quad E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}\bigg|_{\lambda=0}$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots, \quad |\psi_n^{(k)}\rangle = \frac{1}{k!}\frac{d^k|\psi_n\rangle}{d\lambda^k}\bigg|_{\lambda=0}$$

$E_n^{(0)}$, $\lambda E_n^{(1)}$, $\lambda^2 E_n^{(1)}$, ... 和 $|\psi_n^{(0)}\rangle$, $\lambda|\psi_n^{(1)}\rangle$, $\lambda^2|\psi_n^{(2)}\rangle$, ... 分别是能量和波函数的零级、一级和二级修正

薛定谔方程

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots)$$
$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots)$$

$$\left\{\begin{array}{ll} \hat{H}^{(0)}|\psi_n^{(0)}\rangle + & \\ \lambda & [\hat{H}^{(0)}|\psi_n^{(1)}\rangle + \hat{H}^{(1)}|\psi_n^{(0)}\rangle] + \\ \lambda^2 & [\hat{H}^{(0)}|\psi_n^{(2)}\rangle + \hat{H}^{(1)}|\psi_n^{(1)}\rangle] + \\ \lambda^3 & [\cdots\cdots\cdots\cdots] + \\ \cdots\cdots\cdots\cdots & \end{array}\right\} = \left\{\begin{array}{ll} E_n^{(0)}|\psi_n^{(0)}\rangle + & \\ \lambda[E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle] + & \\ \lambda^2 & [E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle] + \\ \lambda^3 & [\cdots\cdots\cdots\cdots] + \\ \cdots\cdots\cdots\cdots & \end{array}\right\}$$

$$\lambda^0: \quad \hat{H}^{(0)}|\psi_n^{(0)}>=E_n^{(0)}|\psi_n^{(0)}>$$

$$\lambda^1: \quad \hat{H}^{(0)}|\psi_n^{(1)}>+\hat{H}^{(1)}|\psi_n^{(0)}>=E_n^{(0)}|\psi_n^{(1)}>+E_n^{(1)}|\psi_n^{(0)}>$$

$$\lambda^2: \quad \hat{H}^{(0)}|\psi_n^{(2)}>+\hat{H}^{(1)}|\psi_n^{(1)}>=E_n^{(0)}|\psi_n^{(2)}>+E_n^{(1)}|\psi_n^{(1)}>+E_n^{(2)}|\psi_n^{(0)}>$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\begin{cases} [\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(0)}>=0 \\ [\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(1)}>=-[\hat{H}^{(1)}-E_n^{(1)}]|\psi_n^{(0)}> \\ [\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(2)}>=-[\hat{H}^{(1)}-E_n^{(1)}]|\psi_n^{(1)}>+E_n^{(2)}|\psi_n^{(0)}> \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{cases}$$

引进λ的目的是为了更清楚地从方程中按数量级分出上述方程组，
实现分离后，将λ省去，将**H$^{(1)}$**理解为**H'**，**En$^{(1)}$**和ψ**n$^{(1)}$**理解为一级修正

（2）态矢量和能量的一级修正

(a) $E_n^{(1)}$

$H^{(0)}$ 的本征函数系$|\psi_n^{(0)}>$组成完全系，任意态可以由它展开，则 有

$$|\psi_n^{(1)}>=\sum_{l=1}^{\infty}|\psi_l^{(0)}><\psi_l^{(0)}|\psi_n^{(1)}>=\sum_{l=1}^{\infty}a_l^{(1)}|\psi_l^{(0)}>$$

$$a_l^{(1)}=<\psi_l^{(0)}|\psi_n^{(1)}>$$

$$\begin{cases}[\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(0)}>=0\\ [\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(1)}>=-[\hat{H}'-E_n^{(1)}]|\psi_n^{(0)}>\end{cases}$$

$$[\hat{H}^{(0)}-E_n^{(0)}]\sum_{l=1}^{\infty}a_l^{(1)}|\psi_l^{(0)}>=-[\hat{H}'-E_n^{(1)}]|\psi_n^{(0)}>$$

$$\sum_{l=1}^{\infty}a_l^{(1)}[E_l^{(0)}-E_n^{(0)}]|\psi_l^{(0)}>=-[\hat{H}'-E_n^{(1)}]|\psi_n^{(0)}>$$

$<\psi_m^{(0)}|\times$

$$\sum_{l=1}^{\infty} a_l^{(1)}[E_l^{(0)} - E_n^{(0)}] < \psi_m^{(0)} | \psi_l^{(0)} > = - < \psi_m^{(0)} | H' | \psi_n^{(0)} > + E_n^{(1)} < \psi_m^{(0)} | \psi_n^{(0)} >$$

$$\sum_{l=1}^{\infty} a_l^{(1)}[E_l^{(0)} - E_n^{(0)}]\delta_{ml} = -H'_{mn} + E_n^{(1)}\delta_{mn}$$

$$\Rightarrow \quad a_m^{(1)}[E_m^{(0)} - E_n^{(0)}] = -H'_{mn} + E_n^{(1)}\delta_{mn}$$

1. m = n $\qquad E_n^{(1)} = H'_{nn} = < \psi_n^{(0)} | H' | \psi_n^{(0)} >$

2. m ≠ n $\qquad a_m^{(1)} = \dfrac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} = \dfrac{< \psi_m^{(0)} | H' | \psi_n^{(0)} >}{E_n^{(0)} - E_m^{(0)}}$

能量一级修正

$$\begin{aligned} E_n &= E_n^{(0)} + E_n^{(1)} \\ &= E_n^{(0)} + < \psi_n^{(0)} | H' | \psi_n^{(0)} > \\ &= E_n^{(0)} + \hat{H}'_{nn} \end{aligned}$$

$$\hat{H}'_{nn} = < \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} >$$

（b）$|\psi_n^{(1)}>$

$$|\psi_n^{(1)}>=\sum_{l=1}^{\infty} a_l^{(1)}|\psi_k^{(0)}>$$

$$[\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(1)}>=[\hat{H}^{(0)}-E_n^{(0)}][\sum_{\substack{l=1\\l\neq n}}^{\infty}{}' a_l^{(1)}|\psi_l^{(0)}>+a_{nn}^{(1)}|\psi_n^{(0)}>]$$

$$[\hat{H}^{(0)}-E_n^{(0)}][\sum_{\substack{l=1\\l\neq n}}^{\infty}{}' a_l^{(1)}|\psi_l^{(0)}>+a_{nn}^{(1)}\bullet 0]=[\hat{H}^{(0)}-E_n^{(0)}]\sum_{\substack{l=1\\l\neq n}}^{\infty}{}' a_l^{(1)}|\psi_l^{(0)}>=-[H'-E_n^{(1)}]|\psi_n^{(0)}>$$

$$\Rightarrow [\hat{H}^{(0)}-E_n^{(0)}]|\psi_n^{(1)'}>=-[H'-E_n^{(1)}]|\psi_n^{(0)}>,\quad |\psi_n^{(1)'}>=\sum_{\substack{l=1\\l\neq n}}^{\infty}{}' a_l^{(1)}|\psi_l^{(0)}>$$

$$|\psi_n^{(1)'}>=\sum_{\substack{k=1\\k\neq n}}^{\infty}{}' a_{kn}^{(1)}|\psi_k^{(0)}>=|\psi_n^{(1)}>\quad (a_{nn}^{(1)}=0)$$

所以 $$|\psi_n^{(1)}>=\sum_{l=1}^{\infty} a_l^{(1)}|\psi_l^{(0)}>=\sum_{\substack{l=1\\l\neq n}}^{\infty}{}' a_l^{(1)}|\psi_l^{(0)}>\quad (a_n^{(1)}=0)$$

（3）能量的二级修正

$$|\psi_n> = |\psi_n^{(0)}> + \sum_{l\neq n}^{\infty} a_l^{(1)} |\psi_l^{(0)}> = |\psi_n^{(0)}> + \sum_{l\neq n}^{\infty} \frac{<\psi_l^{(0)}|H'|\psi_n^{(0)}>}{E_n^{(0)} - E_l^{(0)}} |\psi_l^{(0)}>$$

$$= |\psi_n^{(0)}> + \sum_{l\neq n}^{\infty} \frac{H'_{\ln}}{E_n^{(0)} - E_l^{(0)}} |\psi_l^{(0)}>$$

$$|\psi_n^{(2)}> = \sum_{l=1}^{\infty} |\psi_l^{(0)}><\psi_l^{(0)}|\psi_n^{(2)}> = \sum_{l=1}^{\infty} a_l^{(2)} |\psi_l^{(0)}>$$

$$[\hat{H}^{(0)} - E_n^{(0)}]|\psi_n^{(2)}> = -[H' - E_n^{(1)}]|\psi_n^{(1)}> + E_n^{(2)}|\psi_n^{(0)}>$$

$$[\hat{H}^{(0)} - E_n^{(0)}]\sum_{l=1}^{\infty} a_l^{(2)} |\psi_l^{(0)}> = -[H' - E_n^{(1)}]\sum_{l\neq n}^{\infty} a_l^{(1)} |\psi_l^{(0)}> + E_n^{(2)}|\psi_n^{(0)}>$$

$$\sum_{l=1}^{\infty} [E_l^{(0)} - E_n^{(0)}] a_l^{(2)} |\psi_l^{(0)}> = -[H' - E_n^{(1)}]\sum_{l\neq n}^{\infty} a_l^{(1)} |\psi_l^{(0)}> + E_n^{(2)}|\psi_n^{(0)}>$$

$<\psi_m{}^{(0)}| \times$

$$\sum_{l=1}^{\infty}[E_l^{(0)}-E_n^{(0)}]a_l^{(2)}\boxed{<\psi_m^{(0)}|\psi_l^{(0)}>}=-\sum_{l=1}^{\infty}a_l^{(1)}<\psi_m^{(0)}|H'|\psi_l^{(0)}>$$

$$+E_n^{(1)}\sum_{l=1}^{\infty}a_l^{(1)}\boxed{<\psi_m^{(0)}|\psi_l^{(0)}>}+E_n^{(2)}\boxed{<\psi_m^{(0)}|\psi_n^{(0)}>}$$

$$\sum_{l=1}^{\infty}[E_l^{(0)}-E_n^{(0)}]a_l^{(2)}\delta_{ml}=-\sum_{l=1}^{\infty}a_l^{(1)}<\psi_m^{(0)}|H'|\psi_l^{(0)}>+E_n^{(1)}\sum_{l=1}^{\infty}a_l^{(1)}\delta_{ml}+E_n^{(2)}\delta_{mn}$$

$$[E_m^{(0)}-E_n^{(0)}]a_{mn}^{(2)}=-\sum_{l=1}^{\infty}a_l^{(1)}V_{ml}+E_n^{(1)}a_{mn}^{(1)}+E_n^{(2)}\delta_{mn}$$

$$a_l^{(1)}=\frac{H'_{\ln}}{E_n^{(0)}-E_k^{(0)}}$$

1. m = n $\quad 0=-\sum_{l=1}^{\infty}a_l^{(1)}H'_{ml}+E_n^{(1)}a_{mn}^{(1)}+E_n^{(2)}$

$$E_n^{(2)}=\sum_{l=1}^{\infty}a_l^{(1)}H'_{nl}-H'_{nn}a_{nn}^{(1)}=\sum_{l\neq n}^{\infty}a_{\ln}^{(1)}H'_{nl}=\sum_{l\neq n}^{\infty}\frac{H'_{\ln}}{E_n^{(0)}-E_l^{(0)}}H'_{nl}$$

$$=\sum_{l\neq n}^{\infty}\frac{H'_{\ln}H'^{*}_{\ln}}{E_n^{(0)}-E_l^{(0)}}=\sum_{l\neq n}^{\infty}\frac{|H'_{\ln}|^2}{E_n^{(0)}-E_l^{(0)}}$$

厄米属性

$$H'^{*}_{\ln}=<\psi_l^{(0)}|H'|\psi_n^{(0)}>^{*}=<\psi_n^{(0)}|H'^{+}|\psi_l^{(0)}>$$

$$=<\psi_n^{(0)}|H'|\psi_l^{(0)}>=H'_{nl}$$

2. m ≠ n

$$[E_m^{(0)} - E_n^{(0)}]a_{mn}^{(2)} = -\sum_{l=1}^{\infty} a_l^{(1)} H'_{ml} + E_n^{(1)} a_{mn}^{(1)}$$

$$a_{mn}^{(2)} = \sum_{l \neq n}^{\infty} \frac{a_l^{(1)} H'_{ml}}{E_n^{(0)} - E_m^{(0)}} - \frac{H'_{nn} a_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}}$$

$$= \sum_{l \neq n}^{\infty} \frac{H'_{\ln} V_{ml}}{[E_n^{(0)} - E_m^{(0)}][E_n^{(0)} - E_l^{(0)}]} - \frac{H'_{nn} H'_{mn}}{[E_n^{(0)} - E_m^{(0)}]^2}$$

$$E_n^{(2)} = \sum_{l \neq n}^{\infty} \frac{|H'_{\ln}|^2}{E_n^{(0)} - E_l^{(0)}} = \sum_{l \neq n}^{\infty} \frac{|<\psi_l^{(0)} | H' | \psi_n^{(0)}>|^2}{E_n^{(0)} - E_l^{(0)}} = \sum_{l \neq n}^{\infty} \frac{|<\psi_l^{(0)} | \hat{H}' | \psi_n^{(0)}>|^2}{E_n^{(0)} - E_l^{(0)}}$$

$$= \sum_{l \neq n}^{\infty} \frac{|H'_{\ln}|^2}{E_n^{(0)} - E_l^{(0)}}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = E_n^{(0)} + H'_{nn} + \sum_{l \neq n}^{\infty} \frac{|H'_{\ln}|^2}{E_n^{(0)} - E_l^{(0)}}$$

（4）微扰理论的适用条件

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{l \neq n}^{\infty} \frac{|H'_{ln}|^2}{E_n^{(0)} - E_l^{(0)}} + \cdots$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_{l \neq n}^{\infty} \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} |\psi_l^{(0)}\rangle + \cdots$$

上述级数要收敛，同时，$|\psi_n\rangle$ 主要是由 $|\psi_n^{(0)}\rangle$组成，微扰来自 $|\psi_l^{(0)}\rangle$，所以

$$\left|\frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}}\right| \ll 1 \qquad |H'_{ln}| \ll E_n^{(0)} - E_l^{(0)}, \quad E_n^{(0)} \neq E_l^{(0)}$$

H’很小的明确表示即为上式所示,即适用条件为

（i）$|H'_{ln}| = |\langle\psi_l^{(0)}|H'|\psi_n^{(0)}\rangle|$ 很小，扰动的矩阵元很小

（ii）$|E_n^{(0)} - E_l^{(0)}|$很大，能量间隔很大，如库伦场中的低能级情形

（5）讨论

扰动态 $|\psi_n>$可视为$\psi_k^{(0)}>$的线性叠加

（a）一级近似:

$$|\psi_n> = |\psi_n^{(0)}> + \sum_{l\neq n}^{\infty} \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} |\psi_l^{(0)}>$$

（b）扰动的主要贡献来自 能量与$|\psi_n^{(0)}>$最接近的 $|\psi_l^{(0)}>$，所以只需计算一级修正表达式中有限的几项

（c）对满足条件 $\left|\frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}}\right| << 1$ $\quad |H'_{ln}| << E_n^{(0)} - E_l^{(0)}$， $E_n^{(0)} \neq E_l^{(0)}$

一级修正已经很精确了，如果能量一级修正$H'_{nn}=0$, 则需要二级修正，但波函数仍采用一级修正

（6）例题

例 1. 一电荷为e的线性谐振子受恒定弱电场ε作用，电场沿正x方向，用微小扰动法求体系的定态能量和波函数

解

:（a）哈密顿算符

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \tfrac{1}{2}\mu\omega^2 x^2 - e\varepsilon x$$

$$\begin{cases} \hat{H}_0 = -\dfrac{\hbar^2}{2\mu}\dfrac{d^2}{dx^2} + \tfrac{1}{2}\mu\omega^2 x^2 \\ \hat{H}' = -e\varepsilon x \end{cases}$$

（b）$E^{(0)}$和$\psi_n^{(0)}$

$$\psi_n^{(0)} = N_n e^{-\alpha^2 x^2/2} H_n(\alpha x) \quad \alpha = \sqrt{\frac{\mu\omega}{\hbar}} \quad N_n = \sqrt{\frac{\alpha}{\sqrt{\pi}\, 2^n n!}}$$

$$E_n^{(0)} = \hbar\omega(n + \tfrac{1}{2}) \quad n = 0,1,2,\cdots$$

（c）$E_n^{(1)}$

$$E_n^{(1)} = H'_{nn} = \int_{-\infty}^{\infty} \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} dx = -e\varepsilon \int_{-\infty}^{\infty} \psi_n^{(0)*} x \psi_n^{(0)} dx = 0$$

（d）能量的二级修正

$$H'_{kn}=\int_{-\infty}^{\infty}\psi_k^{(0)*}\hat{H}'\psi_n^{(0)}dx=-e\varepsilon\int_{-\infty}^{\infty}\psi_k^{(0)*}x\psi_n^{(0)}dx$$

由递推关系 $x\psi_n=\frac{1}{\alpha}[\sqrt{\frac{n}{2}}\psi_{n-1}+\sqrt{\frac{n+1}{2}}\psi_{n+1}]$

$$H'_{kn}=-e\varepsilon\int_{-\infty}^{\infty}\psi_k^{(0)*}\frac{1}{\alpha}[\sqrt{\tfrac{n}{2}}\psi_{n-1}^{(0)}+\sqrt{\tfrac{n+1}{2}}\psi_{n+1}^{(0)}]dx$$

$$=-e\varepsilon\frac{1}{\alpha}[\int_{-\infty}^{\infty}\psi_k^{(0)*}\sqrt{\tfrac{n}{2}}\psi_{n-1}^{(0)}dx+\int_{-\infty}^{\infty}\psi_k^{(0)*}\sqrt{\tfrac{n+1}{2}}\psi_{n+1}^{(0)}dx]$$

$$=-\frac{e\varepsilon}{\alpha}[\sqrt{\tfrac{n}{2}}\delta_{k,n-1}+\sqrt{\tfrac{n+1}{2}}\delta_{k,n+1}]$$

$$E_n^{(2)}=\sum_{k\neq n}\frac{|H'_{kn}|^2}{E_n^{(0)}-E_k^{(0)}}=\sum_{k\neq n}\frac{\left|-\frac{e\varepsilon}{\alpha}[\sqrt{\frac{n}{2}}\delta_{k,n-1}+\sqrt{\frac{n+1}{2}}\delta_{k,n+1}]\right|^2}{E_n^{(0)}-E_k^{(0)}}$$

$$=(\tfrac{e\varepsilon}{\alpha})^2\sum_{k\neq n}\frac{1}{E_n^{(0)}-E_k^{(0)}}[\tfrac{n}{2}\delta_{k,n-1}+\tfrac{n+1}{2}\delta_{k,n+1}]$$

$$=(\tfrac{e\varepsilon}{\alpha})^2\left[\frac{n}{2}\frac{1}{E_n^{(0)}-E_{n-1}^{(0)}}+\frac{n+1}{2}\frac{1}{E_n^{(0)}-E_{n+1}^{(0)}}\right]$$

对线性谐振子
$E_n^{(0)}-E_{n-1}^{(0)}=\hbar\omega$,
$E_n^{(0)}-E_{n+1}^{(0)}=-\hbar\omega$，

$$E_n^{(2)}=(\tfrac{e\varepsilon}{\alpha})^2[\tfrac{n}{2}\tfrac{1}{\hbar\omega}+\tfrac{n+1}{2}\tfrac{1}{-\hbar\omega}]=-(\tfrac{e\varepsilon}{\alpha})^2\tfrac{1}{2\hbar\omega}\quad\because\alpha^2=\tfrac{\mu\omega}{\hbar}$$

$$=-\frac{e^2\varepsilon^2}{2\mu\omega^2}$$ 能量变化只与扰动 ε 有关

$$\psi_n^{(1)}=\sum_{k\neq n}\frac{H'_{kn}}{E_n^{(0)}-E_k^{(0)}}\psi_k^{(0)}=\sum_{k\neq n}\frac{-\frac{e\varepsilon}{\alpha}[\sqrt{\frac{n}{2}}\delta_{k,n-1}+\sqrt{\frac{n+1}{2}}\delta_{k,n+1}]}{E_n^{(0)}-E_k^{(0)}}\psi_k^{(0)}$$

$$=-\frac{e\varepsilon}{\alpha}\left[\sqrt{\frac{n}{2}}\frac{1}{E_n^{(0)}-E_{n-1}^{(0)}}\psi_{n-1}^{(0)}+\sqrt{\frac{n+1}{2}}\frac{1}{E_n^{(0)}-E_{n+1}^{(0)}}\psi_{n+1}^{(0)}\right]$$

$$=-\frac{e\varepsilon}{\alpha}\left[\sqrt{\frac{n}{2}}\frac{1}{\hbar\omega}\psi_{n-1}^{(0)}+\sqrt{\frac{n+1}{2}}\frac{1}{-\hbar\omega}\psi_{n+1}^{(0)}\right]=e\varepsilon\sqrt{\frac{1}{2\hbar\mu\omega^3}}\left[\sqrt{n+1}\psi_{n+1}^{(0)}-\sqrt{n}\psi_{n-1}^{(0)}\right]$$

（e）讨论:

e.1 在粒子数表象中秋矩阵元

$$E_n^{(1)}=<n|\hat{H}'|n>=-e\varepsilon<n|x|n>=-e\varepsilon<n|\tfrac{1}{\alpha\sqrt{2}}[\hat{a}+\hat{a}^+]|n>$$

$$=-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[<n|\hat{a}|n>+<n|\hat{a}^+|n>]$$

$$=-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[\sqrt{n}<n|n-1>+\sqrt{n+1}<n|n+1>]=0$$

$$x=\tfrac{1}{\alpha\sqrt{2}}[\hat{a}+\hat{a}^+]$$

$$\hat{a}|n>=\sqrt{n}|n-1>$$

$$\hat{a}^+|n>=\sqrt{n+1}|n+1>$$

$$H'_{mn}=<m|\hat{H}'|n>=-e\varepsilon<m|x|n>=-e\varepsilon<m|\tfrac{1}{\alpha\sqrt{2}}[\hat{a}+\hat{a}^{+}]|n>$$
$$=-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[<m|\hat{a}|n>+<m|\hat{a}^{+}|n>]$$
$$=-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[\sqrt{n}<m|n-1>+\sqrt{n+1}<m|n+1>]$$
$$=-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[\sqrt{n}\delta_{m,n-1}+\sqrt{n+1}\delta_{m,n+1}]$$
$$E_n^{(2)}=\sum_{m\neq n}\frac{|H'_{mn}|^2}{E_n^{(0)}-E_m^{(0)}}=\sum_{m\neq n}\frac{|-e\varepsilon\tfrac{1}{\alpha\sqrt{2}}[\sqrt{n}\delta_{m,n-1}+\sqrt{n+1}\delta_{m,n+1}]|^2}{E_n^{(0)}-E_m^{(0)}}=-\frac{e^2\varepsilon^2}{2\mu\omega^2}$$

e.2　　精确解

$$\hat{H}=-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\tfrac{1}{2}\mu\omega^2x^2-e\varepsilon x$$
$$=-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\tfrac{1}{2}\mu\omega^2[x^2-2\frac{e\varepsilon}{\mu\omega^2}x+(\frac{e\varepsilon}{\mu\omega^2})^2]-\frac{e^2\varepsilon^2}{2\mu\omega^2}$$
$$=-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\tfrac{1}{2}\mu\omega^2[x-\frac{e\varepsilon}{\mu\omega^2}]^2-\frac{e^2\varepsilon^2}{2\mu\omega^2}\quad=-\frac{\hbar^2}{2\mu}\frac{d^2}{dx'^2}+\tfrac{1}{2}\mu\omega^2x'^2-\frac{e^2\varepsilon^2}{2\mu\omega^2}$$

x'=x–[eε/μω²]-----平衡位置为(eε/μω²) 的新线性谐振子

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} = \psi_n^{(0)} + e\varepsilon\sqrt{\frac{1}{2\mu\hbar\omega^3}}[\sqrt{n+1}\psi_{n+1}^{(0)} - \sqrt{n}\psi_{n-1}^{(0)}]$$

例 2. 假定哈密顿的矩阵形式为

$$H = \begin{pmatrix} 1 & c & 0 \\ c & 3 & 0 \\ 0 & 0 & c-2 \end{pmatrix}$$

（1）如果 c << 1, 用微扰理论计算H本征值的二级近似;
（2）计算H的精确本征值;
（3）在何种条件下上述结果符合较好?

解:

(1) c << 1

$$H_0=\begin{pmatrix}1&0&0\\0&3&0\\0&0&-2\end{pmatrix}\quad H'=\begin{pmatrix}0&c&0\\c&0&0\\0&0&c\end{pmatrix}$$

$$E_1^{(0)}=1$$
$$E_2^{(0)}=3$$
$$E_3^{(0)}=-2$$

$$\begin{cases}E_n^{(1)}=H'_{nn}\\[2ex] E_n^{(2)}=\sum\limits_{k\neq n}\dfrac{|H'_{kn}|^2}{E_n^{(0)}-E_k^{(0)}}\end{cases}$$

一级修正:

$$\begin{cases}E_1^{(1)}=H'_{11}=0\\E_2^{(1)}=H'_{22}=0\\E_3^{(1)}=H'_{33}=c\end{cases}$$

二级修正:

$$E_1^{(2)}=\sum_{k\neq n}\frac{|H'_{k1}|^2}{E_1^{(0)}-E_k^{(0)}}=\frac{|H'_{21}|^2}{E_1^{(0)}-E_2^{(0)}}+\frac{|H'_{31}|^2}{E_1^{(0)}-E_3^{(0)}}=-\tfrac{1}{2}c^2$$

$$E_2^{(2)}=\sum_{k\neq n}\frac{|H'_{k2}|^2}{E_2^{(0)}-E_k^{(0)}}=\frac{|H'_{12}|^2}{E_2^{(0)}-E_1^{(0)}}+\frac{|H'_{32}|^2}{E_2^{(0)}-E_3^{(0)}}=\tfrac{1}{2}c^2$$

$$E_3^{(2)}=\sum_{k\neq n}\frac{|H'_{k3}|^2}{E_3^{(0)}-E_k^{(0)}}=\frac{|H'_{13}|^2}{E_3^{(0)}-E_1^{(0)}}+\frac{|H'_{23}|^2}{E_3^{(0)}-E_2^{(0)}}=0$$

精确到二级：
$$\begin{cases} E_1 = 1 - \frac{1}{2}c^2 \\ E_2 = 3 + \frac{1}{2}c^2 \\ E_3 = -2 + c \end{cases}$$

$$\begin{cases} E_1 = 2 - \sqrt{1+c^2} \\ E_2 = 2 + \sqrt{1+c^2} \\ E_3 = -2 + c \end{cases}$$

(2)　精确解

$$\begin{vmatrix} 1-E & c & 0 \\ c & 3-E & 0 \\ 0 & 0 & c-2-E \end{vmatrix} = 0 \Rightarrow (c-2-E)(E^2-4E+3-c^2)=0$$

(3) c<<1：

$$\begin{cases} E_1 = 2-\sqrt{1+c^2} = 1-\frac{1}{2}c^2+\frac{1}{8}c^4+\cdots \\ E_2 = 2+\sqrt{1+c^2} = 3+\frac{1}{2}c^2-\frac{1}{8}c^4+\cdots \\ E_3 = -2+c \end{cases}$$

比较（1）和（2）找到二者符合较好的条件如左所示

§5.2　简并情况下的微扰理论

简短回顾微扰体系的方程求解过程

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \qquad \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \qquad \hat{H}^{(0)}|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$$

$H'=0$，　$|\psi_n\rangle = |\psi_n^{(0)}\rangle$, $E_n = E_n^{(0)}$

$H' \neq 0$，　$E_n^{(0)} \to E_n$, $|\psi_n^{(0)}\rangle \to |\psi_n\rangle$

为明显表示微小程度，微扰项写成如下形式：

$$\hat{H}' = \lambda \hat{H}^{(1)}$$

λ是一个很小的实参数，**En**和ψn都和微扰有关，可以把它们看做是λ的函数，可以将它们展开为的幂级数

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \quad E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}\bigg|_{\lambda=0}$$

$$|\psi_n> = |\psi_n^{(0)}> + \lambda|\psi_n^{(1)}> + \lambda^2|\psi_n^{(2)}> + \cdots, \quad |\psi_n^{(k)}> = \frac{1}{k!}\frac{d^k|\psi_n>}{d\lambda^k}\bigg|_{\lambda=0}$$

薛定谔方程

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|\psi_n^{(0)}> + \lambda|\psi_n^{(1)}> + \lambda^2|\psi_n^{(2)}> + \cdots)$$

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

$$\begin{Bmatrix} \hat{H}^{(0)}|\psi_n^{(0)}> + \\ \lambda \quad [\hat{H}^{(0)}|\psi_n^{(1)}> + \hat{H}^{(1)}|\psi_n^{(0)}>] + \\ \lambda^2 \quad [\hat{H}^{(0)}|\psi_n^{(2)}> + \hat{H}^{(1)}|\psi_n^{(1)}>] + \\ \lambda^3 \quad [\cdots\cdots\cdots\cdots] + \\ \cdots\cdots\cdots\cdots \end{Bmatrix} = \begin{Bmatrix} E_n^{(0)}|\psi_n^{(0)}> + \\ \lambda[E_n^{(0)}|\psi_n^{(1)}> + E_n^{(1)}|\psi_n^{(0)}>] + \\ \lambda^2 \quad [E_n^{(0)}|\psi_n^{(2)}> + E_n^{(1)}|\psi_n^{(1)}> + E_n^{(2)}|\psi_n^{(0)}>] + \\ \lambda^3 \quad [\cdots\cdots\cdots\cdots] + \\ \cdots\cdots\cdots\cdots \end{Bmatrix}$$

简并微扰理论

H$^{(0)}$ E$_n$$^{(0)}$: | n1 >, | n 2 >, ..., | n k >

$<n\alpha|n\beta>=\delta_{\alpha\beta}$

$$[\hat{H}^{(0)} - E_n^{(0)}]|n\alpha>= 0 \qquad \alpha = 1,2,3,\cdots,k$$

$$< n\alpha|[\hat{H}^{(0)} - E_n^{(0)}] = 0 \qquad \alpha = 1,2,3,\cdots,k$$

$$[\hat{H}^{(0)} - E_n^{(0)}]|\psi_n^{(1)}>= -[\hat{H}' - E_n^{(1)}]|\psi_n^{(0)}>$$

$|\psi_n^{(0)}>$ 已归一化

$$|\psi_n^{(0)}> = \sum_{\alpha=1}^{k} c_\alpha |n\alpha>$$

$$[\hat{H}^{(0)} - E_n^{(0)}]|\psi_n^{(1)}> = -[\hat{H}' - E_n^{(1)}]\sum_{\alpha=1}^{k} c_\alpha |n\alpha>$$

$$= E_n^{(1)}\sum_{\alpha=1}^{k} c_\alpha |n\alpha> - \sum_{\alpha=1}^{k} c_\alpha \hat{H}'|n\alpha>$$

$$< n\beta|[\hat{H}^{(0)} - E_n^{(0)}] = 0$$

$$< n\beta|[\hat{H}^{(0)} - E_n^{(0)}]|\psi_n^{(1)}> = E_n^{(1)}\sum_{\alpha=1}^{k} c_\alpha < n\beta|n\alpha> - \sum_{\alpha=1}^{k} c_\alpha < n\beta|\hat{H}'|n\alpha>$$

$$= E_n^{(1)}\sum_{\alpha=1}^{k} c_\alpha \delta_{\beta\alpha} - \sum_{\alpha=1}^{k} c_\alpha H'_{\beta\alpha} = \sum_{\alpha=1}^{k} [E_n^{(1)}\delta_{\beta\alpha} - H'_{\beta\alpha}]c_\alpha$$

$$\sum_{\alpha=1}^{k} [H'_{\beta\alpha} - E_n^{(1)}\delta_{\beta\alpha}]c_\alpha = 0$$

$$H'_{\beta\alpha} = < n\beta|\hat{H}'|n\alpha>$$

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \cdots & \cdots \\ H'_{21} & H'_{22} - E_n^{(1)} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ H'_{k1} & H'_{k2} & \cdots & H'_{kk} - E_n^{(1)} \end{vmatrix} = 0$$

久期方程的解 $\mathbf{E_n^{(1)}}$:

$$\mathbf{E_{n\nu}^{(1)}},\ \nu = 1, 2, \ldots, k.$$

$$\mathbf{E_{n\,\nu} = E_n^{(0)} + E^{(1)}_{n\,\nu}}.$$

$$\sum_{\alpha=1}^{k} [H'_{\beta\alpha} - E_{n\nu}^{(1)} \delta_{\beta\alpha}] c_{\alpha\nu} = 0 \qquad \beta = 1, 2, \cdots, k$$

$$|\psi_{n\nu}^{(0)}> = \sum_{\alpha=1}^{k} c_{\alpha\nu} | n\alpha>$$

§5.3　氢原子的一级斯塔克效应

（1）斯塔克效应

氢原子在外电场作用下所产生的谱线分裂现象

（2）哈密顿算符

$$\hat{H} = \hat{H}_0 + \hat{H}' \qquad \begin{cases} \hat{H}_0 = -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{e_s{}^2}{r} \\ \hat{H}' = e\vec{\varepsilon} \bullet \vec{r} = e\varepsilon z = e\varepsilon r\cos\theta \end{cases}$$

Z 沿外场**ε**的方向.

ε ≈ 10^2 V/m

内场强度 ≈ **10^{11} V/m.**

相比之下, 外场**ε**可视为微扰

（3） H_0

$$\begin{cases} E_n = -\dfrac{m e_s^4}{2\hbar^2 n^2} \qquad n = 1,2,3,\cdots \\ \psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta,\varphi) \end{cases}$$

n = 2, 简并度 $n^2 = 4$

$$E_n = -\frac{m e_s^4}{8\hbar^2} = -\frac{e_s^2}{8a_0} \qquad a_0 = \frac{\hbar^2}{m e_s^2}$$

$$\phi_1 \equiv \psi_{200} = R_{20}Y_{00} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$\phi_2 \equiv \psi_{210} = R_{21}Y_{10} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\theta$$

$$\phi_3 \equiv \psi_{211} = R_{21}Y_{11} = -\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta e^{i\varphi}$$

$$\phi_4 \equiv \psi_{21-1} = R_{21}Y_{1-1} = -\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta e^{-i\varphi}$$

$$\phi_\alpha \Rightarrow |\, 2\alpha > \qquad \alpha = 1,2,3,4.$$

（4）H’

$$H'_{12} = <\phi_1 | \hat{H}' | \phi_2> = e\varepsilon <R_{20}|r|R_{21}><Y_{00}|\cos\theta|Y_{10}>$$

$$H'_{21} = <\phi_2 | \hat{H}' | \phi_1> = e\varepsilon <R_{21}|r|R_{20}><Y_{10}|\cos\theta|Y_{00}>$$

....

根据球谐函数的性质

$$\cos\theta Y_{lm} = \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} Y_{l+1,m} + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}} Y_{l-1,m}$$

得

$$<Y_{l'm'}|\cos\theta|Y_{lm}> = \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} <Y_{l'm'}|Y_{l+1,m}> + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}} <Y_{l'm'}|Y_{l-1,m}>$$

$$= \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} \delta_{l'l+1}\delta_{m'm} + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}} \delta_{l'l-1}\delta_{m'm}$$

所以，**H’**的矩阵元中所有**m’=m**且*l’=l+1*或*l’=l-1*项不为零，从而只有**H’**$_{12}$、**H’**$_{21}$不为零

H'的矩阵元中所有m'=m且 *l'=l+1* **或** *l'=l-1* **项不为零，即非零项条件如右所示**

$$\begin{cases} l' = l+1 \\ l' = l-1 \\ m' = m \end{cases} \Rightarrow \begin{cases} \Delta l = l' - l = \pm 1 \\ \Delta m = m' - m = 0 \end{cases}$$

只有H'_{12}、H'_{21}不为零

$$<Y_{00}|\cos\theta|Y_{10}>=\sqrt{\tfrac{1}{3}}$$

$$H'_{12} = H'_{21} = \tfrac{e\varepsilon}{\sqrt{3}} <R_{20}|r|R_{21}>$$

$$= \tfrac{e\varepsilon}{\sqrt{3}} \int_0^\infty (\tfrac{1}{2a_0})^{3/2}(2-\tfrac{r}{a_0})e^{-r/2a_0} r \tfrac{1}{\sqrt{3}}(\tfrac{1}{2a_0})^{3/2}(\tfrac{r}{a_0})e^{-r/2a_0} r^2 dr$$

$$= \tfrac{e\varepsilon}{24}(\tfrac{1}{a_0})^4 \int_0^\infty (2-\tfrac{r}{a_0})e^{-r/a_0} r^4 dr$$

$$= \tfrac{e\varepsilon}{24}(\tfrac{1}{a_0})^4 [\int_0^\infty 2e^{-r/a_0} r^4 dr - \int_0^\infty \tfrac{r}{a_0} e^{-r/a_0} r^4 dr]$$

$$= \tfrac{e\varepsilon}{24}(\tfrac{1}{a_0})^4 [a_0^5 4!(2-5)]$$

$$= -3e\varepsilon a_0$$

（e）$\mathbf{E}^{(1)}$

$$\begin{vmatrix} -E_2^{(1)} & -3e\varepsilon a_0 & 0 & 0 \\ -3e\varepsilon a_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \qquad \begin{cases} E_{21}^{(1)} = 3e\varepsilon a_0 \\ E_{22}^{(1)} = -3e\varepsilon a_0 \\ E_{23}^{(1)} = 0 \\ E_{24}^{(1)} = 0 \end{cases}$$

（f） $\psi^{(0)}$

$$\sum_{\alpha=1}^{k} (H'_{\beta\alpha} - E_{n\nu}^{(1)}\delta_{\beta\alpha})c_{\alpha\nu} = 0$$

$$\beta = 1,2,\cdots k$$

$$H' - E^{(1)}I = 0$$

$$\begin{cases} -E_2^{(1)}c_1 \quad -3e\varepsilon a_0 c_2 + \quad 0 \quad + \quad 0 = 0 \\ -3e\varepsilon a_0 c_1 - E_2^{(1)}c_2 \quad + \quad 0 \quad + \quad 0 = 0 \\ 0 \quad + \quad 0 \quad -E_2^{(1)}c_3 \quad + \quad 0 = 0 \\ 0 \quad + \quad 0 \quad + \quad 0 \quad -E_2^{(1)}c_4 = 0 \end{cases}$$

$$E_2^{(1)} = E_{21}^{(1)} = 3e\varepsilon a_0 \qquad E_2^{(0)} + 3e\varepsilon a_0$$

$$\begin{cases} c_1 = -c_2 \\ c_3 = c_4 = 0 \end{cases} \qquad \psi_1^{(0)} = \frac{1}{\sqrt{2}}[\phi_1 - \phi_2] = \frac{1}{\sqrt{2}}[\psi_{200} - \psi_{210}]$$

$$E_2^{(1)} = E_{22}^{(1)} = -3e\varepsilon a_0 \qquad E_2^{(0)} - 3e\varepsilon a_0$$

$$\begin{cases} c_1 = c_2 \\ c_3 = c_4 = 0 \end{cases} \qquad \psi_2^{(0)} = \frac{1}{\sqrt{2}}[\phi_1 + \phi_2] = \frac{1}{\sqrt{2}}[\psi_{200} + \psi_{210}]$$

$$E_2^{(1)} = E_{23}^{(1)} = E_{24}^{(1)} = 0 \qquad E_2^{(0)}$$

$$\begin{cases} c_1 = c_2 = 0 \\ c_3 \neq 0 \text{ or } c_4 \neq 0 \end{cases} \qquad \begin{aligned} \psi_3^{(0)}(\psi_4^{(0)}) &= c_3\phi_3 + c_4\phi_4 \\ &= c_3\psi_{211} + c_4\psi_{21-1} \end{aligned}$$

$$\begin{cases} c_3 = 1 \\ c_4 = 0 \end{cases} \text{ 或 } \begin{cases} c_3 = 0 \\ c_4 = 1 \end{cases} \qquad \begin{cases} \psi_3^{(0)} = \psi_{211} \\ \psi_4^{(0)} = \psi_{21-1} \end{cases}$$

§5.4 变分法

微扰法的哈密顿算符 $\hat{H} = \hat{H}_0 + \hat{H}'$

$$\left|\frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}}\right| << 1 \qquad |H'_{kn}| << E_n^{(0)} - E_k^{(0)}, \quad E_n^{(0)} \neq E_k^{(0)}$$

另一种方法是变分法，不受上述条件限制

假设体系能量本征值由小到大顺序和相应的本征函数为

$$E_0 < E_1 < E_2 < \ldots\ldots < E_n < \ldots\ldots$$

$$|\psi_0> \quad |\psi_1> \quad |\psi_2> \quad \ldots\ldots\ldots|\psi_n>\ldots\ldots$$

$$\begin{cases} \hat{H}|\psi_n> = E_n|\psi_n> & n = 0,1,2,\cdots \\ \sum_n |\psi_n><\psi_n| = 1 \\ <\psi_m|\psi_n> = \delta_{mn} \end{cases}$$

$$E = \overline{H} = <\psi|\hat{H}|\psi> \equiv <H> \qquad E \geq E_0$$

$$E = \overline{H} = <\psi|\hat{H}|\psi> = \sum_n <\psi|\hat{H}|\psi_n><\psi_n|\psi> = \sum_n E_n <\psi|\psi_n><\psi_n|\psi>$$

$$\geq E_0 \sum_n <\psi|\psi_n><\psi_n|\psi> = E_0 <\psi|\psi>$$

$$\overline{H} \geq E_0 \qquad \overline{H} = \frac{<\psi|\hat{H}|\psi>}{<\psi|\psi>} \geq E_0$$

$$|\psi\rangle \to |\psi(1)\rangle, |\psi(2)\rangle, \ldots\ldots, |\psi(k)\rangle, \ldots\ldots$$

$$\overline{H} \to \overline{H}_1, \overline{H}_2, \cdots\cdots \overline{H}_k$$

$$Min\ [\overline{H}_1,\ \overline{H}_2,\ \cdots\cdots\ \overline{H}_k] \approx E_0$$

变分法求基态能量的步骤:

选取含有参量λ的尝试波函数ψ(λ)代入方程求<H(λ)>，即H的平均值，然后对其求λ的一阶导数为零时的结果，求出H(λ)的最小值，所得结果即为E_0的近似值

$$< H > = < \psi | \hat{H} | \psi > = < \psi(\lambda) | \hat{H} | \psi(\lambda) > = < H(\lambda) > = \overline{H}(\lambda)$$

$$\frac{d\overline{H}(\lambda)}{d\lambda} \equiv \frac{d < H(\lambda) >}{d\lambda} = 0$$

§5.5 氦原子基态（变分法）

氦原子核质量比电子大得多，可认为核是固定不动的，其体系哈密顿算符可写为

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e_s^{\ 2}}{r_1} - \frac{2e_s^{\ 2}}{r_2} + \frac{e_s^{\ 2}}{r_{12}}$$

用变分法求解基态能量

（1）哈密顿算符

$$\hat{H} = \hat{H}_0 + \hat{H}_{12}$$

$$\hat{H}_0 = \left[-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e_s^{\ 2}}{r_1}\right] + \left[-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e_s^{\ 2}}{r_2}\right] = \hat{H}_1(\vec{r}_1) + \hat{H}_2(\vec{r}_2)$$

$$\hat{H}_{12} = \frac{e_s^{\ 2}}{r_{12}}$$

（2）尝试波函数

H₀的本征函数

假定：
$$\begin{cases}\hat{H}_1\psi(\vec{r}_1)=\varepsilon_1\psi(\vec{r}_1)\\ \hat{H}_2\psi(\vec{r}_2)=\varepsilon_2\psi(\vec{r}_2)\end{cases}$$

$$\Psi(\vec{r}_1,\vec{r}_2)=\psi(\vec{r}_1)\psi(\vec{r}_2)$$

H_1，H_2

$$\psi_{100}(\vec{r})=\frac{1}{\sqrt{\pi}}[\frac{z}{a_0}]^{3/2}e^{-Zr/a_0}$$

^4He $\quad Z=2$

$$\Psi(\vec{r}_1,\vec{r}_2)=\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)=\frac{Z^3}{\pi a_0^3}e^{-Z(r_1+r_2)/a_0}$$

尝试波函数

（3）选择变分参数　考虑两电子相互屏蔽，选Z为参数

（4）基态能量

$$\overline{H}=<\Psi|\hat{H}|\Psi>=<\Psi|\hat{H}_1|\Psi>+<\Psi|\hat{H}_2|\Psi>+<\Psi|\hat{H}_{12}|\Psi>$$

$$<\Psi|\hat{H}_1|\Psi>=<\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)|\hat{H}_1|\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)>$$

$$=<\psi_{100}(\vec{r}_1)|\hat{H}_1|\psi_{100}(\vec{r}_1)><\psi_{100}(\vec{r}_2)|\psi_{100}(\vec{r}_2)>$$

$$=<\psi_{100}(\vec{r}_1)|-\frac{\hbar^2}{2\mu}\nabla_1^2-\frac{2e_s^2}{r_1}|\psi_{100}(\vec{r}_1)>$$

$$=<\psi_{100}(\vec{r}_1)|\frac{\hat{p}_1^2}{2\mu}|\psi_{100}(\vec{r}_1)>-2e_s^2<\psi_{100}(\vec{r}_1)|\frac{1}{r_1}|\psi_{100}(\vec{r}_1)>$$

$$<\Psi|\hat{H}_1|\Psi>=\frac{Z^2e_s^{\ 2}}{2a_0}-\frac{2Ze_s^{\ 2}}{a_0}$$，同理，$$<\Psi|\hat{H}_2|\Psi>=\frac{Z^2e_s^{\ 2}}{2a_0}-\frac{2Ze_s^{\ 2}}{a_0}$$

$$<\Psi|\hat{H}_0|\Psi>=<\Psi|\hat{H}_1|\Psi>+<\Psi|\hat{H}_2|\Psi>=\frac{Z^2e_s^{\ 2}}{a_0}-\frac{4Ze_s^{\ 2}}{a_0}$$

$$<\Psi|\hat{H}_{12}|\Psi>=<\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)|\frac{e_s^{\ 2}}{r_{12}}|\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)>$$

$$=\iint e_s|\psi_{100}(\vec{r}_1)|^2\frac{1}{r_{12}}e_s|\psi_{100}(\vec{r}_2)|^2 d\tau_1 d\tau_2$$

$$=\iint\frac{\rho(r_1)}{r_{12}}\rho(r_2)d\tau_1 d\tau_2$$

$$=\iint\left(\frac{Z^3}{\pi a_0^3}\right)^2\frac{e_s^{\ 2}}{r_{12}}e_s^{\ -2Z(r_1+r_2)/a_0}d\tau_1 d\tau_2$$

$$=\left(\frac{Z^3}{\pi a_0^3}\right)^2\bullet\frac{5\pi^2e_s^{\ 2}}{8(Z/a_0)^5}=\frac{5Ze_s^{\ 2}}{8a_0}$$

$$\rho(r_i)=e_s|\psi_{100}(\vec{r}_i)|^2$$

$$=e_s\frac{Z^3}{\pi a_0}e^{-2Zr/a_0}$$

$i=1,2.$

$$\overline{H}=\frac{Z^2 e_s{}^2}{a_0}-\frac{4Ze_s{}^2}{a_0}+\frac{5Ze_s{}^2}{8a_0}$$

$$\frac{d\overline{H}}{dZ}=\frac{2Ze_s{}^2}{a_0}-\frac{4e_s{}^2}{a_0}+\frac{5e_s{}^2}{8a_0}=0$$

$$2Z_{\min}-4+\frac{5}{8}=0$$

$$Z_{\min}=\frac{27}{16}=1.69$$

$$E_0 \approx -2.85\,\frac{e_s{}^2}{a_0} \qquad E_0(\exp) = -2.904\,\frac{e_s{}^2}{a_0}$$

$$\Psi(\vec{r}_1,\vec{r}_2)=\frac{1}{\pi}\left(\frac{27}{16a_0}\right)^3 e^{\frac{-27(r_1+r_2)}{16a_0}}$$

作业

5.1
5.2
5.3

§5.6 与时间有关的微扰理论

以上章节讨论的是定态微扰问题，体系的哈密顿算符不含时间，求解的是定态薛定谔方程，本节讨论体系哈密顿算符含有与时间相关的微扰情况，即

$$\hat{H}(t) = \hat{H}_0 + H'(t)$$

由于哈密顿算符与时间有关，体系的波函数要由含时间的薛定谔方程准确解出，通常是很困难的.下面要讨论的与时间有关的微扰理论，能够由$\mathbf{H_0}$的定态波函数近似地计算出有微扰时的波函数，从而可计算无微扰体系在微扰作用下由一个量子态跃迁到另一个量子态的跃迁概率.将这些结果可用于讨论原子的光发射和吸收等问题.

(1) 含时微扰理论

$$\hat{H}_0\phi_n = \varepsilon_n\phi_n \quad \Phi_n = \phi_n e^{-\frac{i}{\hbar}\varepsilon_n t} \quad i\hbar\frac{\partial}{\partial t}\Phi_n = \hat{H}_0\Phi_n \quad \Psi = \sum_n a_n(t)\Phi_n$$

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}(t)\Psi \qquad i\hbar\frac{\partial}{\partial t}\sum_n a_n(t)\Phi_n = \hat{H}(t)\sum_n a_n(t)\Phi_n$$

$$i\hbar\sum_n\frac{da_n(t)}{dt}\Phi_n + \boxed{i\hbar\sum_n a_n(t)\frac{\partial\Phi_n}{\partial t}} = \boxed{\sum_n a_n(t)\hat{H}_0\Phi_n} + \sum_n a_n(t)\hat{H}'(t)\Phi_n$$

$$i\hbar\sum_n\frac{da_n(t)}{dt}\Phi_n = \sum_n a_n(t)\hat{H}'(t)\Phi_n$$

$$i\hbar\sum_n\left[\frac{da_n(t)}{dt}\right]\int\Phi_m^*\Phi_n d\tau = \sum_n a_n(t)\int\Phi_m^*\hat{H}'(t)\Phi_n d\tau$$

$$i\hbar\sum_n\frac{da_n(t)}{dt}\delta_{mn} = \sum_n a_n(t)\int\phi_m^*\hat{H}'(t)\phi_n e^{i[\varepsilon_m-\varepsilon_n]t/\hbar}d\tau$$

$$i\hbar\sum_n \frac{da_n(t)}{dt}\delta_{mn} = \sum_n a_n(t)\int \phi_m^* \hat{H}'(t)\phi_n e^{i[\varepsilon_m-\varepsilon_n]t/\hbar}d\tau$$

$$i\hbar\frac{da_m(t)}{dt} = \sum_n a_n(t)\hat{H}'_{mn}e^{i\omega_{mn}t}$$ 薛定谔方程

$$\begin{cases} \hat{H}'_{mn} = \int \varphi_m^* \hat{H}'(t)\varphi_n d\tau & \text{微扰矩阵元} \\ \omega_{mn} = \frac{1}{\hbar}[\varepsilon_m - \varepsilon_n] & \text{波尔频率} \end{cases}$$

记 $\hat{H}'(t) = \lambda\hat{H}^{(1)}(t)$，将 $a_n(t)$ 展开成 λ 的幂级数

$$a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \cdots$$

$$i\hbar\left[\frac{da_m^{(0)}}{dt} + \lambda\frac{da_m^{(1)}}{dt} + \lambda^2\frac{da_m^{(2)}}{dt} + \cdots\right] = \sum_n [a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \cdots]\hat{H}'_{mn}e^{i\omega_{mn}t}$$

$$= \sum_n [\lambda a_n^{(0)} + \lambda^2 a_n^{(1)} + \lambda^3 a_n^{(2)} + \cdots]\hat{H}'^{(1)}_{mn}e^{i\omega_{mn}t}$$

$$\begin{cases} \dfrac{da_m^{(0)}}{dt} = 0 \\ i\hbar \dfrac{da_m^{(1)}}{dt} = \sum_n a_n^{(0)} \hat{H}'_{mn} e^{i\omega_{mn} t} \\ i\hbar \dfrac{da_m^{(2)}}{dt} = \sum_n a_n^{(1)} \hat{H}'_{mn} e^{i\omega_{mn} t} \\ \cdots\cdots\cdots\cdots = \cdots\cdots\cdots\cdots \end{cases}$$

设微扰**H'**在**t=0**时开始引入，**t=0**时体系处于Φ_k态且λ=0，则有

$$t=0,\ \Psi = \Phi_k = \sum_n a_n(0)\Phi_n = \sum_n \delta_{nk}\Phi_n$$

$$= \sum_n [a_n^{(0)}(0) + \lambda a_n^{(1)}(0) + \cdots]\Phi_n = \sum_n a_n^{(0)}(0)\Phi_n$$

$$\delta_{nk} = a_n^{(0)}(0) = a_n^{(0)}(t)$$

t ≥ 0 可得方程： $i\hbar \dfrac{da_m^{(1)}}{dt} = \sum_n \delta_{nk} \hat{H}'_{mn} e^{i\omega_{mn} t} = \hat{H}'_{mk} e^{i\omega_{mk} t}$

可求得一级近似解： $a_m^{(1)} = \dfrac{1}{i\hbar}\int_0^t \hat{H}'_{mk} e^{i\omega_{mk} t} dt$

$$a_m(t) = a_m^{(0)}(t) + a_m^{(1)}(t) + \cdots = \delta_{mk} + \frac{1}{i\hbar}\int_0^t H'_{mk} e^{i\omega_{mk} t} dt + \cdots$$

$$\Psi = \sum_m a_m(t)\Psi_m \qquad W_{k\to m} = |a_m^{(1)}(t)|^2 = \left| \frac{1}{i\hbar}\int_0^t H'_{mk} e^{i\omega_{mk} t} dt \right|^2$$

§ 5.7 跃迁概率

（1）常微扰

$$\hat{H}' = \begin{cases} 0 & t < 0 \\ \hat{H}'(\vec{r}) & 0 \le t \le t_1 \\ 0 & t > t_1 \end{cases}$$

（a） $a_m^{(1)}$

$$a_m^{(1)}(t) = \frac{1}{i\hbar}\int_0^t H'_{mk} e^{i\omega_{mk}t} dt = \frac{H'_{mk}}{i\hbar}\int_0^t e^{i\omega_{mk}t} dt = \frac{H'_{mk}}{i\hbar}\frac{1}{i\omega_{mk}}\left[e^{i\omega_{mk}t}\right]\Big|_0^t$$

$$= -\frac{H'_{mk}}{\hbar\omega_{mk}}\left[e^{i\omega_{mk}t} - 1\right] = -\frac{H'_{mk}}{\hbar\omega_{mk}}\left[e^{i\omega_{mk}t} - 1\right] = -\frac{H'_{mk}}{\hbar\omega_{mk}} e^{i\omega_{mk}t/2}\left[e^{i\omega_{mk}t/2} - e^{-i\omega_{mk}t/2}\right]$$

$$= -\frac{H'_{mk}}{\hbar\omega_{mk}} 2i e^{i\omega_{mk}t/2} \sin(\tfrac{1}{2}\omega_{mk}t)$$

（b）跃迁概率与跃迁速率

$$W_{k\to m}=|a_m^{(1)}(t)|^2 = \left|-\frac{H'_{mk}}{\hbar\omega_{mk}}2ie^{i\omega_{mk}t/2}\sin(\tfrac{1}{2}\omega_{mk}t)\right|^2=\frac{4|H'_{mk}|^2\sin^2(\tfrac{1}{2}\omega_{mk}t)}{\hbar^2\omega_{mk}{}^2}$$

$$\lim_{\alpha\to\infty}\frac{\sin^2(\alpha x)}{\pi\alpha x^2}=\delta(x)$$

$$t\to\infty \qquad \lim_{t\to\infty}\frac{\sin^2(\tfrac{1}{2}\omega_{mk}t)}{\tfrac{1}{4}\omega_{mk}{}^2t}=\pi\delta(\tfrac{1}{2}\omega_{mk})$$

$$=2\pi\delta\left(\frac{\varepsilon_m-\varepsilon_k}{\hbar}\right)=2\pi\hbar\delta(\varepsilon_m-\varepsilon_k)$$

$$W_{k\to m}=\frac{2\pi t}{\hbar}|H'_{mk}|^2\delta(\varepsilon_m-\varepsilon_k)$$

$$\omega_{k\to m}=\frac{W_{k\to m}}{t}=\frac{2\pi}{\hbar}|H'_{mk}|^2\delta(\varepsilon_m-\varepsilon_k)$$

补充:

$$\lim_{\alpha\to\infty}\frac{\sin^2(\alpha x)}{\pi\alpha x^2}=\delta(x) \qquad \int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}dx=\pi$$

$$\sin^2\alpha=\frac{1-\cos 2\alpha}{2}$$

$$\cos^2\alpha=\frac{1+\cos 2\alpha}{2}$$

证明

$$\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}dx=\frac{1}{2}\int_{-\infty}^{+\infty}\frac{1-\cos 2x}{x^2}dx=\frac{1}{2}[\int_{-\infty}^{+\infty}\frac{1}{x^2}dx-\int_{-\infty}^{+\infty}\frac{\cos 2x}{x^2}dx]=$$

$$=\frac{1}{2}[\int_{-\infty}^{+\infty}d(-x^{-1})-\int_{-\infty}^{+\infty}\frac{\cos 2x}{x^2}dx]=-\frac{1}{2}\int_{-\infty}^{+\infty}\frac{\cos 2x}{x^2}dx$$

$$=\int_{-\infty}^{+\infty}\frac{\sin 2x}{x}dx\overset{y=2x}{=}\int_{-\infty}^{+\infty}\frac{\sin y}{y}dy=2\int_{0}^{+\infty}\frac{\sin y}{y}dy=\pi$$

http://en.wikipedia.org/wiki/List_of_integrals_of_trigonometric_functions

$$\int\frac{\cos ax}{x^n}dx=-\frac{\cos ax}{(n-1)x^{n-1}}-\frac{a}{n-1}\int\frac{\sin ax}{x^{n-1}}dx \qquad (\text{for } n\neq 1)$$

http://en.wikipedia.org/wiki/Dirichlet_integral

$$\int_0^{\infty}\frac{\sin\omega}{\omega}d\omega=\frac{\pi}{2}$$

（c）讨论

$$\omega_{k\to m}=\frac{W_{k\to m}}{t}=\frac{2\pi}{\hbar}|H'_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k)$$

i). 对长时间的常微扰，跃迁与时间无关，只有当末态与初态能量接近$\varepsilon_m\approx\varepsilon_k$才有显著的跃迁

ii). 能量守恒体现在$\delta(\varepsilon_m-\varepsilon_k)$

iii). 费米黄金定则

若能量在$\varepsilon_m+d\varepsilon_m$范围的状态数目为$\rho(\varepsilon_m)d\varepsilon_m$，则跃迁速率为

$$\omega=\int d\varepsilon_m\rho(\varepsilon_m)\omega_{k\to m}=\int d\varepsilon_m\rho(\varepsilon_m)\frac{2\pi}{\hbar}|H'_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k)$$

$$=\frac{2\pi}{\hbar}|H'_{mk}|^2\,\rho(\varepsilon_m)$$

（2） 谐微扰

（a）哈密顿算符

$$\hat{H}'(t)=\begin{cases}0 & t<0\\ \hat{A}\cos\omega t & t>0\end{cases}$$

$$\hat{H}'(t)=\begin{cases}0 & t<0\\ \hat{F}[e^{i\omega t}+e^{-i\omega t}] & t>0\end{cases}$$

F 与时间t无关

（b） $a_m^{(1)}(t)$

$$\begin{aligned}H'_{mk} &=<\phi_m|\hat{H}'(t)|\phi_k>\\ &=<\phi_m|\hat{F}[e^{i\omega t}+e^{-i\omega t}]|\phi_k>\\ &=<\phi_m|\hat{F}|\phi_k>[e^{i\omega t}+e^{-i\omega t}]\\ &=F_{mk}[e^{i\omega t}+e^{-i\omega t}]\end{aligned}$$

$$a_m^{(1)}(t) = \frac{F_{mk}}{i\hbar}\int_0^t [e^{i\omega t} + e^{-i\omega t}]e^{i\omega_{mk} t}dt$$

$$= \frac{F_{mk}}{i\hbar}\int_0^t [e^{i[\omega_{mk}+\omega]t} + e^{i[\omega_{mk}-\omega]t}]dt$$

$$= \frac{F_{mk}}{i\hbar}\left[\frac{e^{i[\omega_{mk}+\omega]t}}{i[\omega_{mk}+\omega]} + \frac{e^{i[\omega_{mk}-\omega]t}}{i[\omega_{mk}-\omega]}\right]_0^t$$

$$= -\frac{F_{mk}}{\hbar}\left[\frac{e^{i[\omega_{mk}+\omega]t}-1}{[\omega_{mk}+\omega]} + \frac{e^{i[\omega_{mk}-\omega]t}-1}{[\omega_{mk}-\omega]}\right]$$

（c）讨论

(i) $\omega = \omega_{mk}$=波尔频率,对上式第二项有

$$\lim_{\omega\to\omega_{mk}} \frac{e^{i[\omega_{mk}-\omega]t}-1}{[\omega_{mk}-\omega]} = it$$

$$a_m^{(1)}(t) = -\frac{F_{mk}}{\hbar}\left[\frac{e^{i2\omega_{mk}t}-1}{2\omega_{mk}} + it\right]$$

it 是主项

(ii) $\omega = -\omega_{mk}$

$$a_m^{(1)}(t) = -\frac{F_{mk}}{\hbar}\left[it + \frac{e^{i2\omega_{mk}t}-1}{2\omega_{mk}}\right]$$

it 是主项

(iii) $\omega \neq \pm\omega_{mk}$，两项都不随时间增加

综上，只有当$\omega=\pm\omega_{mk}=\pm(\varepsilon_m-\varepsilon_k)/\hbar$ 或$\varepsilon_m=\varepsilon_k\pm\hbar\omega$时，才出现明显的跃迁.这就是说，只有当外界微扰含有频率ω_{mk}时，体系才能从φ_k态跃迁到φ_m,这说明所讨论的跃迁是一个共振现象.故只需要讨论 $\hbar\omega\approx\pm\hbar\omega_{mk}$ 的情况

（d）跃迁概率

$\omega=\omega_{mk}$ $$a_m^{(1)} = -\frac{F_{mk}}{\hbar}\left[\frac{e^{i[\omega_{mk}-\omega]t}-1}{\omega_{mk}-\omega}\right]$$

与常微扰情形类似，对其进行代换后得 $$a_m^{(1)} = -\frac{H'_{mk}}{\hbar\omega_{mk}}\left[e^{i\omega_{mk}t}-1\right]$$ $H'_{mk} \to F_{mk}$，$\omega_{mk} \to \omega_{mk}-\omega$

$$W_{k\to m} = \frac{|F_{mk}|^2}{\hbar^2}2\pi t\delta(\omega_{mk}-\omega) = \frac{2\pi t}{\hbar^2}|F_{mk}|^2\,\delta(\tfrac{1}{\hbar}[\varepsilon_m-\varepsilon_k]-\omega)$$

$$= \frac{2\pi t}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k-\hbar\omega)$$

$\omega=-\omega_{mk}$ $$W_{k\to m} = \frac{2\pi t}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k+\hbar\omega)$$

综上 $$W_{k\to m} = \frac{2\pi t}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k\pm\hbar\omega)$$

（e） 跃迁速率

$$\omega_{k\to m} = \frac{W_{k\to m}}{t} = \frac{2\pi}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m - \varepsilon_k \pm \hbar\omega)$$

或

$$\omega_{k\to m} = \frac{2\pi}{\hbar^2}|F_{mk}|^2\,\delta(\omega_{mk} \pm \omega)$$

（f）讨论

f.1 $\delta(\varepsilon_m-\varepsilon_k\pm\hbar\omega)$ 体现能量守恒$\varepsilon_m-\varepsilon_k\pm\hbar\omega= 0$

f.2 $\varepsilon_k > \varepsilon_m$

$$\omega_{k\to m} = \frac{2\pi}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m - \varepsilon_k + \hbar\omega)$$

$\varepsilon_m=\varepsilon_k - \hbar\omega$ $\hbar\omega$--- 光子

f.3 $\varepsilon_k < \varepsilon_m$

$$\omega_{k\to m} = \frac{2\pi}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m - \varepsilon_k - \hbar\omega)$$

f.4　m 跃迁到 k 态

$$\omega_{m\to k}=\frac{2\pi}{\hbar}|F_{km}|^2\,\delta(\varepsilon_k-\varepsilon_m\pm\hbar\omega)$$

F是厄米算符

$$=\frac{2\pi}{\hbar}|F_{mk}|^2\,\delta(-[\varepsilon_m-\varepsilon_k\mp\hbar\omega])$$

$$=\frac{2\pi}{\hbar}|F_{mk}|^2\,\delta(\varepsilon_m-\varepsilon_k\mp\hbar\omega)$$

$$=\omega_{k\to m}$$

（3）能量时间的不确定关系

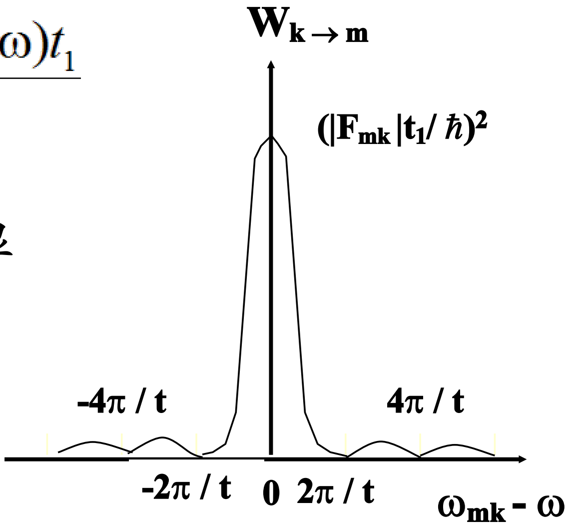
初态Φ_k 分立 ,末态 Φ_m 连续，且 $(\varepsilon_m > \varepsilon_k)$

$$\hat{H}'(t)=\begin{cases}0 & t<0\\ \hat{F}(e^{i\omega t}+e^{-i\omega t}) & 0<t<t_1\\ 0 & t>t_1\end{cases}$$

$t \geq t_1$，$\Phi_k \rightarrow \Phi_m$

$$W_{k\to m}=\frac{4|F_{mk}|^2 \sin^2\frac{1}{2}(\omega_{mk}-\omega)t_1}{\hbar^2(\omega_{mk}-\omega)^2}$$

（a）$(-2\pi/t_1, 2\pi/t_1)$ $W_{k\to m}$ 很明显



（b）能量守恒 $\varepsilon_m=\varepsilon_k+\hbar\omega$ 或 $\omega_{mk}=\omega$ 只在原点严格成立. 在区间 $[-2\pi/t_1 , 2\pi/t_1]$，跃迁概率明显不为零，ω_{mk}可以取 ω，还可以取 $\omega-2\pi/t_1 < \omega_{mk} <\omega+2\pi/t_1$，其不确定范围是 $\Delta\omega_{mk}= (4\pi/t_1) \sim (1/t_1)$，

考虑k是分立能级，则有

$$\Delta\omega_{mk}=\Delta\left(\frac{\varepsilon_m-\varepsilon_k}{\hbar}\right)=\frac{1}{\hbar}\Delta\varepsilon_m\approx\frac{1}{t_1}\qquad t_1\Delta\varepsilon_m\approx\hbar$$

测量时间的间隔是 Δt，能量不确定程度是 ΔE，则

$$\Delta E\,\Delta t\approx\hbar$$

这就是能量时间的不确定关系

（4）例题

t＝0时，一带电荷e 的线性谐振子处于基态， t＞0时，施加沿x正向的恒定外场Σ，现计算线性谐振子处于任意态时的概率

解: $\hat{H}' = e\Sigma x \qquad a_m^{(1)}(t) = \frac{1}{i\hbar}\int_0^t H'_{mk} e^{i\omega_{mk}t} dt$

$$x_{m0} = \int_{-\infty}^{\infty} \psi_m^*(x) x \psi_0(x) dx$$

$$= \int_{-\infty}^{\infty} \psi_m^*(x) \frac{1}{\alpha}\sqrt{\frac{1}{2}} \psi_1(x) dx$$

$$= \frac{1}{\alpha}\sqrt{\frac{1}{2}}\delta_{m1}$$

$$= \frac{e\Sigma}{i\hbar}\int_0^t x_{mk} e^{i\omega_{mk}t} dt$$

t=0
k=0

$$= \frac{e\Sigma}{i\hbar}\int_0^t x_{m0} e^{i\omega_{m0}t} dt$$

$$= \frac{1}{\alpha}\sqrt{\frac{1}{2}}\frac{e\Sigma}{i\hbar}\delta_{m1}\int_0^t e^{i\omega_{m0}t} dt =$$

$$\frac{1}{\alpha}\sqrt{\frac{1}{2}}\frac{e\Sigma}{i\hbar}\delta_{m1}\left[\frac{e^{i\omega_{m0}t}}{i\omega_{m0}}\right]_0^t = -\frac{e\Sigma}{\sqrt{2}\alpha\hbar\omega_{m0}}\delta_{m1}[e^{i\omega_{m0}t} - 1]$$

$$a_1^{(1)}(t) = -\frac{e\Sigma}{\sqrt{2\alpha\hbar\omega_{10}}}(e^{i\omega_{10}t} - 1)$$

$$W_{0\to 1} = \left|a_1^{(1)}\right|^2 = \left|-\frac{e\Sigma}{\sqrt{2\alpha\hbar\omega_{10}}}(e^{i\omega_{10}t} - 1)\right|^2$$

$$= \frac{e^2\Sigma^2}{2\alpha^2\hbar^2\omega_{10}{}^2}(e^{i\omega_{10}t} - 1)(e^{-i\omega_{10}t} - 1)$$

$$= \frac{e^2\Sigma^2}{2\alpha^2\hbar^2\omega_{10}{}^2}[2 - (e^{i\omega_{10}t} + e^{-i\omega_{10}t})]$$

$$= \frac{e^2\Sigma^2}{\alpha^2\hbar^2\omega_{10}{}^2}[1 - \cos(\omega_{10}t)]$$

结论:

ψ_0 — ψ_1	$W = W_{0\to 1}$
ψ_0 — $\psi_{2,3,\ldots}$	$W = 0$

§5.8 光的发射和吸收

原子对光的发射和吸收是原子体系与光相互作用所产生的现象。彻底地用量子理论解释这类现象属于量子电动力学的范围。可以采用较简单的讨论方式，即用量子力学处理原子体系，而光波则仍用经典理论中的电磁波描写，但这样的讨论只能解释吸收与受激发射，不能说明自发发射，为了把自发发射包括在讨论中，先介绍爱因斯坦关于发射系数和吸收系数的一般讨论。

为了描述原子在能级**m**和**k**间的跃迁概率，爱因斯坦引进三个系数A_{mk},B_{mk},B_{km}，A_{mk}为**m**到**k**的自发发射系数，表示单位时间的跃迁概率.其中，B_{mk}为受激发射系数，B_{km}为吸收系数，它们的意义如下：设作用于原子的光波在ω至$\omega+d\omega$频率范围内的能量密度为$I(\omega)d\omega$,则在单位时间内原子由**m**能级受激跃迁到**k**能级的概率是$B_{mk}I(\omega)$,由**k**能级跃迁到**m**能级的概率是$B_{km}I(\omega)$.

（1）自发发射系数 A_{mk}

i) A_{mk}

没有光的辐射，单位时间从Φ_m跃迁至Φ_k态（$\varepsilon_m > \varepsilon_k$）的概率为$A_{mk}$.

ii) A_{mk}，B_{mk}，B_{km}

在光的辐射下，从ε_m跃迁到ε_k 的概率为

$$A_{mk} + B_{mk} I(\omega_{mk})$$

从ε_k跃迁至ε_m的概率为 $B_{km} I(\omega_{mk})$

在温度T时的热平衡态

能级ε_m的原子数

能级ε_k的原子数

$$N_m [A_{mk} + B_{mk} I(\omega_{mk})] = N_k B_{km} I(\omega_{mk})$$

iii) 能量密度

$$I(\omega_{mk}) = \frac{N_m A_{mk}}{N_k B_{km} - N_m B_{mk}} = \frac{A_{mk}}{\frac{N_k}{N_m} B_{km} - B_{mk}} = \frac{A_{mk}}{B_{km}} \frac{1}{e^{\frac{\hbar\omega_{mk}}{kT}} - \frac{B_{mk}}{B_{km}}}$$

麦克斯韦-玻尔兹曼分布

$$\begin{cases} N_k = C(T)e^{-\varepsilon_k/kT} \\ N_m = C(T)e^{-\varepsilon_m/kT} \end{cases}$$

$$\frac{N_k}{N_m} = e^{(\varepsilon_m - \varepsilon_k)/kT} = e^{\hbar\omega_{mk}/kT}$$

热平衡时

$$\rho(\nu)d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1}d\nu$$

$$\rho(\nu)d\nu = I(\omega)d\omega$$

$$\omega = 2\pi\nu, \quad d\omega = 2\pi d\nu$$

$$\rho(\nu) = 2\pi I(\omega)$$

$$\frac{A_{mk}}{B_{km}} \frac{1}{e^{\frac{\hbar\omega_{mk}}{kT}} - \frac{B_{mk}}{B_{km}}} = \frac{4h\nu_{mk}^3}{c^3}\frac{1}{e^{h\nu_{mk}/kT} - 1}$$

$$\hbar\omega_{mk} = h\nu_{mk}, B_{km} = B_{km}$$

$$A_{mk} = \frac{4h\nu_{mk}^3}{c^3} B_{km} = \frac{\hbar\omega_{mk}^3}{c^3\pi^2} B_{mk}$$

(2) 用微扰理论计算发射和吸收系数

（a）两点近似

i） 忽略光波中磁场的影响

(CGS
)

$$U_E = e\vec{E} \bullet \vec{r} \approx eEa \qquad a = \frac{\hbar^2}{\mu e_s^{\,2}}$$ （波尔半径

$$U_B = -\vec{M} \bullet \vec{B} \approx -\frac{-e}{2\mu c} L_z B \approx \frac{e}{\mu c} \hbar E$$

$\mathbf{B} \approx \mathbf{E}$

$$\frac{U_B}{U_E} \approx \frac{\dfrac{e}{\mu c}\hbar E}{eEa} = \frac{\dfrac{e}{\mu c}\hbar E}{eE\dfrac{\hbar^2}{\mu e_s^{\,2}}} = \frac{e_s^{\,2}}{\hbar c} = \frac{1}{137} \equiv \alpha$$

ii)　近均匀电场近似

$$\begin{cases} E_x = E_0 \cos(\frac{2\pi}{\lambda} z - \omega t) \\ E_y = E_z = 0 \end{cases}$$

原子线度 $z \approx a \approx 10^{-10}$m　　可见光 $\lambda \approx 10^{-6}$m

$$\frac{2\pi}{\lambda} z \approx \frac{2\pi}{\lambda} a \approx 10^{-4} << 1$$

$$E_x = E_0 \cos \omega t$$

（b）微扰哈密顿算符

$$\hat{H}' = exE_x = exE_0 \cos\omega t = \tfrac{1}{2} exE_0[e^{i\omega t} + e^{-i\omega t}] = \hat{F}[e^{i\omega t} + e^{-i\omega t}]$$

$$\hat{F} = \tfrac{1}{2} exE_0$$

（c） $\omega_{k\to m}$

i) 吸收情形，$\varepsilon_k < \varepsilon_m$

$$\omega_{k\to m} = \frac{2\pi}{\hbar} |F_{mk}|^2 \delta(\varepsilon_m - \varepsilon_k - \hbar\omega) = \frac{2\pi}{\hbar} |\tfrac{1}{2} eE_0 x_{mk}|^2 \delta(\varepsilon_m - \varepsilon_k - \hbar\omega)$$

$$= \frac{\pi e^2 E_0^{\ 2}}{2\hbar^2} |x_{mk}|^2 \delta(\omega_{mk} - \omega)$$

ii) E_0

光的能量密度 (CGS)

$$I = \frac{1}{8\pi}\overline{(E^2 + B^2)}$$

一个周期的平均值

$$\overline{E^2} = \frac{1}{T}\int_0^T E_0^2 \cos^2 \omega t dt = \tfrac{1}{2} E_0^2$$

$$\overline{E^2} = \overline{B^2} = \tfrac{1}{2} E_0^2 \qquad I = \frac{1}{8\pi} E_0^2 \Rightarrow E_0^2 = 8\pi I$$

iii) 跃迁速率

$$\omega_{k\to m} = \frac{\pi e_s^{\ 2} E_0^2}{2\hbar^2} |x_{mk}|^2 \delta(\omega_{mk} - \omega) = \frac{4\pi^2 e_s^{\ 2}}{\hbar^2} I |x_{mk}|^2 \delta(\omega_{mk} - \omega)$$

（d）自然光

i） 单色到 $\longrightarrow$ 多色光

考虑在某一频率范围连续分布的光，能量密度是 ω 的函数 -- I(ω)。在 ω→ ω + dω 间隔内，其能量密度为： I(ω)dω，所以

$$d\omega_{k\to m}=\frac{4\pi^2 e_s^{\ 2}}{\hbar^2}I(\omega)\,|x_{mk}|^2\,\delta(\omega_{mk}-\omega)d\omega$$

$$\omega_{k\to m}=\frac{4\pi^2 e_s^{\ 2}}{\hbar^2}|x_{mk}|^2\int I(\omega)\delta(\omega_{mk}-\omega)d\omega\ =\frac{4\pi^2 e_s^{\ 2}}{\hbar^2}|x_{mk}|^2\,I(\omega_{mk})$$

ii）偏振光 $\longrightarrow$ 非偏振光

$$\omega_{k\to m}=\frac{4\pi^2 e_s^{\ 2}}{3\hbar^2}I(\omega_{mk})[|x_{mk}|^2+|y_{mk}|^2+|z_{mk}|^2]=\frac{4\pi^2 e_s^{\ 2}}{3\hbar^2}I(\omega_{mk})\,|\vec{r}_{mk}|^2$$

$$=\frac{4\pi^2}{3\hbar^2}I(\omega_{mk})\,|\vec{D}_{mk}|^2 \qquad \vec{D}_{mk}=e\vec{r}_{mk}$$ 电子的电偶极矩

基于以上两点近似（偶极近似）得到偶极跃迁

$$\omega_{m\to k}=\frac{4\pi^2 e_s^{\ 2}}{3\hbar^2}I(\omega_{mk})\,|\vec{r}_{km}|^2$$

iii）吸收系数 B_{km}

$$\omega_{k\to m} = B_{km} I(\omega_{mk})$$ **$I(\omega)$，$\Phi_k \to \Phi_m$ （$\varepsilon_m > \varepsilon_k$）**

微扰理论

$$\omega_{k\to m} = \frac{4\pi^2 e_s^{\ 2}}{3\hbar^2} I(\omega_{mk}) |\vec{r}_{mk}|^2 \qquad B_{km} = \frac{4\pi^2 e_s^{\ 2}}{3\hbar^2} |\vec{r}_{mk}|^2$$

iv）受激发射系数 B_{mk}

Φ_m 至 Φ_k态（$\varepsilon_m > \varepsilon_k$）

$$B_{mk} = \frac{4\pi^2 e_s^{\ 2}}{3\hbar^2} |\vec{r}_{km}|^2$$

$$\omega_{m\to k} = B_{mk} I(\omega_{mk})$$

r 是厄米算符

$$|\vec{r}_{km}|^2 = |\vec{r}_{mk}|^2 \qquad B_{km} = B_{mk}$$

v）自发发射系数

$$A_{mk} = \frac{\hbar\omega_{mk}^{3}}{\pi^{2}c^{3}} \boxed{B_{mk}} = \frac{\hbar\omega_{mk}^{3}}{\pi^{2}c^{3}} \boxed{\frac{4\pi^{2}e_{s}^{2}}{3\hbar^{2}} |\vec{r}_{mk}|^{2}} = \frac{4e_{s}^{2}\omega_{mk}^{3}}{3\hbar c^{3}} |\vec{r}_{mk}|^{2}$$

vi）辐射强度J_{mk}

$$J_{mk} = N_{m} A_{mk} \hbar\omega_{mk} = N_{m} \frac{4e_{s}^{2}\omega_{mk}^{3}}{3\hbar c^{3}} |\vec{r}_{km}|^{2} \hbar\omega_{mk}$$

$$= N_{m} \frac{4e_{s}^{2}\omega_{mk}^{4}}{3c^{3}} |\vec{r}_{km}|^{2}$$

vii）激发态原子的寿命

$$dN_m = -A_{mk} N_m dt$$

$$N_m = N_m^{(0)} e^{-A_{mk} t} = N_m^{(0)} e^{-t/\tau_{mk}}$$

平均寿命

$$A_m = \sum_{k=1}^{i} A_{mk}$$

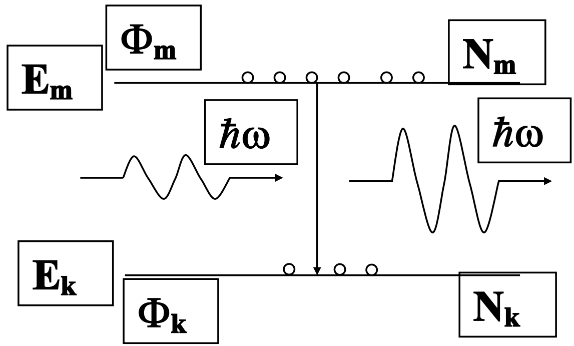
$$\tau_m = \frac{1}{A_m} = \frac{1}{\sum_k A_{mk}}$$

viii）微波量子放大器和激光

（a）受激发射

微波量子放大器和激光器都是应用受激发射现象的器件. 前者受激发射的频率在微波区，后者在可见光区和红外区.

$$\omega = \frac{1}{\hbar}(E_m - E_k)$$



（b）受激发射条件

1）高能态粒子数大于低能态粒子数，粒子数反转

2）自发发射远小于受激发射. 对于微波，波长较长，自发发射概率远小于受激发射概率，条件自动满足; 对于激光，用谐振腔来产生辐射场，使辐射密度远大于热平衡时的数值，以增加受激发射的概率

§5.9 选择定则

（1）禁戒跃迁

$$\omega_{k\to m} \propto |\vec{r}_{mk}|^2$$

$$|\mathbf{r}_{mk}|^2 = 0 \qquad \omega_{k\to m} = 0$$

$$|r_{mk}|^2 \neq 0 \qquad |x_{mk}|^2 + |y_{mk}|^2 + |z_{mk}|^2 \neq 0$$

（2）选择定则

i) 波函数和$\mathbf{r}_{mk}$

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\varphi) = |n\ l\ m\rangle = |n\ l\rangle\ |l\ m\rangle$$

$$\omega_{m\to k} = \frac{4\pi^2 e_s^{\ 2}}{3\hbar^2} I(\omega_{mk})\,|\vec{r}_{km}|^2$$

$$\begin{cases} x = r\sin\theta\cos\varphi = \dfrac{r}{2}\sin\theta[e^{i\varphi} + e^{-i\varphi}] \\ y = r\sin\theta\sin\varphi = \dfrac{r}{2i}\sin\theta[e^{i\varphi} - e^{-i\varphi}] \\ z = r\cos\theta \end{cases}$$

$$\begin{cases} x_{mk} = <n'l'm'|\dfrac{r}{2}\sin\theta\ \ [e^{i\varphi} + e^{-i\varphi}]|nlm> \ \ \propto \ \ <n'l'm'|r\sin\theta\ \ e^{\pm i\varphi}|nlm> \\ y_{mk} = <n'l'm'|\dfrac{r}{2i}\sin\theta\ \ [e^{i\varphi} - e^{-i\varphi}]|nlm> \ \ \propto \ \ <n'l'm'|r\sin\theta\ \ e^{\pm i\varphi}|nlm> \\ z_{mk} = <n'l'm'|r\cos\theta|nlm> \end{cases}$$

$$\begin{cases} <n'l'm'|r\sin\theta\ \ e^{\pm i\varphi}|nlm> = <n'l'|r|nl><l'm'|\sin\theta\ \ e^{\pm i\varphi}|lm> \\ z = <n'l'|r|nl><l'm'|\cos\theta|lm> \end{cases}$$

ii) <l'm'|cosθ|lm>

$$\boxed{\cos\theta\,|\,lm> = \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}\,|\,l+1,m> + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}\,|\,l-1,m>}$$

$$<l'm'\,|\cos\theta|\,lm> =$$

$$= \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} <l'm'\,|\,l+1,m> + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}} <l'm'\,|\,l-1,m>$$

$$= \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}\delta_{l',l+1}\delta_{m'm} + \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}\delta_{l',l-1}\delta_{m'm} \neq 0$$

$$\begin{cases} l' = l \pm 1 \\ m' = m \end{cases} \Rightarrow \begin{cases} \Delta l = l' - l = \pm 1 \\ \Delta m = m' - m = 0 \end{cases}$$

iii) $<l'm'|\sin\theta\ e^{\pm i\varphi}|l\ m>$

$$\boxed{\sin\theta e^{\pm i\varphi}\,|\,lm>=}$$

$$\boxed{=\mp\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}\,|\,l+1,m\pm1>\pm\sqrt{\frac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}\,|\,l-1,m\pm1>}$$

$$<l'm'\,|\sin\theta e^{\pm i\varphi}\,|\,lm>=$$

$$=\mp\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}<l'm'\,|\,l+1,m\pm1>\pm\sqrt{\frac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}<l'm'\,|\,l-1,m\pm1>$$

$$=\mp\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}\delta_{l',l+1}\delta_{m',m\pm1}\pm\sqrt{\frac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}\delta_{l',l-1}\delta_{m',m\pm1}$$

$$\begin{cases} l'=l\pm1 \\ m'=m\pm1 \end{cases}\Rightarrow\begin{cases} \Delta l=l'-l=\pm1 \\ \Delta m=m'-m=\pm1 \end{cases}$$

补充:

$$(\ell - m + 1)P_{\ell+1}^{m}(x) = (2\ell+1)xP_{\ell}^{m}(x) - (\ell+m)P_{\ell-1}^{m}(x)$$

$$\begin{cases} e^{\pm i\varphi}\sin\theta Y_{lm}(\theta,\varphi) = \mp\sqrt{\dfrac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}Y_{l+1,m\pm1}(\theta,\varphi) \pm \\ \qquad\qquad \pm\sqrt{\dfrac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}Y_{l-1,m\pm1}(\theta,\varphi) \\ \cos\theta Y_{lm}(\theta,\varphi) = \sqrt{\dfrac{(l+1)^2-m^2}{(2l+1)(2l+3)}}Y_{l+1,m}(\theta,\varphi) + \sqrt{\dfrac{l^2-m^2}{(2l-1)(2l+1)}}Y_{l-1,m}(\theta,\varphi) \end{cases}$$

http://en.wikipedia.org/wiki/Associated_Legendre_functions

iv) 选择定则

$$\begin{cases} \Delta l = l' - l = \pm 1 \\ \Delta m = m' - m = 0, \pm 1 \end{cases}$$

（3）严格禁戒跃迁

如果跃迁概率为零，则需计算比偶极近似更高的高级近似.如果在任何级近似中跃迁概率为零，则这种跃迁为严格禁戒跃迁

作业

5.4
5.5
5.7
5.8