跃迁理论

主要整理自陈新、郭永老师讲义

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0.1 线性谐振子

势能

$$V(x) = \frac{1}{2}m\omega^2 x^2.$$

其中 ω 为谐振子固有圆频率.

$$\frac{\partial^2\psi}{\partial x^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2\right)\psi = 0.$$

做变换 $\xi = \sqrt{\frac{m\omega}{\hbar}}x,\ \lambda = \frac{2E}{\hbar\omega}$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} + (\lambda - \xi^2)\psi = 0.$$

当 $x \to \infty$, 方程近似为

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} - \xi^2\psi = 0, \quad \Rightarrow \quad \psi \sim \mathrm{e}^{\pm\xi^2/2}.$$

由束缚态要求，解应有形式 $\psi(\xi) = \mathrm{e}^{-\xi^2/2}H(\xi)$,

$$\frac{\mathrm{d}^2H}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}H}{\mathrm{d}\xi} + (\lambda - 1)H = 0.$$

此即 Hermite 方程，用级数解得系数

$$c_{k+2} = \frac{2k+1-\lambda}{(k+1)(k+2)}c_k,$$

注意到 $k \to \infty$

$$\frac{c_{k+2}}{c_k} \to \frac{2}{k}, \quad H(\xi) \sim \sum_{i=i_0}^{\infty}\frac{\xi^{2i}}{i!} = \mathrm{e}^{\xi^2}.$$

仍使 $\psi(\xi)$ 发散．除非 $H(\xi)$ 的项有限 $\lambda = 2k+1$ 且只能出现奇或偶次幂．

故能量本征值

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, \ldots \tag{0.1}$$

基态能量不为 0．

对应 Hermite 方程

$$H_n'' - 2\xi H_n' + 2nH_n = 0.$$

解称为 Hermite 多项式

$$H_n(x) = (-1)^n \,\mathrm{e}^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}x^n} \,\mathrm{e}^{-x^2}.$$

例 0.1.1: Hermite 多项式

前几项

$$\begin{aligned} &H_0 = 1, && H_2 = 4x^2 - 2, && H_4 = 16x^4 - 48x^2 + 12, \\ &H_1 = 2x, && H_3 = 8x^3 - 12x, && H_5 = 32x^5 - 160x^3 + 120x. \end{aligned}$$

Hermite 多项式的内积

$$\int_{-\infty}^{+\infty} H_n H_{n'} \,\mathrm{e}^{-x^2} \,\mathrm{d}x = 2^n n! \,\delta_{nn'}.$$

因此本征态

$$\psi_n = \sqrt[4]{\frac{m\omega}{\pi\hbar}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) \,\mathrm{e}^{-\xi^2/2}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x. \tag{0.2}$$

宇称为 $(-1)^n$．

递推关系

$$x\,|n\rangle = \frac{1}{\sqrt{2}\alpha}\left[\sqrt{n}\,|n-1\rangle + \sqrt{n+1}\,|n+1\rangle\right]; \tag{0.3}$$

$$x^2\,|n\rangle = \frac{1}{2\alpha^2}\left[\sqrt{n(n-1)}\,|n-2\rangle + (2n+1)\,|n\rangle + \sqrt{(n+1)(n+2)}\,|n+2\rangle\right]. \tag{0.4}$$

0.2　角动量算符

顺承经典力学中的定义，角动量算符

$$\hat{\boldsymbol{L}} := \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}\,.$$

直角坐标表象下

$$\begin{aligned}\hat{\boldsymbol{L}} &= [\hat{x}, \hat{y}, \hat{z}]^\top \times [\hat{p}_x, \hat{p}_y, \hat{p}_z]^\top \\ &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x]^\top =: [\hat{L}_x, \hat{L}_y, \hat{L}_z]^\top.\end{aligned}$$

易证 $\hat{L}_x, \hat{L}_y, \hat{L}_z$ 是 Hermite 的．对易子

$$[\hat{L}_x, \hat{L}_y] = (\hat{p}_z\hat{z} - \hat{z}\hat{p}_z)(\hat{y}\hat{p}_x - \hat{x}\hat{p}_y) = \mathrm{i}\hbar\,\hat{L}_z.$$

$[\hat{L}_y, \hat{L}_z]$ 等同理，因此

$$\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}} = \mathrm{i}\hbar\hat{\boldsymbol{L}}\,. \tag{0.5}$$

另一方面，角动量平方算符 $\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ 与 $\hat{L}_z$ 等分量对易

$$\begin{aligned}[\hat{L}^2, \hat{L}_z] &= [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + 0 \\ &= \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x + \hat{L}_y[\hat{L}_y, \hat{L}_z] + [\hat{L}_y, \hat{L}_z]\hat{L}_y \\ &= -\mathrm{i}\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) + \mathrm{i}\hbar(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y) = 0.\end{aligned} \tag{0.6}$$

联级 Stern-Gerlach 实验证明，在确定银原子的 $\hat{L}_z$ 时，其 $\hat{L}_x, \hat{L}_y$ 没有确定值，即 $\hat{L}_x, \hat{L}_y, \hat{L}_z$ 不能同时有确定值．

回顾球坐标系下

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{1}{r}\frac{\partial}{\partial \theta}, \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right]_{\mathrm{Sp}}^\top.$$

Laplace 算符

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

定义 $\hat{\boldsymbol{L}} = -\mathrm{i}\hbar\,\hat{\boldsymbol{\Lambda}}$

$$\hat{\boldsymbol{\Lambda}} := \hat{\boldsymbol{r}} \times \nabla = \left[0, -\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}, \frac{\partial}{\partial\theta}\right]_{\mathrm{Sp}}^\top.$$

特别的，代回直角坐标系后，有

$$\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}; \tag{0.7}$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{0.8}$$

由 $\hat{L}_z, \hat{L}^2$ 对易，二者有共同本征函数.

$\hat{L}_z$ 的本征态　设本征值为 $m\hbar$，本征函数 $\psi_m(\varphi)$

$$\hat{L}_z\psi_m = -\mathrm{i}\hbar\frac{\partial\psi_m}{\partial\varphi} = m\hbar\psi_m \quad \Rightarrow \quad \psi_m = C\,\mathrm{e}^{\mathrm{i}m\varphi}.$$

且本征态应具有周期性 $\psi_m(\varphi+2\pi) = \psi_m(\varphi)$，故 $m = 0, \pm1, \pm2, \dots$

$$(\psi_m, \psi_m) = |C|^2\int_0^{2\pi}\mathrm{d}\varphi = 1, \quad \Rightarrow \quad C = \frac{1}{\sqrt{2\pi}}.$$

$\hat{L}^2$ 的本征态　设本征值为 $\lambda\hbar^2$，本征函数 $Y(\theta,\varphi)$

$$\hat{\Lambda}^2 Y = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -\lambda Y.$$

分离变量 $Y(\theta,\varphi) = \varTheta(\theta)\varPhi(\varphi)$

$$\frac{\varPhi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\varTheta}{\mathrm{d}\theta}\right) + \frac{\varTheta}{\sin^2\theta}\frac{\mathrm{d}^2\varPhi}{\mathrm{d}\varphi^2} = -\lambda\varTheta\varPhi.$$

即

$$\frac{\sin\theta}{\varTheta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\varTheta}{\mathrm{d}\theta}\right) + \lambda\sin^2\theta = -\frac{1}{\varPhi}\frac{\partial^2\varPhi}{\partial\varphi^2} = m^2.$$

引入 $w := \cos\theta$, $P(w) := \varTheta(\arccos w) = \varTheta(\theta)$

$$\frac{\mathrm{d}}{\mathrm{d}w}\left[\left(1-w^2\right)\frac{\mathrm{d}P}{\mathrm{d}w}\right] + \left(\lambda - \frac{m^2}{1-w^2}\right)P = 0. \tag{0.9}$$

这是缔合 Legendre 方程，±1 是方程的奇点，只有

$$\lambda = \ell(\ell+1), \quad \ell = |m|\,, |m|+1, \dots$$

时，方程才有收敛解 $P_\ell^m(w)$.

特别的，当 $m=0$ 时，

$$\frac{\mathrm{d}}{\mathrm{d}w}\left[\left(1-w^2\right)\frac{\mathrm{d}P}{\mathrm{d}w}\right] + \ell(\ell+1)P = 0.$$

便是 Legendre 方程，其解是 Legendre 多项式

$$P_\ell(w)=\frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}w^\ell}\left(w^2-1\right)^\ell.$$

对应的，当 $m>0$ 时，缔合 Legendre 函数

$$P_\ell^m(w)=\left(1-w^2\right)^{m/2}\frac{\mathrm{d}^m}{\mathrm{d}w^m}P_\ell(w).$$

而对于 $m<0$ 的情形，其实应当与 $|m|$ 相同；若对正负均沿用原定义，则

$$P_\ell^{-m}=(-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m,\quad m>0.$$

Legendre 多项式的奇偶性由 ℓ 决定.

例 0.2.1: Legendre 函数表

$\ell=0,1,2,3$ 的 Legendre 多项式 P_ℓ 和缔合 Legendre 函数 $P_\ell^m(\cos\theta)$

$$\begin{aligned}
&P_0=1, && P_0^0=1; && \\
&P_1=x, && P_1^0=\cos\theta, && P_1^1=\sin\theta; \\
&P_2=\frac{1}{2}(3x^2-1), && P_2^0=\frac{1}{2}(3\cos^2\theta-1), && P_2^1=3\sin\theta\cos\theta, \\
& && P_2^2=3\sin^2\theta; && \\
&P_3=\frac{1}{2}(5x^3-3x), && P_3^0=\frac{1}{2}(5\cos^3\theta-3\cos\theta), && P_3^1=\frac{3}{2}\sin\theta(5\cos^2\theta-1), \\
& && P_3^2=15\sin^2\theta\cos\theta, && P_3^3=15\sin^3\theta;
\end{aligned}$$

轨道角动量本征函数最后为

$$Y_{\ell m}(\theta,\varphi)=N_{\ell m}P_\ell^m(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\varphi},$$

由于

$$\int_{-1}^{1}P_\ell^m(x)P_{\ell'}^{m'}(x)\,\mathrm{d}x=\frac{2}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\delta_{\ell\ell'}\,\delta_{mm'}.$$

得

$$N_{\ell m}=(-1)^m\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}$$

称 $Y_{\ell m(\theta,\varphi)}$ 为球谐函数，ℓ 为角量子数，m 为磁量子数．原子物理中将 $\ell=0,1,2,3,\ldots$ 的状态分别称为 s, p, d, f 态．

$\hat{L}^2$ 的本征值 ℓ 下有 $2\ell+1$ 个可能的 m，简并度为 $2\ell+1$．

例 0.2.2: 球谐函数表

$\ell=0,1,2,3$ 已归一化后的 Y_ℓ^m

$$
\begin{aligned}
Y_0^0 &= \frac{1}{2\sqrt{\pi}}, & Y_2^{\pm 2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta\,\mathrm{e}^{\pm 2\mathrm{i}\phi}, \\
Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta, & Y_3^0 &= \sqrt{\frac{7}{16\pi}}(5\cos^3\theta-3\cos\theta), \\
Y_1^{\pm 1} &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}, & Y_3^{\pm 1} &= \mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta-1)\,\mathrm{e}^{\pm\mathrm{i}\phi}, \\
Y_2^0 &= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1), & Y_3^{\pm 2} &= \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\,\mathrm{e}^{\pm 2\mathrm{i}\phi}, \\
Y_2^{\pm 1} &= \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}, & Y_3^{\pm 3} &= \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\,\mathrm{e}^{\pm 3\mathrm{i}\phi}.
\end{aligned}
$$

球谐函数是 $\hat{L}^2$ 和 $\hat{L}_z$ 的共同本征函数

$$
\begin{cases}
\hat{L}^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}, & \ell = 0,1,2,\dots \\
\hat{L}_z Y_{\ell m} = m\hbar Y_{\ell m}, & m = -\ell,-\ell+1,\dots,\ell
\end{cases}
$$

宇称 作空间反射变换 $\boldsymbol{r}\to-\boldsymbol{r}$，对应球坐标中 $(r,\theta,\varphi)\to(r,\pi-\theta,\pi+\varphi)$

$$
P_\ell^m(\cos(\pi-\theta)) = P_\ell^m(-\cos\theta) = (-1)^{\ell-m}P_\ell^m(\cos\theta)
$$

$$
\mathrm{e}^{im(\pi+\varphi)} = (-1)^m\,\mathrm{e}^{im\varphi}
$$

$$
Y_{\ell m}(\pi-\theta,\pi+\varphi) = (-1)^\ell Y_{\ell m}(\theta,\varphi)
$$

因此 $Y_{\ell m}(\theta,\varphi)$ 的宇称为 $(-1)^\ell$.

递推关系

$$
\cos\theta Y_\ell^m = \sqrt{\frac{(\ell+1)^2-m^2}{(2\ell+1)(2\ell+3)}}Y_{\ell+1}^m + \sqrt{\frac{\ell^2-m^2}{(2\ell-1)(2\ell+1)}}Y_{\ell-1}^m. \tag{0.10}
$$

$$
\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi}Y_\ell^m = \pm\sqrt{\frac{(\ell\pm m+1)(\ell\pm m+2)}{(2\ell+1)(2\ell+3)}}Y_{\ell+1}^{m+1} + \sqrt{\frac{(\ell\mp m)(\ell\mp m+1)}{(2\ell-1)(2\ell+1)}}Y_{\ell-1}^{m\pm 1}. \tag{0.11}
$$

1 跃迁理论

若体系的 Hamilton 量 $\hat{H}_0$ 不显含时间，能量本征值问题的解为

$$\hat{H}_0 \left|n\right\rangle = E_n \left|n\right\rangle.$$

若 $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$ 显含时间，体系将有一定的概率离开初态 $\left|k\right\rangle$ 而处于其它定态 $\left|k'\right\rangle$，这就是**量子跃迁**.

1.1 量子态随时间的变化

状态随时间的演化由 Schrödinger 方程决定

$$\begin{cases} \mathrm{i}\hbar\dfrac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}(t)\left|\psi(t)\right\rangle, \\ \left|\psi(0)\right\rangle = \left|k\right\rangle. \end{cases} \tag{1.1}$$

采用能量 $\hat{H}_0$ 表象

$$\left|\psi(0)\right\rangle = \sum_n C_{nk}(t)\left|n\right\rangle \mathrm{e}^{-\mathrm{i}E_n t/\hbar}, \quad C_{nk}(0) = \delta_{nk}. \tag{1.2}$$

体系 t 时刻跃迁到定态 $\left|k'\right\rangle$ 的概率为 $|C_{k'k}(t)|^2$.

为求出跃迁概率，将表象表达式带入 Schrödinger 方程，假定 $\hat{H}'$ 中不包括 $\partial/\partial t$ 作用

$$\mathrm{i}\hbar\sum_n\left[\dot{C}_{nk}(t) - \cancel{\frac{\mathrm{i}E_nC_{nk}(t)}{\hbar}}\right]\left|n\right\rangle\mathrm{e}^{-\mathrm{i}E_nt/\hbar} = \sum_n C_{nk}(t)\left[\cancel{E_n} + \hat{H}'(t)\right]\left|n\right\rangle\mathrm{e}^{-\mathrm{i}E_nt/\hbar}.$$

$$\mathrm{i}\hbar\sum_n\dot{C}_{nk}(t)\left|n\right\rangle\mathrm{e}^{-\mathrm{i}E_nt/\hbar} = \sum_n C_{nk}(t)\hat{H}'(t)\left|n\right\rangle\mathrm{e}^{-\mathrm{i}E_nt/\hbar}. \tag{1.3}$$

与 $\left|k'\right\rangle$ 内积

$$\mathrm{i}\hbar\dot{C}_{k'k}(t)\,\mathrm{e}^{-\mathrm{i}E_{k'}t/\hbar} = \sum_n C_{nk}(t)\left\langle k'\right|\hat{H}'(t)\left|n\right\rangle\mathrm{e}^{-\mathrm{i}E_nt/\hbar} \tag{1.4}$$

定义

$$H'_{k'n}(t) := \left\langle k'\right|\hat{H}'(t)\left|n\right\rangle, \quad \omega_{k'n} = \frac{E_{k'} - E_n}{\hbar}. \tag{1.5}$$

得到跃迁振幅 $C_{k'k}(t)$ 满足

$$\begin{cases} \mathrm{i}\hbar\dfrac{\mathrm{d}}{\mathrm{d}t}C_{k'k}(t) = \displaystyle\sum_n H'_{k'n}(t)\,\mathrm{e}^{\mathrm{i}\omega_{k'n}t}C_{nk}(t), \\ C_{k'k}(0) = \delta_{k'k}. \end{cases} \tag{1.6}$$

两边对 t 积分

$$C_{k'k}(t)=C_{k'k}(0)+\frac{1}{\mathrm{i}\hbar}\int_0^t\sum_n H'_{k'n}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'n}\tau}C_{nk}(\tau)\,\mathrm{d}\tau \tag{1.7}$$

这是一个积分方程，可采用迭代求解.

迭代一次

$$\begin{aligned}C_{k'k}(t)&=\delta_{k'k}+\frac{1}{\mathrm{i}\hbar}\int_0^t\sum_n H'_{k'n}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'n}\tau}\cdot\\&\quad\left[\delta_{nk}+\frac{1}{\mathrm{i}\hbar}\int_0^\tau\sum_n H'_{k'n}(\pi)\,\mathrm{e}^{\mathrm{i}\omega_{k'n}\pi}C_{nk}(\pi)\,\mathrm{d}\pi\right]\mathrm{d}\tau\\&=\delta_{k'k}+\frac{1}{\mathrm{i}\hbar}\int_0^t H'_{k'k}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'k}\tau}\,\mathrm{d}\tau+\cdots\end{aligned}$$

零级近似

$$C^{(0)}_{k'k}=\delta_{k'k};$$

一级近似

$$C^{(1)}_{k'k}=\frac{1}{\mathrm{i}\hbar}\int_0^t H'_{k'k}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'k}\tau}\,\mathrm{d}\tau,$$

代表直接从初态 $|k\rangle$ 跃迁到末态 $\left|k'\right\rangle$，故跃迁概率

$$P_{k'k}(t)=\frac{1}{\hbar^2}\left|\int_0^t H'_{k'k}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'k}\tau}\,\mathrm{d}\tau\right|^2. \tag{1.8}$$

由 $\hat{H}'$ 是 Hermite 的. 故 $P_{k'k}=P_{kk'}$，即从初态到末态的跃迁概率等于从末态到初态的跃迁概率.

对于初态 $|k\rangle$ 和末态 $\left|k'\right\rangle$ 都有简并的情况，计算跃迁概率应对 $|k\rangle$ 能级各简并态求平均，而对 $\left|k'\right\rangle$ 能级各简并态求和，此时跃迁概率不一定相等.

二级近似

$$C^{(2)}_{k'k}=\frac{1}{(\mathrm{i}\hbar)^2}\sum_n\int_0^t H'_{k'n}(\tau)\,\mathrm{e}^{\mathrm{i}\omega_{k'n}\tau}\int_0^\tau H'_{nk}(\pi)\,\mathrm{e}^{\mathrm{i}\omega_{nk}\pi}\,\mathrm{d}\pi\,\mathrm{d}\tau,$$

代表从初态 $|k\rangle$ 经中间态 $|n\rangle$ 跃迁到末态 $\left|k'\right\rangle$.

1.2　周期微扰和常微扰

没讲

1.3　光的吸收与辐射

光与原子的相互作用包括受激吸收、受激辐射和自发辐射. 其中自发辐射是前面的理论无法解释的，Einstein 基于热力学和统计物理中的平衡概念给出过半唯象的理论，巧妙地导出了自发辐射系数.

电偶极跃迁　若入射光为理想单色偏振光，

$$\boldsymbol{E}=\boldsymbol{E}_0\cos(\omega t-\boldsymbol{k}\cdot\boldsymbol{r}),\quad \boldsymbol{B}=\frac{\boldsymbol{k}}{|k|}\times\boldsymbol{E}. \tag{CGS}$$

对电子的作用

$$\boldsymbol{f}=-e\left(\boldsymbol{E}+\frac{\boldsymbol{v}}{c}\times\boldsymbol{B}\right), \tag{CGS}$$

原子中电子的速度 $v\ll c$，故可仅考虑电场的作用.

对于可见光和紫外光[I]波长 $\lambda\gg a$ (Bohr 半径)，故在原子范围内电场可视为均匀场

$$\boldsymbol{E}\doteq\boldsymbol{E}_0\cos\omega t.$$

光对原子的作用可近似表示成电子的电偶极矩与电场的相互作用

$$\hat{H}'(t)=-\boldsymbol{D}\cdot\boldsymbol{E}=W\cos\omega t.$$

其中电子的电偶极矩 $\boldsymbol{D}=-e\boldsymbol{r}$，电偶极矩与电场作用引起的跃迁称为电偶极跃迁.

$$\begin{aligned}C^{(1)}_{k'k}(t)&=\frac{1}{\mathrm{i}\hbar}\int_0^t H'_{k'k}(\tau)\,\mathrm{e}^{-\mathrm{i}\omega_{k'k}\tau}\,\mathrm{d}\tau=\frac{W_{k'k}}{\mathrm{i}\hbar}\int_0^t\cos\omega\tau\,\mathrm{e}^{-i\omega_{k'k}\tau}\,\mathrm{d}\tau\\&=-\frac{W_{k'k}}{2\hbar}\left[\frac{\mathrm{e}^{\mathrm{i}(\omega_{k'k}+\omega)t}-1}{\omega_{k'k}+\omega}+\frac{\mathrm{e}^{\mathrm{i}(\omega_{k'k}-\omega)t}-1}{\omega_{k'k}-\omega}\right].\end{aligned}$$

下面讨论原子吸收光的跃迁，$E_{k'}>E_k$，只有当入射光 $\omega\doteq\omega_{k'k}$ 时，才会引起 $E_k\to E_{k'}$ 跃迁，此时

$$C^{(1)}_{k'k}(t)=-\frac{W_{k'k}}{2\hbar}\frac{\mathrm{e}^{\mathrm{i}(\omega_{k'k}-\omega)t}-1}{\omega_{k'k}-\omega}.$$

从 $k\to k'$ 的概率为

$$P_{k'k}(t)=\left|C^{(1)}_{k'k}(t)\right|^2=\frac{|W_{k'k}|^2}{4\hbar^2}\left[\frac{\sin(\omega_{k'k}-\omega)t/2}{(\omega_{k'k}-\omega)/2}\right]^2 \tag{1.9}$$

[I] X 光并不满足.

$t \to \infty$ 时，有

$$P_{k'k}(t) = \frac{\pi t}{2\hbar^2} \left|W_{k'k}\right|^2 \delta\left(\omega_{k'k} - \omega\right); \tag{1.10}$$

跃迁速率

$$w_{k'k} = \frac{\mathrm{d}}{\mathrm{d}t} P_{k'k} = \frac{\pi}{2\hbar^2} \left|W_{k'k}\right|^2 \delta\left(\omega_{k'k} - \omega\right) \tag{1.11}$$

$$= \frac{\pi}{2\hbar^2} \left|\boldsymbol{D}_{k'k}\right|^2 E_0^2 \cos^2\theta \, \delta\left(\omega_{k'k} - \omega\right), \tag{1.12}$$

θ 为电子的电偶极矩与电场的夹角.

而对于非偏振光，应对 $\cos^2\theta$ 取平均

$$\left\langle \cos^2\theta \right\rangle = \frac{1}{4\pi} \int_0^{2\pi}\int_0^{\pi} \cos^2\theta \sin\theta \, \mathrm{d}\theta \mathrm{d}\phi = \frac{1}{3}.$$

跃迁速率

$$w_{k'k} = \frac{\pi}{6\hbar^2} \left|\boldsymbol{D}_{k'k}\right|^2 E_0^2 \, \delta\left(\omega_{k'k} - \omega\right). \tag{1.13}$$

对于非单色光，总跃迁速率是对各种频率求和

$$w_{\mathrm{tot}} = \int_{-\infty}^{+\infty} \omega_{k'k} \, \mathrm{d}\omega = \frac{\pi}{6\hbar^2} \left|\boldsymbol{D}_{k'k}\right|^2 E_0^2(\omega_{k'k}). \tag{1.14}$$

频率为 ω 的电磁波能量密度的时间平均值

$$\rho(\omega) = \frac{1}{8\pi} \left\langle E^2 + B^2 \right\rangle = \frac{1}{8\pi} E_0^2(\omega). \tag{CGS}$$

故非偏振自然光引起的跃迁速率

$$w_{k'k} = \frac{4\pi^2}{3\hbar^2} \left|\boldsymbol{D}_{k'k}\right|^2 \rho(\omega_{k'k}) = \frac{4\pi^2 e^2}{3\hbar^2} \left|\boldsymbol{r}_{k'k}\right|^2 \rho(\omega_{k'k}). \tag{1.15}$$

由 $\boldsymbol{r}$ 为奇宇称算符，只有 $|k\rangle, |k'\rangle$ 宇称相反时，$\left|\boldsymbol{r}_{k'k}\right|^2$ 才不为 0. 又

$$\boldsymbol{r} = r[\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta]$$

由第 6 页的球谐函数递推式知，跃迁态间需满足 $\Delta\ell = \pm 1$, $\Delta m = 0, \pm 1$.

Einstein 跃迁理论