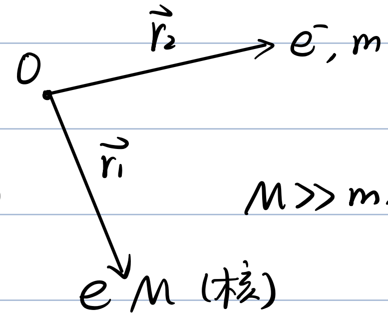
4. 氢原子(三维中心力场定态问题)



$$\left[-\frac{\hbar^2}{2M}\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\nabla_{r_2}^2 + V(|\vec{r}_1-\vec{r}_2|)\right]\psi(\vec{r}_1,\vec{r}_2) = E\,\psi(\vec{r}_1,\vec{r}_2)$$

令 $\begin{cases}\vec{R} = \frac{m}{M+m}\vec{r}_2 + \frac{M}{M+m}\vec{r}_1 \\ \vec{r} = \vec{r}_1 - \vec{r}_2\end{cases}$

变量代换后得到

$$\left[-\frac{\hbar^2}{2(M+m)}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(|\vec{r}|)\right]\psi(\vec{r}_1,\vec{r}_2) = E\,\psi(\vec{r}_1,\vec{r}_2)$$

令 $\psi(\vec{r}_1,\vec{r}_2) = \psi_c(\vec{R})\,\psi(\vec{r})$ $\quad \mu = \frac{Mm}{M+m} \xrightarrow{M\gg m} m.$

$$\Rightarrow \left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(|\vec{r}|)\right]\psi(\vec{r}) = E\,\psi(\vec{r}) \quad \text{Born-Oppenheimer 近似}$$

球坐标下

$-\frac{\hat{l}^2}{\hbar^2 r^2}$ 在球坐标下的表示

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

分离变量，令 $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

$$\left\{\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\} + \frac{1}{Y(\theta,\varphi)}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\} = 0.$$

$\hat{l}^2$ 的本征方程.

我们有 $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -l(l+1)\,Y(\theta,\varphi)$

$$\Rightarrow \hat{l}^2|\psi\rangle = l(l+1)\hbar^2|\psi\rangle$$

解为球谐函数 $Y_l^m(\theta,\varphi)$, $\quad l = 0, 1, 2\ldots \quad m = -l, -l+1 \ldots l-1, l$

$|l,m\rangle$ 球坐标表象

径向方程，令 $u(r) = rR(r)$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u(r) = Eu(r)$$

当 $V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$ 首先进行无量纲化处理.

令 $K = \sqrt{\frac{-2mE}{\hbar^2}}$ 则 $\rho = Kr$ 无量纲.

此时方程化为：

$$\frac{d^2u(\rho)}{d\rho^2} - \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u(\rho) = 0,\ \text{其中}\ \rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar K}$$

渐近行为 $\rho \to \infty$ $u'' - u = 0 \Rightarrow u \sim Ae^{-\rho} + \boxed{Be^{\rho}}$ X

$\rho \to 0$ $u'' - \frac{l(l+1)}{\rho^2}u = 0 \Rightarrow u \sim A\rho^{l+1} + \boxed{B\rho^{-l}}$ X

由此，取通解形式为：

$$u = \rho^{l+1}e^{-l}v(\rho)$$

$$\Rightarrow \rho v'' + 2(l+1-\rho)v' + (\rho_0 - 2l - 2)v = 0$$

令 $v = \sum_k C_k\rho^k \Rightarrow C_{k+1} = \frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)}C_k$

当 $k \to \infty$ 时，$C_k = \frac{2^k}{k!}C_0$ $v(\rho) \sim e^{2\rho}$，此时 $u(\rho)$ 发散.

因此 C_k 应被截断.

$$\Rightarrow \rho_0 = 2(k_{max} + l + 1) = 2n,\quad n = 1, 2\ldots$$

得到 $E_n = -\frac{\hbar^2K^2}{2m} = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2}$，$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ (玻尔半径)

波函数：

$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \to$ 广义 Lagurre 多项式

$$\Rightarrow$$

$$\psi_{nlm}(\vec{r}) = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{n-l-1}{2n[(n+l)!]^3}}\, e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)Y_l^m(\theta,\varphi)$$

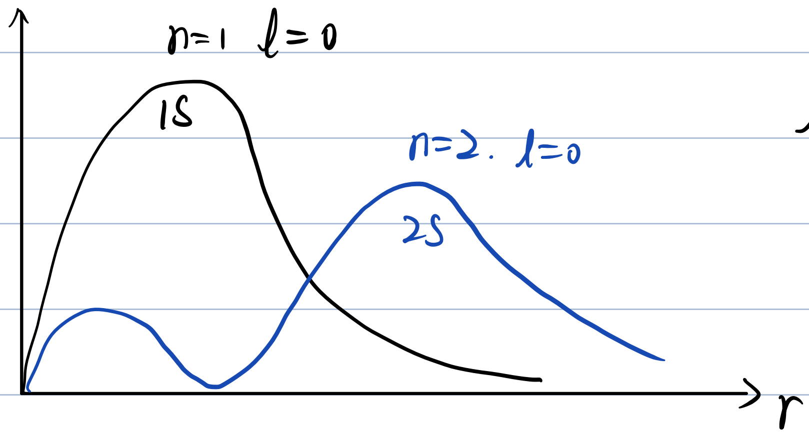
$$= \langle\vec{r}\,|\,nlm\rangle$$

$E_n \sim \frac{1}{n^2}$，而态为 $|nlm\rangle \Longrightarrow E_n$ 有简并.

简并度 $\sum_{l=0}^{n-1}(2l+1) = n^2$ （不考虑自旋）

考虑自旋后为 $2n^2$

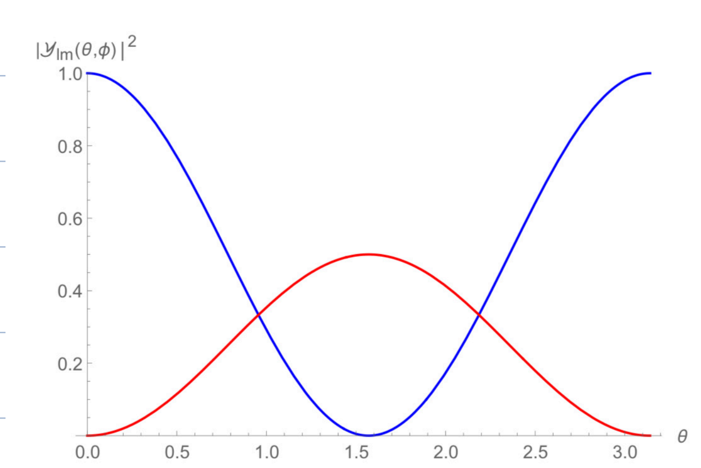
i) $u^2 = |rR_{nl}|^2$

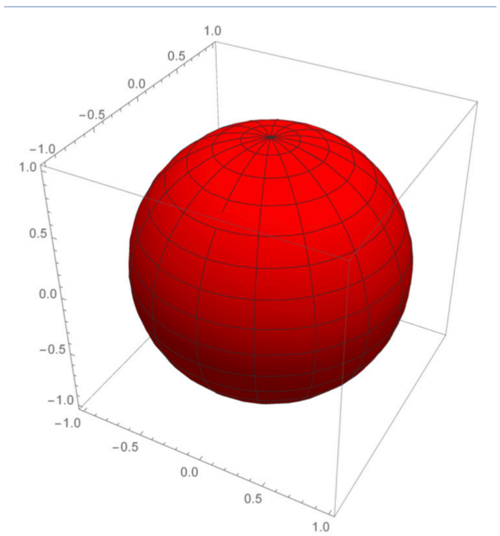


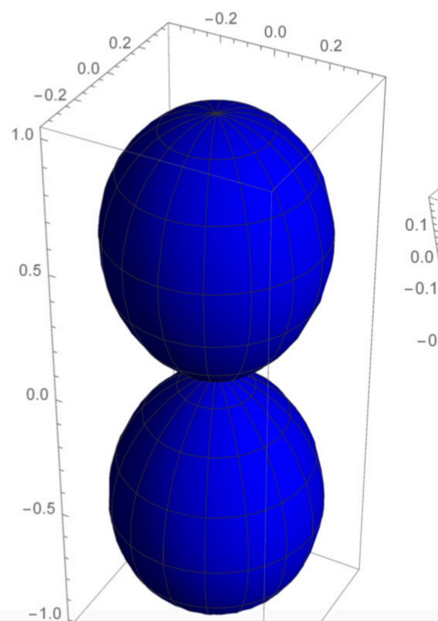
$l = 0, 1, 2 \dots$

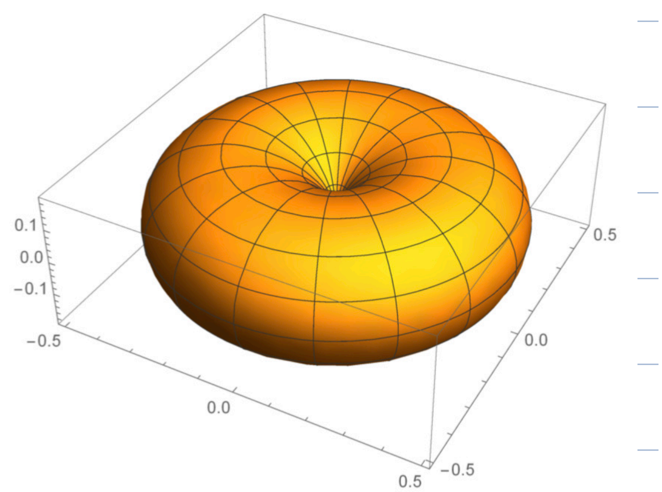
s p d ...

$Y_{lm}(\theta, \varphi)$









1) 零级近似

① 相对论修正

② 自旋一轨道耦合 } 精细结构

③ 核自旋耦合 } 超精细结构

第七章 角动量与自旋

1. 轨道角动量

$\hat{\vec{l}} = \hat{\vec{r}} \times \hat{\vec{p}}$ 性质：$[\hat{l}_i, \hat{l}_j] = i\hbar \varepsilon_{ijk} \hat{l}_k \quad (ijk = x, y, z)$

$[\hat{l}^2, \hat{l}_i] = 0$

↳ 存在 $\hat{l}_i$ 与 $\hat{l}^2$ 的共同本征态

在坐标表象下：

$\hat{l}^2 : (\hat{\vec{r}} \times \hat{\vec{p}}) \cdot (\hat{\vec{r}} \times \hat{\vec{p}}) f$

$\Rightarrow [\vec{r} \times (-i\hbar\nabla)][\vec{r} \times (-i\hbar\nabla)] f$

$= -\hbar^2 (\vec{r} \times \nabla) \cdot (\vec{r} \times \nabla) f$

球坐标系下：$\nabla f = \frac{\partial f}{\partial r} \vec{e}_r + \frac{1}{r} \frac{\partial f}{\partial \theta} \vec{e}_\theta + \frac{1}{r\sin\theta} \frac{\partial}{\partial \varphi} f \vec{e}_\varphi$

$$\nabla \times \vec{A} = \frac{1}{r\sin\theta} \left[\frac{\partial}{\partial \theta} (A\sin\theta) - \frac{\partial A_\theta}{\partial \varphi} \right] \vec{e}_r$$

$$+ \frac{1}{r} \left[\frac{1}{\sin\theta} \frac{\partial A_r}{\partial \varphi} - \frac{\partial}{\partial r} (rA_\varphi) \right] \vec{e}_\theta$$

$$+ \frac{1}{r} \left[\frac{\partial}{\partial r} (rA_\theta) - \frac{\partial A_r}{\partial \theta} \right] \vec{e}_\varphi$$

则 $\hat{l}^2 f$

$$\Rightarrow -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right] f$$

即 $\hat{l}^2$ 在球坐标表象下为 $-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right]$

$\hat{l}_z: (\hat{\vec{r}} \times \hat{\vec{p}})_z f = -i\hbar \left(\frac{\partial f}{\partial \theta} \vec{e}_\varphi - \frac{1}{\sin\theta} \frac{\partial f}{\partial \varphi} \vec{e}_\theta \right) \cdot \vec{e}_z$

$= (-i\hbar \frac{\partial}{\partial \varphi}) f$

即 $\hat{l}_z$ 在球坐标表象下为 $(-i\hbar \frac{\partial}{\partial\varphi})$

$\hat{l}_z$ 的本征波函数

$-i\hbar \frac{\partial}{\partial \varphi} \phi_m(\varphi) = A\, \phi_m(\varphi) \Rightarrow \phi_m(\varphi) \sim e^{i\frac{A}{\hbar}\varphi}$

A为实数

单值性要求我们有: $e^{i\frac{A}{\hbar}\varphi} = e^{i\frac{A}{\hbar}(\varphi+2\pi)} \Rightarrow A = m\hbar$ $\boxed{m为整数}$ 角动量量子化

则 $\phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$ $\int_0^{2\pi} \phi_m^*(\varphi)\, \phi_m(\varphi)\, d\varphi = 1$

令 $\hat{l}^2 Y(\theta,\varphi) = \lambda \hbar^2 Y(\theta,\varphi)$

$\hat{l}_z Y(\theta,\varphi) = m\hbar\, Y(\theta,\varphi)$

再令 $Y(\theta,\varphi) = \Theta(\theta)\, \phi_m(\varphi)$

$\Rightarrow (1-\xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi \frac{d\Theta}{d\xi} + (\lambda - \frac{m^2}{1-\xi^2})\Theta = 0$

其中 $\xi = \cos\theta$. (连带 Legendre 方程)

解为 $P_l^m(\cos\theta)$ $\lambda = l(l+1)$, $l = 0, 1, 2 \cdots$

则 $Y_l^m(\theta,\varphi) = (-1)^m \sqrt{\frac{(l-m)!\,(2l+1)}{(l+m)!\,4\pi}}\, P_l^m(\cos\theta)\, e^{im\varphi}$

(球谐函数)

PS. 在 Dirac 的符号语言中, 上面的波函数可抽象为 $|l,m\rangle$

则 $Y_l^m(\theta,\varphi) = \langle r | l, m\rangle$

$$\begin{cases} \hat{l}^2 |l,m\rangle = l(l+1)\hbar^2 |l,m\rangle \\ \hat{l}_z |l,m\rangle = m\hbar\, |l,m\rangle \end{cases}$$

性质:

① 正交性

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \, Y_{lm}^*(\theta,\varphi) Y_{l'm'}(\theta,\varphi) = \delta_{ll'}\delta_{mm'}$$

$$\Longrightarrow \langle l,m|l',m'\rangle = \delta_{ll'}\delta_{mm'}$$

② 完备性

1) $\sum_{lm} Y_{lm}(\theta,\varphi) Y_{lm}^*(\theta',\varphi') = \delta(\Omega-\Omega') = \frac{1}{\sin\theta}\delta(\theta-\theta')\delta(\varphi-\varphi')$

$$\Longrightarrow \sum_{lm} |l,m\rangle\langle l,m| = \hat{I}$$

2) $\varphi(\theta,\varphi) = \sum_{lm} C_{lm} Y_{lm}(\theta,\varphi)$ for any $\varphi(\theta,\varphi)$

例: 已知 $Y_{00} = \frac{1}{\sqrt{4\pi}}$ $\quad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}$ $\quad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$.

求波函数 $\psi = (r+x+2y+2z)f(r)$ 上测 $\hat{l}^2$, $\hat{l}_z$ 的可能值与几率.

解: $x = r\sin\theta\cos\varphi \quad y = r\sin\theta\sin\varphi \quad z = r\cos\theta$.

则 $Y_{1,1} = -\sqrt{\frac{3}{8\pi}}\left(\frac{x}{r} + i\frac{y}{r}\right)$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\left(\frac{x}{r} - i\frac{y}{r}\right)$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\left(\frac{z}{r}\right)$$

则 $\psi = \left(1 + \frac{x}{r} + \frac{2y}{r} + \frac{2z}{r}\right) r f(r)$

$$= \propto \sqrt{4\pi}\, Y_{00} + \sqrt{\frac{2\pi}{3}}(Y_{1,-1} - Y_{1,1}) + 2i\sqrt{\frac{2\pi}{3}}(Y_{1,-1} + Y_{11}) + 2\sqrt{\frac{4\pi}{3}}\, Y_{1,0}$$

$\xrightarrow{\text{归一化}}$ $\frac{1}{2}\left(Y_{00} + \sqrt{\frac{1}{6}}(1+2i)Y_{1,-1} + \sqrt{\frac{1}{6}}(-1+2i)Y_{11} + 2\sqrt{\frac{1}{3}}Y_{10}\right)$

则测 $\hat{l}^2$ 可得: $\begin{cases} l=0 \Rightarrow \hbar^2 l(l+1) = 0,\ P = \frac{1}{4} \\ l=1 \Rightarrow \hbar^2 l(l+1) = 2\hbar^2,\ P = \frac{3}{4} \end{cases}$

测 $\hat{l}_z$ 可得：$\begin{cases} m=1 \Rightarrow m\hbar=\hbar, & P=\frac{5}{24} \\ m=-1 \Rightarrow m\hbar=-\hbar, & P=\frac{5}{24} \\ m=0 \Rightarrow m\hbar=0, & P=\frac{7}{12} \end{cases}$

在坐标表象下，我们作如下轮换：

$x \to y$，$y \to z$，$z \to x$，则有 $\hat{l}_x \to \hat{l}_y$，$\hat{l}_y \to \hat{l}_z$，$\hat{l}_z \to \hat{l}_x$

可求其它方向的本征函数. 要测哪个方向，令哪个方向为z

2. 角动量的一般定义及代数性质.

定义：$[\hat{j}_\alpha, \hat{j}_\beta] = i\hbar\,\varepsilon_{\alpha\beta\gamma}\,\hat{j}_\gamma$ $\quad \hat{\vec{j}} = \hat{j}_x \vec{e}_x + \hat{j}_y \vec{e}_y + \hat{j}_z \vec{e}_z$

$\Updownarrow$ $\quad (\alpha, \beta, \gamma = x, y, z)$

$\hat{\vec{j}} \times \hat{\vec{j}} = i\hbar \hat{\vec{j}}$

引入升降算符

$\hat{j}_\pm = \hat{j}_x \pm i\hat{j}_y \qquad \hat{j}_- = \hat{j}_+^+$

基本性质：① $[\hat{j}^2, \hat{j}_\alpha] = 0$，$\alpha = x, y, z$.

② $[\hat{j}_z, \hat{j}_\pm] = \pm\hbar \hat{j}_\pm$

③ $\hat{j}_\pm \hat{j}_\mp = \hat{j}^2 - \hat{j}_z^2 \pm \hbar \hat{j}_z$

目的：求解 $\{\hat{j}^2, \hat{j}_z\}$ 的本征问题

定义：$\begin{cases} \hat{j}^2 |j,m\rangle = \lambda\hbar^2 |j,m\rangle \\ \hat{j}_z |j,m\rangle = m\hbar\, |j,m\rangle \end{cases}$

① $\hat{j}^2 \hat{j}_\pm |j,m\rangle = \hat{j}_\pm \hat{j}^2 |j,m\rangle = \lambda\hbar^2 \hat{j}_\pm |j,m\rangle$

即 $\hat{j}_\pm |j,m\rangle$ 也为 $\hat{j}^2$ 的本征值为 $\lambda\hbar^2$ 的本征态

② $\hat{J}_z\hat{J}_\pm|j,m\rangle = \hat{J}_\pm\hat{J}_z|j,m\rangle \pm \hbar\hat{J}_\pm|j,m\rangle$

$= (m\pm\hbar)\hat{J}_\pm|j,m\rangle$

$\hat{J}_\pm|j,m\rangle$ 为 $\hat{J}_z$ 本征值为 $(m\pm\hbar)$ 的本征态

$\Longrightarrow \hat{J}_\pm|j,m\rangle \begin{cases} \text{是 } \hat{J}^2 \text{ 的本征值为 } \lambda\hbar^2 \text{ 的本征态} \\ \text{是 } \hat{J}_z \text{ 本征值为 } (m\pm\hbar) \text{ 的本征态} \end{cases}$

则 $\hat{J}_\pm|j,m\rangle = C_\pm|j,m\pm1\rangle$ (此处先假设无简并)

令 $C_\pm$ 为实数.

考察 $\langle j,m|\hat{J}_\mp\hat{J}_\pm|j,m\rangle = |C_\pm|^2$

利用 $\hat{J}_\pm\hat{J}_\mp = \hat{J}^2 - \hat{J}_z^2 \pm \hbar\hat{J}_z$

$= \langle j,m|(\hat{J}^2 - \hat{J}_z^2 \mp \hbar\hat{J}_z)|j,m\rangle$

$= \lambda\hbar^2 - m^2\hbar^2 \mp m\hbar^2 = C_\pm^2$

$\Rightarrow C_\pm = \sqrt{\lambda - m(m\pm1)}\ \hbar$

② λ, m 的取值范围.

$C_\pm$ 为实数, 则对给定 λ, m 有最大值. 记为 $\overline{m}$

$\Rightarrow \hat{J}_+|j,\overline{m}\rangle = 0$, $\lambda = \overline{m}(\overline{m}+1)$

同时, m 有最小值, 记为 $\underline{m}$

$\Rightarrow \hat{J}_-|j,\underline{m}\rangle = 0$, $\lambda = \underline{m}(\underline{m}-1)$

$\Longrightarrow \overline{m}(\overline{m}+1) = \underline{m}(\underline{m}-1)$ 且 $\overline{m} > \underline{m} \Rightarrow \overline{m} = -\underline{m}$

可记 $\overline{m} = j$, 则 $\overline{m} - \underline{m} = 2j$

而 从 $|j,\underline{m}\rangle$ 连续作用 N 次可得到 $|j,\overline{m}\rangle$

$\Rightarrow 2j = N$

所以 $j=0,\frac{1}{2},1,\frac{3}{2}\cdots$ 对应的 $m=-j,-j+1\cdots j$

$\lambda=j(j+1)$

③ $\hat{J}^2|j,m\rangle=j(j+1)\hbar^2|j,m\rangle$ $j=0,\frac{1}{2},1,\frac{3}{2}\cdots$

$\hat{J}_z|j,m\rangle=m\hbar|j,m\rangle$ 对应 $m=-j,-j+1\cdots j$

(轨道角动量对应 j 为自然数)

$$\hat{J}_\pm|j,m\rangle=\sqrt{j(j+1)-m(m\pm1)}\,\hbar|j,m\pm1\rangle$$
$$=\sqrt{(j\mp m)(j\pm m+1)}\,\hbar|j,m\pm1\rangle$$ ☆记住.

前反 后正.

记住 "$J_+|j,j\rangle=0$" $\Rightarrow C_{jj}=0$

j 为整数 $\longrightarrow$ 轨道角动量.

j 为半整数 $\longrightarrow$ 粒子自旋.

注：角动量的不对易本质是来自于转动的不对易.

定义无穷小转动算符：$\hat{D}(\vec{n},d\varphi)=1-i\left(\frac{\hat{J}\cdot\vec{n}}{\hbar}\right)d\varphi$.

则 $\hat{D}(\varphi)=\lim\limits_{N\to\infty}\left[1-\frac{i(\hat{J}\cdot\vec{n})}{\hbar}\left(\frac{\varphi}{N}\right)\right]^N$

$$=e^{-\frac{i\hat{J}\cdot\vec{n}}{\hbar}\varphi} \xLeftrightarrow{\text{类比}} e^{-\frac{i\hat{p}\cdot\vec{a}}{\hbar}}$$

转动算符 平移算符

例：$l=1$ 的子空间代数.

$l=1$, $m=-1,0,1$ 空间的基：$\{|l,m\rangle\}$

$\hat{L}_z$ 对应矩阵：$\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\hbar$

$\hat{l}_x$对应矩阵的计算:

$$\hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-)$$

$$\langle m|\hat{l}_x|m'\rangle = \langle m|\frac{1}{2}(\hat{l}_+ + \hat{l}_-)|m'\rangle$$

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

易算得:

$$\hat{l}_+|1\rangle = 0 \qquad \hat{l}_-|1\rangle = \sqrt{2}\hbar|0\rangle$$

$$\hat{l}_+|0\rangle = \sqrt{2}\hbar|1\rangle \qquad \hat{l}_-|0\rangle = \sqrt{2}\hbar|-1\rangle$$

$$\hat{l}_+|-1\rangle = \sqrt{2}\hbar|0\rangle \qquad \hat{l}_-|-1\rangle = 0$$

于是 $\hat{l}_x$ 的对应矩阵为:

$$\frac{\sqrt{2}}{2}\hbar\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

同理,利用 $\hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-)$

可得 $\hat{l}_y$ 的对应矩阵为

$$\frac{\sqrt{2}\hbar}{2i}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\hat{l}_+ : \sqrt{2}\hbar\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \qquad \hat{l}_- : \sqrt{2}\hbar\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$\hat{l}_x$的本征问题

$$\frac{\sqrt{2}}{2}\hbar\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

由于对称性可知 $\hat{l}_x$ 的本征值应当为 $-\hbar, 0, \hbar$.

$\lambda=\hbar$ 时，得到归一的本征态 $|\alpha\rangle=\frac{1}{2}(1,\sqrt{2},1)^T$

$\lambda=0$ 时，得到归一的本征态 $|\beta\rangle=\frac{\sqrt{2}}{2}(1,0,-1)^T$

$\lambda=-\hbar$ 时，得到归一的本征态 $|\gamma\rangle=\frac{1}{2}(1,-\sqrt{2},1)^T$

$|\alpha\rangle=|l=1,m_x=1\rangle \quad |\beta\rangle=|l=1,m_x=0\rangle \quad |\gamma\rangle=|l=1,m_x=-1\rangle$

处于 $\hat{l}_z$ 本征态上测 $\hat{l}_x$？

$$|l=1,m_z=1\rangle=\begin{pmatrix}1\\0\\0\end{pmatrix}=\frac{1}{2}\left[\frac{1}{2}\begin{pmatrix}1\\\sqrt{2}\\1\end{pmatrix}+\frac{\sqrt{2}}{2}\begin{pmatrix}1\\0\\-1\end{pmatrix}+\frac{1}{2}\begin{pmatrix}1\\-\sqrt{2}\\1\end{pmatrix}\right]$$

$$=\frac{1}{2}\left(|\alpha\rangle+\sqrt{2}|\beta\rangle+|\gamma\rangle\right)$$

因为

$$(|\alpha\rangle,|\beta\rangle|\gamma\rangle)=\frac{1}{2}\begin{pmatrix}1&\sqrt{2}&1\\\sqrt{2}&0&-\sqrt{2}\\1&-\sqrt{2}&1\end{pmatrix}(|m_z=1\rangle\,|m_z=0\rangle\,|m_z=-1\rangle)$$

则

$$(|m_z=1\rangle\,|m_z=0\rangle\,|m_z=-1\rangle)=\frac{1}{2}\begin{pmatrix}1&\sqrt{2}&1\\\sqrt{2}&0&-\sqrt{2}\\1&-\sqrt{2}&1\end{pmatrix}(|\alpha\rangle|\beta\rangle|\gamma\rangle)$$

同时

$$\frac{1}{4}\begin{pmatrix}1&\sqrt{2}&1\\\sqrt{2}&0&-\sqrt{2}\\1&-\sqrt{2}&1\end{pmatrix}l_x\begin{pmatrix}1&\sqrt{2}&1\\\sqrt{2}&0&-\sqrt{2}\\1&-\sqrt{2}&1\end{pmatrix}=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}$$

变换到 $\hat{l}_x$ 本征态的基对应的矩阵.

再考察

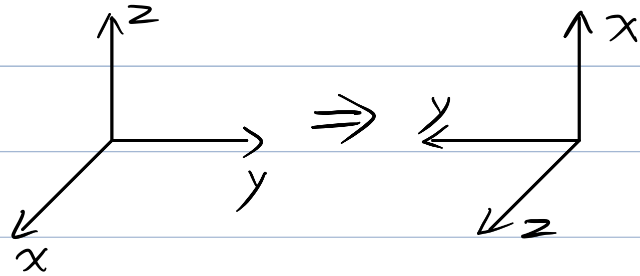
$$\frac{1}{4}\begin{pmatrix}1 & \sqrt{2} & 1\\ \sqrt{2} & 0 & -\sqrt{2}\\ 1 & -\sqrt{2} & 1\end{pmatrix} l_z \begin{pmatrix}1 & \sqrt{2} & 1\\ \sqrt{2} & 0 & -\sqrt{2}\\ 1 & -\sqrt{2} & 1\end{pmatrix} = \frac{\sqrt{2}}{2}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\hbar$$

$\hat{l}_z$在$\hat{l}_x$本征态下的矩阵表示

再考察$\hat{l}_y$

$$\frac{1}{4}\begin{pmatrix}1 & \sqrt{2} & 1\\ \sqrt{2} & 0 & -\sqrt{2}\\ 1 & -\sqrt{2} & 1\end{pmatrix} l_y \begin{pmatrix}1 & \sqrt{2} & 1\\ \sqrt{2} & 0 & -\sqrt{2}\\ 1 & -\sqrt{2} & 1\end{pmatrix} = \frac{\sqrt{2}}{2i}\begin{pmatrix}0 & -1 & 0\\ 1 & 0 & -1\\ 0 & 1 & 0\end{pmatrix}\hbar$$

在图像上表记为



3. 自旋

① 历史

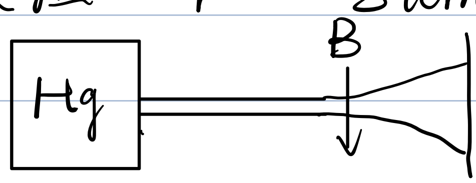
反常 Zeeman 效应.无法用原有量子理论解释.

1925年 { Uhlenbeck, Goudsmit, Kröning } 提出"自旋"概念.

1927年 Pauli matrix.

1928年 Dirac equation.

实验: 1922 Stern-Gerlach.



② 电子自旋 $(j=\frac{1}{2})$ $s=\frac{1}{2}$

在 $\{\hat{S}^2, \hat{S}_z\}$ 的共同本征态的基下讨论. $|s, m_s\rangle$

$s=\frac{1}{2}$. $m_s=-\frac{1}{2}, \frac{1}{2}$. 略写 s.

即基矢为 $\{|m_s\rangle\}=\{|1\rangle, |-1\rangle\}/\{|+\rangle, |-\rangle\}/\{|\uparrow\rangle |\downarrow\rangle\}$

$\hat{\vec{S}}=\hat{S}_x\vec{e}_x+\hat{S}_y\vec{e}_y+\hat{S}_z\hat{e}_z$ 且 $[\hat{S}_i, \hat{S}_j]=i\hbar\varepsilon_{ijk}\hat{S}_k$

再定义 $\hat{S}_\pm=\hat{S}_x\pm i\hat{S}_y$.

$\Longrightarrow$ $\hat{S}_z|\uparrow\rangle=\frac{1}{2}\hbar|\uparrow\rangle$, $\hat{S}_z|\downarrow\rangle=-\frac{1}{2}\hbar|\downarrow\rangle$

$\hat{S}_x|\uparrow\rangle=\frac{1}{2}(\hat{S}_++\hat{S}_-)|\uparrow\rangle=\frac{1}{2}\hat{S}_-|\uparrow\rangle$

$=\frac{\hbar}{2}\sqrt{(\frac{1}{2}+\frac{1}{2})(\frac{1}{2}-\frac{1}{2}+1)}|\downarrow\rangle$

$=\frac{\hbar}{2}|\downarrow\rangle$

同理 $\hat{S}_x|\downarrow\rangle=\frac{1}{2}\hbar|\uparrow\rangle$

$\hat{S}_y|\uparrow\rangle=\frac{1}{2}\hbar|\downarrow\rangle$

$\hat{S}_y|\downarrow\rangle=-\frac{1}{2}\hbar|\uparrow\rangle$

定义: Pauli 算符 $\hat{\vec{\sigma}}=\frac{2}{\hbar}\hat{\vec{S}}=\sigma_x\vec{e}_x+\sigma_y\vec{e}_y+\sigma_z\vec{e}_z$

相应的有 $[\hat{\sigma}_i, \hat{\sigma}_j]=2i\varepsilon_{ijk}\hat{\sigma}_k$.

同时有 $\{\hat{\sigma}_i, \hat{\sigma}_j\}=2\delta_{ij}$

$\Big\}\Rightarrow \underline{\hat{\sigma}_i\hat{\sigma}_j=\delta_{ij}+i\varepsilon_{ijk}\hat{\sigma}_k}$

Pauli 矩阵: Pauli 算符在 $\{|\uparrow\rangle, |\downarrow\rangle\}$ 基下的矩阵表示.

$$\sigma_x=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_y=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_z=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

任何 2x2 的矩阵均可用 $\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$ 及 Pauli 矩阵展开.

例：电子处于 $(\alpha,\beta)^T$ 自旋态，求测 $\hat{S}_y$ 时的测值与几率分布.

解：首先求解 σ_y 的本征问题.

$$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \Rightarrow \lambda=\pm 1,\ \text{相应的本征矢为}\ \underset{\Downarrow}{\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ i \end{pmatrix}}_{|1\rangle},\ \underset{\Downarrow}{\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ -i \end{pmatrix}}_{|-1\rangle}$$

则

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = |1\rangle\langle 1|\begin{pmatrix} \alpha \\ \beta \end{pmatrix} + |-1\rangle\langle -1|\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$= \frac{\sqrt{2}}{2}(\alpha-i\beta)\left[\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ i \end{pmatrix}\right] + \frac{\sqrt{2}}{2}(\alpha+i\beta)\left[\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ -i \end{pmatrix}\right]$$

$$= \frac{\sqrt{2}}{2}(\alpha-i\beta)|1\rangle + \frac{\sqrt{2}}{2}(\alpha+i\beta)|-1\rangle$$

同时

$$\frac{1}{2}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

注：一般 Pauli 阵的构造为：$\begin{pmatrix} \langle\uparrow|\uparrow\rangle & \langle\uparrow|\downarrow\rangle \\ \langle\downarrow|\uparrow\rangle & \langle\downarrow|\downarrow\rangle \end{pmatrix}$

$$\frac{\sqrt{2}}{2}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{2}}{2}(\alpha-i\beta) \\ \frac{\sqrt{2}}{2}(\alpha+i\beta) \end{pmatrix}$$

例：转动算符的矩阵表示（$\vec{n}$ 为转轴方向的单位向量）

$$e^{\frac{-i\hat{S}\cdot\vec{n}}{\hbar}\varphi} = e^{\frac{-i\hat{\sigma}\cdot\vec{n}}{2}\varphi}$$

$$(\hat{\sigma}\cdot\vec{a})(\hat{\sigma}\cdot\vec{b}) = \sum_{jk}\hat{\sigma}_j a_j \hat{\sigma}_k b_k = \sum_{jk}\left(\frac{1}{2}\{\hat{\sigma}_j,\hat{\sigma}_k\} + \frac{1}{2}[\hat{\sigma}_j,\hat{\sigma}_k]\right)a_j b_k$$

$$= \sum_{jk}(\delta_{jk} + i\varepsilon_{jki}\hat{\sigma}_i)a_j b_k$$

$$= \sum_j a_j b_j + i\sum_{jk}\varepsilon_{jki}a_j b_k\hat{\sigma}_i$$

$$= \vec{a}\cdot\vec{b} + i\hat{\vec{\sigma}}\cdot(\vec{a}\times\vec{b})$$

之后考察 $(\hat{\vec{\sigma}}\cdot\vec{n})^2 = \vec{n}\cdot\vec{n} + i\hat{\vec{\sigma}}\cdot(\vec{n}\times\vec{n}) = 1$

则 $$e^{-i\frac{\varphi}{2}(\hat{\vec{\sigma}}\cdot\vec{n})} = \left[1 - \frac{(\hat{\vec{\sigma}}\cdot\vec{n})^2}{2!}\left(\frac{\varphi}{2}\right)^2 + \frac{(\hat{\vec{\sigma}}\cdot\vec{n})^4}{4!}\left(\frac{\varphi}{2}\right)^4 + \cdots\right]$$

$$+ \left[-i(\hat{\vec{\sigma}}\cdot\vec{n})\frac{\varphi}{2} + i\frac{(\hat{\vec{\sigma}}\cdot\vec{n})^3}{3!}\left(\frac{\varphi}{2}\right)^3 + \cdots\right]$$

$$= \cos\left(\frac{\varphi}{2}\right)\hat{I} - i(\hat{\vec{\sigma}}\cdot\vec{n})\sin\left(\frac{\varphi}{2}\right) = e^{-\frac{i}{\hbar}\varphi\hat{\vec{S}}\cdot\vec{n}}$$

$$\Rightarrow \quad e^{-i\varphi(\hat{\vec{\sigma}}\cdot\vec{n})} = \cos\varphi\,\hat{I} - i(\hat{\vec{\sigma}}\cdot\vec{n})\sin(\varphi) \quad ☆☆$$

例：转动算符：在 $\hat{S}_z$ 本征基下求 $\hat{\vec{S}}$ 在 $\vec{e}_r = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\varphi)$ 方向上分量的矩阵表示与本征态.

解：

① $$\hat{u} = e^{-i\varphi\frac{(\hat{\vec{S}}\cdot\hat{n}_z)}{\hbar}} e^{-i\theta\frac{(\hat{\vec{S}}\cdot\hat{n}_y)}{\hbar}} = e^{-i\frac{\varphi}{2}\hat{\sigma}_z} e^{-i\frac{\theta}{2}\hat{\sigma}_y}$$

$$= \left(\cos\frac{\varphi}{2} - i\hat{\sigma}_z\sin\frac{\varphi}{2}\right)\left(\cos\frac{\theta}{2} - i\hat{\sigma}_y\sin\frac{\theta}{2}\right)$$

$$= \cos\frac{\varphi}{2}\cos\frac{\theta}{2} - i\cos\frac{\varphi}{2}\sin\frac{\theta}{2}\hat{\sigma}_y - i\sin\frac{\varphi}{2}\cos\frac{\theta}{2}\hat{\sigma}_z + i\sin\frac{\varphi}{2}\sin\frac{\theta}{2}\hat{\sigma}_x$$

$$\Rightarrow \quad \hat{u} \Rightarrow \begin{pmatrix} \cos\frac{\theta}{2}e^{-i\frac{\varphi}{2}} & -\sin\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\varphi}{2}} & \cos\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$$

$$\Rightarrow \quad \hat{u}\hat{\sigma}_z\hat{u}^+ \Rightarrow \begin{pmatrix} \cos\theta & \sin\theta e^{-i\varphi} \\ \sin\theta e^{i\varphi} & -\cos\theta \end{pmatrix}$$

在 $\{\hat{\vec{S}}^2, \hat{S}_z\}$ 表象下沿 $\vec{e}_r$ 方向上的 $\hat{\sigma}_r$

$\theta = 0,\ \varphi = 0$ 时为 $\hat{\sigma}_z$

$\theta = \frac{\pi}{2},\ \varphi = 0$ 时为 $\hat{\sigma}_x$

$\theta = \frac{\pi}{2},\ \varphi = \frac{\pi}{2}$ 时为 $\hat{\sigma}_y$

则 $|\uparrow\rangle_r \to \hat{u}|\uparrow\rangle_z \Rightarrow \begin{pmatrix} \cos\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$ $|\uparrow\rangle_r, |\downarrow\rangle_r$ 为上面矩阵的本征态

$|\downarrow\rangle_r \to \hat{u}\,|\downarrow\rangle_z \Rightarrow \begin{pmatrix} -\sin\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \cos\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$

② $\hat{S}_r = \hat{\vec{S}}\cdot\vec{e}_r = \sin\theta\cos\varphi\,\hat{S}_x + \sin\theta\sin\varphi\,\hat{S}_y + \cos\varphi\,\hat{S}_z$

$$= \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta e^{-i\varphi} \\ \sin\theta e^{i\varphi} & -\cos\theta \end{pmatrix}$$ ($\{\hat{S}^2, \hat{S}_z$表象下$\}$)

对角化得本征值为$\pm\frac{\hbar}{2}$.

本征态 $\begin{pmatrix} \cos\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$ $\begin{pmatrix} -\sin\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \cos\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$

$e^{-i\varphi(\hat{S}\cdot\vec{n})}$ 可以类比 $e^{-i\hat{H}t/\hbar}$，时间演化对应相空间的某种旋转

例：自旋$\frac{1}{2}$的电子，在外磁场中的哈密顿量为$\hat{H} = -\frac{e}{m_e c}\hat{\vec{S}}\cdot\vec{B}$

定义 $A = -\frac{e}{m_e c}$，假设磁场方向为z方向，电子初态为$\hat{S}_x$本征值为$\frac{\hbar}{2}$的本征态，求t时刻电子态，$\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$的期望值及测量几率分布.

解：　　　　　　　　　　　　　　$\{\hat{S}^2, \hat{S}_z\}$基下

$\hat{H} = AB\hat{S}_z$　　$e^{-i\frac{AB}{2}\hat{\sigma}_z t} \Rightarrow \begin{pmatrix} e^{-i\frac{AB}{2}t} & 0 \\ 0 & e^{\frac{iAB}{2}t} \end{pmatrix}$

$\hat{S}_x$的本征态 $|\uparrow\rangle_x \Rightarrow \frac{\sqrt{2}}{2}(1,\ 1)^T$

$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \Rightarrow \frac{\sqrt{2}}{2}\left(e^{-\frac{i\varphi t}{\hbar}}\ \ e^{\frac{i\varphi t}{\hbar}}\right)$, $\varphi = AB$

测量：

$\hat{S}_z$: $\begin{cases} \frac{\hbar}{2} & P=\frac{1}{2} \\ -\frac{\hbar}{2} & P=\frac{1}{2} \end{cases} \Rightarrow \langle\hat{S}_z\rangle_t = 0$

$\hat{S}_x$: $\begin{cases} \frac{\hbar}{2} & P=\left|\frac{\sqrt{2}}{2}(1,1)\cdot\frac{\sqrt{2}}{2}(e^{-\frac{i\varphi t}{2}}, e^{\frac{i\varphi t}{2}})^T\right|^2=\cos^2\frac{\varphi t}{2} \\ -\frac{\hbar}{2} & P=\left|\frac{\sqrt{2}}{2}(1,-1)\cdot\frac{\sqrt{2}}{2}(e^{-\frac{i\varphi t}{2}}, e^{\frac{i\varphi t}{2}})^T\right|^2=\sin^2\frac{\varphi t}{2} \end{cases}$

$$\langle \hat{S}_x \rangle_t = \frac{\hbar}{2}\cos\varphi t$$

$\hat{S}_y$: $\begin{cases} \frac{\hbar}{2} & P=\frac{1}{2}(1+\sin\varphi t) \\ -\frac{\hbar}{2} & P=\frac{1}{2}(1-\sin\varphi t) \end{cases}$ $\quad \langle \hat{S}_y \rangle_t = \frac{\hbar}{2}\sin\varphi t$

Dirac's notation:

$$|\psi(t)\rangle = \frac{\sqrt{2}}{2}e^{-\frac{i\varphi t}{2}}|\uparrow\rangle_z + \frac{\sqrt{2}}{2}e^{\frac{i\varphi t}{2}}|\downarrow\rangle_z$$

而 $\begin{cases} |\uparrow\rangle_z = \frac{\sqrt{2}}{2}(|\uparrow\rangle_x + |\downarrow\rangle_x) \\ |\downarrow\rangle_z = \frac{\sqrt{2}}{2}(|\uparrow\rangle_x - |\downarrow\rangle_x) \end{cases}$

代入得

$$|\psi(t)\rangle = \underline{\left(\frac{1}{2}e^{-i\frac{\varphi t}{2}} + \frac{1}{2}e^{i\frac{\varphi t}{2}}\right)}|\uparrow\rangle_x + \left(\frac{1}{2}e^{\frac{i\varphi t}{2}} - \frac{1}{2}e^{-\frac{i\varphi t}{2}}\right)|\downarrow\rangle_x$$

$|\uparrow\rangle_x$ 由两个方向相反的转动叠加而成，类似于干涉.
因此随时间演化.

例: Bloch球与2x2的体系.

$$H = \underline{AI} + B\sigma_x + C\sigma_y + D\sigma_z$$

类似于势函数中的常数项，可以去掉.

$\Rightarrow \quad H = E\vec{\sigma}\cdot\vec{n} \qquad B, C, D \in \mathbb{R}.$

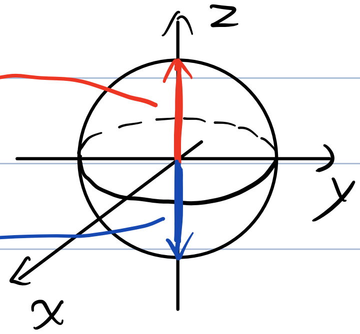
$$\vec{n} = \left(\frac{B}{\sqrt{B^2+C^2+D^2}}, \frac{C}{\sqrt{B^2+C^2+D^2}}, \frac{D}{\sqrt{B^2+C^2+D^2}}\right)$$

$$\text{or} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$$

本征态 $\begin{pmatrix} \cos\frac{\theta}{2}e^{-\frac{i\varphi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$ $\quad \begin{pmatrix} -\sin\frac{\theta}{2}e^{-i\frac{\varphi}{2}} \\ \cos\frac{\theta}{2}e^{i\frac{\varphi}{2}} \end{pmatrix}$ 用球面上的点对应.

$\begin{pmatrix}1\\0\end{pmatrix} \Rightarrow \theta=0 \quad (\varphi=0)$

$\begin{pmatrix}0\\1\end{pmatrix} \Rightarrow \theta=\pi \quad (\varphi=0)$

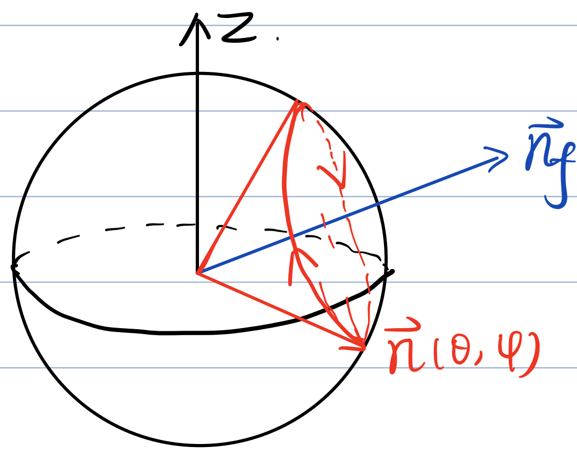


任意(θ,φ) 用 $\hat{U}(\theta,\varphi)\begin{pmatrix}1\\0\end{pmatrix}$ 可以得到

$\Rightarrow$ $\vec{n}(\theta,\varphi)$ 的正/反向代表 $(\hat{\sigma}\cdot\vec{n})$ 的本征态

含时演化

$$e^{-iE(\hat{\sigma}\cdot\vec{n}_f)t/\hbar}\begin{pmatrix}\cos\frac{\theta}{2}\, e^{-i\frac{\varphi}{2}}\\ \sin\frac{\theta}{2}\, e^{i\frac{\varphi}{2}}\end{pmatrix}$$



$\vec{n}$绕$\vec{n}_f$转动

$\varphi = 2Et$

注：哈密顿量中的非对角元对应耦合项，物理上代表跃迁。

4. 角动量耦合

考虑两个独立的角动量算符 $\hat{j}_1, \hat{j}_2$

$\hookrightarrow [\hat{j}_{1\alpha}, \hat{j}_{2\beta}]=0. \quad (\alpha,\beta=x,y,z)$

如定义 $\hat{j}=\hat{j}_1+\hat{j}_2$，则 $[\hat{j}_\alpha, \hat{j}_\beta]=0$，即 $\hat{j}$ 也为角动量算符

我们研究 $\{\hat{j}^2, \hat{j}_z\}$ 的本征问题.（耦合问题）

eg: $\hat{L}+\hat{S}=\hat{J}$ ⇒ 氢原子的轨道角动量与自旋的耦合

$\hat{S}_1+\hat{S}_2=\hat{S}$ ⇒ 两个电子的角动量耦合.

性质:

$[\hat{j}_\alpha, \hat{j}_1^2]=0 \quad [\hat{j}^2, \hat{j}_1^2]=0$

$[\hat{j}_\alpha, \hat{j}_2^2]=0 \quad [\hat{j}^2, \hat{j}_2^2]=0$

我们可以选取以下两组力学量完备集

$\{\hat{j}_1^2, \hat{j}_2^2, \hat{j}_{1z}, \hat{j}_{2z}\} \quad \{\hat{j}_1^2, \hat{j}_2^2, \hat{j}^2, \hat{j}_z\}$

① $\{\hat{j}_1^2, \hat{j}_2^2, \hat{j}_{1z}, \hat{j}_{2z}\}$: 非耦合表象

本征态: $|j_1 m_1\rangle \otimes |j_2, m_2\rangle \,/\, |j_1, m_1; j_2, m_2\rangle$

$\hat{j}_1^2 |j_1, m_1; j_2, m_2\rangle = j_1(j_1+1)\hbar^2 |j_1, m_1; j_2, m_2\rangle$

$\hat{j}_2^2 |j_1, m_1; j_2, m_2\rangle = j_2(j_2+1)\hbar^2 |j_1, m_1; j_2, m_2\rangle$

$\hat{j}_{1z}^2 |j_1, m_1; j_2, m_2\rangle = m_1\hbar |j_1, m_1; j_2, m_2\rangle$

$\hat{j}_{2z}^2 |j_1, m_1; j_2, m_2\rangle = m_2\hbar |j_1, m_1; j_2, m_2\rangle$

$\langle j_1, m_1; j_2, m_2 | j_1, m_1'; j_2, m_2'\rangle = \delta_{m_1m_1'}\delta_{m_2m_2'} \quad \sum_{m_1m_2} |j_1m_1; j_2m_2\rangle\langle j_1m_1; j_2m_2| = \hat{I}$

② $\{\hat{j}_1^2, \hat{j}_2^2, \hat{j}^2, \hat{j}_z\}$: 耦合表象

本征态: $|j_1, j_2, j, m\rangle$

两者维数相同

$\hat{j}_1^2 |j_1, j_2, j, m\rangle = j_1(j_1+1)\hbar^2 |j_1, j_2, j, m\rangle$

$\hat{j}_2^2 |j_1, j_2, j, m\rangle = j_2(j_2+1)\hbar^2 |j_1, j_2, j, m\rangle$

$\hat{j}^2 |j_1, j_2, j, m\rangle = j(j+1)\hbar^2 |j_1, j_2, j, m\rangle$

$\hat{j}_z |j_1, j_2, j, m\rangle = m\hbar |j_1, j_2, j, m\rangle$

$\langle j_1j_2jm | j_1j_2j'm'\rangle = \delta_{jj'}\delta_{mm'} \quad \sum_{j,m} |j_1j_2jm\rangle\langle j_1j_2jm| = \hat{I}$

③ 表象变换与 Clebsh-Gordan 系数 (C.G.系数)

$$|j_1,j_2,j,m\rangle=\sum_{m_1m_2}\underbrace{\langle j_1,m_1;j_2,m_2|j_1,j_2,j,m\rangle}|j_1,m_1;j_2,m_2\rangle$$

(给定 j_1,j_2)

C.G.系数(变换矩阵的矩阵元).

由于非耦合表象与耦合表象均为我们所研究问题的完备基，因此存在表象变换.(CG系数)的由来.

C.G.系数的性质

i) 非零C.G.系数要求 $m=m_1+m_2$ (Z方向角动量守恒)

$$\hat{j}_z-\hat{j}_{1z}-\hat{j}_{2z}=0 \quad (\hat{\vec{j}}=\hat{\vec{j}}_1+\hat{\vec{j}}_2)$$

Prof: $\langle j_1,m_1;j_2,m_2|\hat{j}_z-\hat{j}_{1z}-\hat{j}_{2z}|j_1,j_2,j,m\rangle=0$

$$=(m-m_1-m_2)\hbar\langle j_1,m_1;j_2m_2|j_1,j_2j,m\rangle=0$$

ii) 非零C.G.系数要求 $|j_1-j_2|\le j\le j_1+j_2$

$m=m_1+m_2$

$\bar{m}_1=j_1 \quad\Rightarrow\quad \bar{m}=j_1+j_2 \quad\Rightarrow\quad j\le j_1+j_2$

$\bar{m}_2=j_2$

j 的取值 从 $j_1+j_2,\ j_1+j_2-1\ \dots\ \underline{j}$

下面利用两个表象的维度相同求 $\underline{j}$ (至于为什么维度相同，我们可以认为是找到了两套力学完备集)

	非耦合表象(固定 j_1,j_2)		耦合表象
维数:	$(2j_1+1)\times(2j_2+1)$	$=$	$\sum_{j=\underline{j}}^{j_1+j_2}(2j+1)$

$$\Rightarrow \underline{j}=|j_1-j_2|$$

iii) C.G.系数一般取实数

求和定理: $\langle j_1j_2jm|j_1m_1';j_2,m_2'\rangle$

$$\sum_{jm} \langle j_1 m_1; j_2, m_2 | j_1 j_2 j\, m\rangle \langle j_1 m_1'; j_2\, m_2' | j_1\, j_2\, j\, m\rangle = \delta_{m_1 m_1'}\delta_{m_2 m_2'}$$

$$\sum_{m_1 m_2} \langle j_1 m_1; j_2 m_2 | j_1 j_2 j\, m\rangle \langle j_1 m_1 j_2\, m_2 | j_1 j_2\, j'\, m'\rangle = \delta_{jj'}\delta_{mm'}$$

$$\langle j_1\, m_1; j_2\, m_2 | j_1 j_2\, j m\rangle = (-1)^{j_1-j_2+m}\sqrt{2j+1}\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m\end{pmatrix}$$

$$= C(j_1 j_2 j; m_1\, m_2\, m)$$

Wigner 3-j 符号

例：自旋一轨道耦合

$\{j_1, m_1\}$ $\{j_2=\frac{1}{2}, m_2 = \pm\frac{1}{2}\}$

$$\hat{j}_{2+} \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle = 0 \qquad \hat{j}_{2-} \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle = \hbar \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle$$

$\sqrt{(\frac{1}{2}+\frac{1}{2})(\frac{1}{2}-\frac{1}{2}+1)}\ \hbar$

$$\hat{j}_{2+} \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle = \hbar\left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle \qquad \hat{j}_{2-} \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle = 0$$

则 $|j_1\ \overset{j_2}{\tfrac{1}{2}}\ j\, m\rangle = \sum_{m_1 m_2} \langle j_1, m_1; \tfrac{1}{2}, m_2 | j_1\ \tfrac{1}{2}\ j m\rangle |j_1\, m_1; \tfrac{1}{2}\, m_2\rangle$

(利用 $m=m_1+m_2$)

$$= \underbrace{\langle j_1, m+\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2} | j_1, \tfrac{1}{2}, j, m\rangle}_{C_{-\frac{1}{2}}} |j_1, m+\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$+ \underbrace{\langle j_1, m-\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2} | j_1, \tfrac{1}{2}, j, m\rangle}_{C_{\frac{1}{2}}} |j_1, m-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\rangle$$

利用 $\hat{\vec{j}}^2 = (\hat{\vec{j}}_1+\hat{\vec{j}}_2)(\hat{\vec{j}}_1+\hat{\vec{j}}_2) = \hat{\vec{j}}_1^{\,2} + \hat{\vec{j}}_2^{\,2} + 2\hat{\vec{j}}_1\cdot\hat{\vec{j}}_2$ 重要的等式！

$$= \underbrace{\hat{j}_1^2 + \hat{j}_2^2 + 2\hat{j}_{1z}\hat{j}_{2z} + \hat{j}_{1+}\hat{j}_{2-} + \hat{j}_{1-}\hat{j}_{2+}}_{\text{可作用于非耦合表象}}$$

可作用于耦合表象

同时有 $2\hat{\vec{j}}_1\cdot\hat{\vec{j}}_2 = 2\hat{j}_{1z}\hat{j}_{2z} + \hat{j}_{1+}\hat{j}_{2-} + \hat{j}_{1-}\hat{j}_{2+}$

用 $\hat{j}^2$ 同时作用得到

$$j(j+1)\hbar^2 |j_1, \tfrac{1}{2}, j, m\rangle =$$

$$C_{-\frac{1}{2}}\Big\{ [j_1(j_1+1)\hbar^2 + \tfrac{1}{2}(\tfrac{1}{2}+1) + 2(m+\tfrac{1}{2})(-\tfrac{1}{2})\hbar^2 |j_1, m+\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$+ \sqrt{(j_1+m+\tfrac{1}{2})(j_1-m-\tfrac{1}{2}+1)}\ \hbar^2 |j_1, m-\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle\Big\}$$

$$+C_{\frac{1}{2}}\{[j_1(j_1+1)+\tfrac{1}{2}(\tfrac{1}{2}+1)+2(m-\tfrac{1}{2})(\tfrac{1}{2})\hbar^2|j_1,m-\tfrac{1}{2};\tfrac{1}{2},\tfrac{1}{2}\rangle$$
$$+\sqrt{(j_1-m+\tfrac{1}{2})(j_1+m-\tfrac{1}{2}+1)}\,\hbar^2|j_1,m+\tfrac{1}{2};\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

等式两边左乘 $\langle j_1,m+\frac{1}{2};\frac{1}{2},-\frac{1}{2}|$

$$\Rightarrow j(j+1)C_{-\frac{1}{2}}=[j_1(j_1+1)+\tfrac{1}{4}-m]\,C_{-\frac{1}{2}}+\sqrt{(j_1-m+\tfrac{1}{2})(j_1+m+\tfrac{1}{2})}\,C_{\frac{1}{2}}$$

等式两边左乘 $\langle j_1,m-\frac{1}{2};\frac{1}{2},\frac{1}{2}|$

$$\Rightarrow j(j+1)C_{\frac{1}{2}}=\sqrt{(j_1+m+\tfrac{1}{2})(j_1-m+\tfrac{1}{2})}\,C_{-\frac{1}{2}}+[(j_1+1)j_1+\tfrac{1}{4}+m]\,C_{\frac{1}{2}}$$

但上面两个条件等价. (Surprise).

我们再利用 $C_{-\frac{1}{2}}^2+C_{\frac{1}{2}}^2=1$ (归一化条件&求和约定)

由于 $j=j_1\pm\frac{1}{2}$ $(j_1\neq 0)$

如 $j=j_1+\frac{1}{2}$

$$\begin{cases}\sqrt{j_1+m+\tfrac{1}{2}}\,C_{-\frac{1}{2}}=\sqrt{j_1-m+\tfrac{1}{2}}\,C_{\frac{1}{2}}\\ C_{-\frac{1}{2}}^2+C_{\frac{1}{2}}^2=1\end{cases}$$

$$\Rightarrow \begin{pmatrix}C_{-\frac{1}{2}}\\ C_{\frac{1}{2}}\end{pmatrix}=\frac{1}{\sqrt{2j_1+1}}\begin{pmatrix}\sqrt{j_1-m+\frac{1}{2}}\\ \sqrt{j_1+m+\frac{1}{2}}\end{pmatrix}=\frac{1}{\sqrt{2j}}\begin{pmatrix}\sqrt{j-m}\\ \sqrt{j+m}\end{pmatrix}$$

即:

$$|j_1,\overset{j_2}{\tfrac{1}{2}},j,m\rangle=\sqrt{\frac{j-m}{2j}}\,|j_1,\overset{m_1}{m+\tfrac{1}{2}};\overset{j_2}{\tfrac{1}{2}},\overset{m_2}{-\tfrac{1}{2}}\rangle+\sqrt{\frac{j+m}{2j}}\,|j_1,\overset{m_1}{m-\tfrac{1}{2}};\overset{j_2}{\tfrac{1}{2}},\overset{m_2}{\tfrac{1}{2}}\rangle$$

考试会给.

如 $j=j_1-\frac{1}{2}$

$$\begin{cases}\sqrt{j_1-m+\tfrac{1}{2}}\,C_{-\frac{1}{2}}=-\sqrt{j_1+m+\tfrac{1}{2}}\,C_{\frac{1}{2}}\\ C_{\frac{1}{2}}^2+C_{-\frac{1}{2}}^2=1\end{cases}$$

$$\Rightarrow \begin{pmatrix}C_{-\frac{1}{2}}\\ C_{\frac{1}{2}}\end{pmatrix}=\frac{1}{\sqrt{2j_1+1}}\begin{pmatrix}\sqrt{j_1+m+\frac{1}{2}}\\ -\sqrt{j_1-m+\frac{1}{2}}\end{pmatrix}=\frac{1}{\sqrt{2j+2}}\begin{pmatrix}\sqrt{j+m+1}\\ -\sqrt{j-m+1}\end{pmatrix}$$

即：
$$|j_1,\tfrac{1}{2};j,m\rangle=\sqrt{\frac{j+m+1}{2j+2}}\,|j_1,m+\tfrac12;\tfrac12,-\tfrac12\rangle-\sqrt{\frac{j-m+1}{2j+2}}\,|j_1,m-\tfrac12;\tfrac12,\tfrac12\rangle$$

我们可以通过迭代关系得到高阶 C.G. 系数 (Sakurai P210)

例：自旋－自旋耦合 (He原子/第II主族原子)

$S_1=\frac12 \quad S_2=\frac12, \quad S=0,1.$

$\hat{S}=\hat{S}_1+\hat{S}_2$

交换反对称

$S=0 \quad |0,0\rangle=\frac{\sqrt2}{2}(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle)$ 自旋单态

$S=1 \begin{cases}|1,1\rangle=|\uparrow\uparrow\rangle\\ |1,-1\rangle=|\downarrow\downarrow\rangle\\ |1,0\rangle=\frac{\sqrt2}{2}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)\end{cases}$ 自旋三重态

交换对称

He原子电子态

由于电子自旋在Schrödinger的理论体系中写不出波函数。

我们用 χ_{spin} 抽象表示

我们要求 $\psi(\vec r_1,\vec r_2)\cdot\chi_{spin}$ 交换对称

则 自旋单态 $\Rightarrow \psi(\vec r_1,\vec r_2)$ 交换对称 $\Rightarrow$ 平均间距小 $\Downarrow$ 库仑排斥能大

自旋三重态 $\Rightarrow \psi(\vec r_1,\vec r_2)$ 交换反对称 $\Rightarrow$ 平均间距大 $\Downarrow$ 库仑排斥小

eg： 1S2S.

	$L=0$	$L=0$
He光谱.	$S=0$	$S=1$
	$J=0$	$J=1$
	${}^1S_0$	${}^3S_1 \rightarrow {}^{2S+1}L_J$.

1S2S ${}^1S_0$ —— ${}^3S_1$ —— 第一激发态

注：He原子基态 1S1S 不存在 $^3S_1$，而第一激发态 1S2S 有 $^3S_1$

因为 1S 2S 中空间波函数可以构造为：

$\psi = \psi_{1s}\psi_{2s}$（交换对称项）

$\psi' = \frac{\sqrt{2}}{2}(\psi_{1s}\psi_{2s} - \psi_{2s}\psi_{1s})$（交换反对称项）

所以 χ_{spin} 可以有单态与三重态

但对于 1S1S

$\psi = \psi_{1s}\psi_{1s}$. $\quad \psi' = \frac{\sqrt{2}}{2}(\psi_{1s}\psi_{1s} - \psi_{1s}\psi_{1s}) = 0$

因此空间波函数无反对称项，χ_{spin} 为反对称

（Pauli不相容原理）

例：(1) 求 $\langle j\, m_j | \hat{l}_z | j\, m_j \rangle \quad \hat{L} + \hat{S} = \hat{J}$

$$\langle j\, m_j | \hat{l}_z | j\, m_j \rangle = \sum_{m_l m_s} \langle j\, m_j | m_l m_s \rangle \langle m_l m_s | \hat{l}_z | j\, m_j \rangle$$

① $j = l + \frac{1}{2}$：$\langle \hat{l}_z \rangle_{jm_j} = (m_j + \frac{1}{2})\frac{j - m_j}{2j}\hbar + (m_j - \frac{1}{2})\frac{j+m_j}{2j}\hbar = \frac{2j-1}{2j} m_j \hbar$

② $j = l - \frac{1}{2}$：$\langle \hat{l}_z \rangle_{jm_j} = (m_j + \frac{1}{2})\frac{j+m_j+1}{2j+2}\hbar + (m_j - \frac{1}{2})\frac{j-m_j+1}{2j+2}\hbar = m_j\hbar + \frac{m_j}{2j+2}\hbar$

(2) 求 $\langle j\, m_j | \hat{S}_z | j\, m_j \rangle$

① $j = l + \frac{1}{2} \quad \frac{j-m_j}{2j}(-\frac{1}{2}\hbar) + \frac{j+m_j}{2j}(\frac{1}{2})\hbar = \frac{m_j}{2j}\hbar$

② $j = l - \frac{1}{2} \quad \frac{j+m_j+1}{2j+2}(-\frac{1}{2})\hbar + \frac{j-m_j+1}{2j+2}(\frac{1}{2})\hbar = -\frac{m_j}{2j+2}\hbar$

(3) $\langle \hat{l}_z \rangle_{jm_j} + \langle \hat{S}_z \rangle_{jm_j} \quad \begin{cases} j = l + \frac{1}{2}, & m_j\hbar \\ j = l - \frac{1}{2}, & m_j\hbar \end{cases}$（角动量守恒）

$$\langle \hat{l}_z\rangle_{jm_j} + 2\langle \hat{S}_z\rangle_{jm_j} \quad \begin{cases} j = l+\frac{1}{2}, & (m_j + \frac{m_j}{2j})\hbar \\ j = l-\frac{1}{2}, & (m_j - \frac{m_j}{2j+2})\hbar \end{cases}$$

例：两自旋 $\frac{1}{2}$ 粒子的张量势写作．

$$\hat{V} = 3\frac{(\hat{\vec{\sigma}}_1\cdot\vec{r})(\hat{\vec{\sigma}}_2\cdot\vec{r})}{r^2} - \hat{\vec{\sigma}}_1\cdot\hat{\vec{\sigma}}_2$$

$\vec{r}$ 为相对位矢，将 $\hat{V}$ 表示为 $\hat{\vec{S}} = \hat{\vec{S}}_1 + \hat{\vec{S}}_2$ 与 $\vec{r}$ 的势数．

解 $$\hat{V} = \frac{4}{\hbar^2}\left(\frac{3(\hat{\vec{S}}_1\cdot\vec{r})(\hat{\vec{S}}_2\cdot\vec{r})}{r^2} - \hat{\vec{S}}_1\cdot\hat{\vec{S}}_2\right)$$

定义 $\vec{n} = \frac{\vec{r}}{r}$ $\quad \hat{S}_n = \hat{\vec{S}}\cdot\vec{n} = \hat{\vec{S}}_1\cdot\vec{n} + \hat{\vec{S}}_2\cdot\vec{n} = \hat{S}_{1n} + \hat{S}_{2n}$

$$\hat{S}_n^2 = \hat{S}_{1n}^2 + \hat{S}_{2n}^2 + 2\hat{S}_{1n}\hat{S}_{2n} \quad 而 \quad S_1 = \frac{1}{2} \quad m_{s_1} = \pm\frac{1}{2}$$

$$= \frac{\hbar^2}{4} + \frac{\hbar^2}{4} + 2\hat{S}_{1n}\hat{S}_{2n} \qquad S_2 = \frac{1}{2} \quad m_{s_2} = \pm\frac{1}{2}$$

$$\hat{S}_{1n}\hat{S}_{2n} = \frac{\hat{S}_n^2 - \frac{\hbar^2}{2}}{2}$$

而 $$\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2 = \frac{\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2}{2} = \frac{1}{2}\hat{S}^2 - \frac{3}{4}\hbar^2\hat{I} \quad (\hat{S}_1^2 \longrightarrow \frac{1}{2}(\frac{1}{2}+1)\hbar^2\hat{I})$$

$$\hat{V} = \frac{4}{\hbar^2}\left(\frac{3}{2}S_n^2 - \frac{3}{4}\hbar^2\hat{I} - \frac{1}{2}\hat{S}^2 + \frac{3}{4}\hbar^2\hat{I}\right) = \frac{1}{\hbar^2}\left[6(\hat{\vec{S}}\cdot\hat{\vec{n}})^2 - 2\hat{\vec{S}}^2\right]$$

例：耦合量子数 $\hat{\vec{L}} + \hat{\vec{S}} = \hat{\vec{J}}$

如 $L=1$．$S=\frac{1}{2}$．

$J=\frac{1}{2}$，$m_j = \pm\frac{1}{2}$，2个基态

$J=\frac{3}{2}$，$m_j = \pm\frac{1}{2}, \pm\frac{3}{2}$，4个基态．

如 $L=1$ $\quad S=1$．

$J=0$ $\quad m_j = 0$． 1个基态．

$J=1$ $\quad m_j = 0, \pm1$，3个基态．

$J=2$． $\quad m_j = 0, \pm1, \pm2$，5个基态．

对于 (1S 2p).

$\begin{cases} L=1 \\ S=0 \end{cases}$ $J=1,\ m_j=\pm1,0$ 3个基态

$\begin{cases} L=1 \\ S=1 \end{cases}$ $J=0/1/2.$ $m_j=\cdots$ 1/3/5个基态

一共12个基态 ⇒ 12维子空间 (耦合表象)

在非耦合表象中. (考试大概率会考)

1S: $m_s=\pm\frac{1}{2}$. 2个基态.

2p: $m_l=\pm1,0$ $m_s=\pm\frac{1}{2}$, 6个基态 } ⇒ 12维子空间

④ C.G.系数的应用.

碱金属 (^{23}Na)

3p	$n=3$ $l=1$	$S=\frac{1}{2}$	$J=\frac{3}{2}$ $J=\frac{1}{2}$	$^2P_{\frac{3}{2}}$ $^2P_{\frac{1}{2}}$
3s	$n=3$ $l=0$	$S=\frac{1}{2}$	$J=\frac{1}{2}$	$^2S_{\frac{1}{2}}$

m_j : $-\frac{3}{2}$ $-\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$

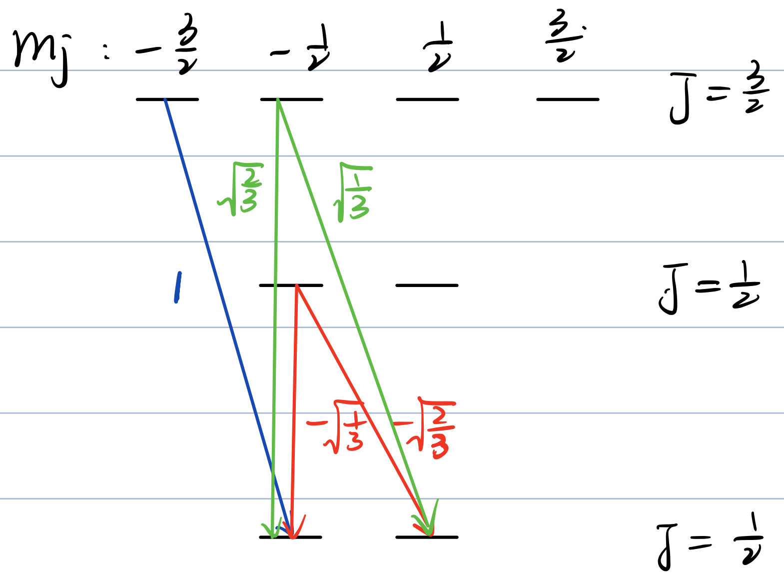
$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	
—	—	—	—	$J=\frac{3}{2}$
	—	—		$J=\frac{1}{2}$
	—	—		$J=\frac{1}{2}$

Wigner – Eckert theorem

$$\langle\alpha',j',m'|\underset{\text{光场项}.\ k=1,\ q=\pm1,0.}{\hat{T}^{(k)}_q}|\alpha,j\,m\rangle = \langle \overset{j_1\,m_1}{j\,m};\overset{j_2\,m_2}{k\,q}|\overset{j_1 j_2}{j\,k}\,\overset{j\ \ m}{j'\,m'}\rangle\left(\frac{\langle\alpha',j'\|T^{(k)}\|\alpha,j\rangle}{\sqrt{2j'+1}}\right)$$

上式告诉我们,电子与光场的耦合最后的结果与C.G.系数有关,本质上为光子与电子角动量守恒.由此告诉我们选择

定则



第八章 近似方法.

1. 定态微扰论.(不含时微扰)

求 $\hat{H}|\psi\rangle = E|\psi\rangle$

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

划分原则：① $\hat{H}_0$尽量简单,本征问题可解.

② $\langle\hat{V}\rangle \ll \langle\hat{H}_0\rangle$ (但原则可以被打破)

已知: $\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$

$$\Longrightarrow \quad |\psi_n^{(0)}\rangle \xrightarrow{\hat{V}} |\psi_n\rangle = \sum_m C_m|\psi_m^{(0)}\rangle$$

$$E_n^{(0)} \xrightarrow{\hat{V}} E_n$$

a. 非简并微扰论 ($|\psi_n^{(0)}\rangle$不在简并子空间中)

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

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}$$

$$|\psi_k\rangle = |\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \cdots$$

由 $\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$

$\Rightarrow$ λ的0次项： $\hat{H}_0|\psi_k^{(0)}\rangle = E_k^{(0)}|\psi_k^{(0)}\rangle$

λ的1次项： $\hat{H}_0|\psi_k^{(1)}\rangle + \hat{V}|\psi_k^{(0)}\rangle = E_k^{(0)}|\psi_k^{(1)}\rangle + E_k^{(1)}|\psi_k^{(0)}\rangle$

λ的2次项： $\hat{H}_0|\psi_k^{(2)}\rangle + \hat{V}|\psi_k^{(1)}\rangle = E_k^{(0)}|\psi_k^{(2)}\rangle + E_k^{(1)}|\psi_k^{(1)}\rangle + E_k^{(2)}|\psi_k^{(0)}\rangle$

设 $|\psi_k^{(1)}\rangle = \sum_n C_n^{(1)}|\psi_n^{(0)}\rangle$

代入λ的1次项等式中，同时用 $\langle\psi_m^{(0)}|$ 在两边作用.

$\Rightarrow \quad E_m^{(0)}C_m^{(1)} + V_{mk} = E_k^{(0)}C_m^{(1)} + E_k^{(1)}\delta_{mk}$

其中 $V_{mk} = \langle\psi_m^{(0)}|\hat{V}|\psi_k^{(0)}\rangle$

当 $m=k$ 时 $\quad E_k^{(1)} = V_{kk} = \langle\psi_n^{(0)}|\hat{V}|\psi_n^{(0)}\rangle$

当 $m\neq k$ 时. $\quad C_m^{(1)} = \dfrac{V_{mk}}{E_k^{(0)} - E_m^{(0)}}$

记住

$$\Rightarrow \begin{cases} E_k \approx E_k^{(0)} + V_{kk} & \text{能量的1级近似(准确到1级修正)} \\ |\psi_k\rangle \approx |\psi_k^{(0)}\rangle & \text{波函数0级近似} \end{cases}$$

同时我们有： $|\psi_k^{(1)}\rangle = \sum_{n\neq k} \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}|\psi_n^{(0)}\rangle$

① 非简并： $E_k^{(0)} \neq E_n^{(0)} \ (n\neq k)$

② $\langle\psi_k^{(0)}|\psi_k^{(1)}\rangle = 0 \Rightarrow$ 微扰修正来自于 $\hat{V}$ 耦合与 $|\psi_k^{(0)}\rangle$ 正交的本征态

能量的2级修正.

设 $|\psi_k^{(2)}\rangle = \sum_n C_n^{(2)}|\psi_n^{(0)}\rangle$

代入λ的2次项的等式中得到：

$$\hat{H}_0\Big(\sum_n C_n^{(2)}|\psi_n^{(0)}\rangle\Big)+\hat{V}\sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)}-E_n^{(0)}}|\psi_n^{(0)}\rangle$$

$$=E_k^{(0)}\sum_n C_n^{(2)}|\psi_n^{(0)}\rangle+V_{kk}\sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)}-E_n^{(0)}}|\psi_n^{(0)}\rangle+E_k^{(2)}|\psi_k^{(0)}\rangle$$

两边左乘 $\langle\psi_m^{(0)}|$

$$\Rightarrow\quad E_m^{(0)}C_m^{(2)}+\sum_{n\neq k}\frac{V_{mn}V_{nk}}{E_k^{(0)}-E_n^{(0)}}=E_k^{(0)}C_m^{(2)}+\frac{V_{kk}V_{mk}}{E_k^{(0)}-E_m^{(0)}}(1-\delta_{mk})+E_k^{(2)}\delta_{mk}$$

当 $m=k$ 时

$$E_k^{(2)}=\sum_{n\neq k}\frac{|V_{nk}|^2}{E_k^{(0)}-E_n^{(0)}}$$

当 $m\neq k$ 时

$$C_m^{(2)}=\frac{1}{E_k^{(0)}-E_m^{(0)}}\Big(\sum_{n\neq k}\frac{V_{mn}V_{nk}}{E_k^{(0)}-E_n^{(0)}}-\frac{V_{kk}V_{mk}}{E_k^{(0)}-E_m^{(0)}}\Big)$$

记住

$$\Rightarrow\begin{cases}E_k\approx E_k^{(0)}+V_{kk}+\sum\limits_{n\neq k}\dfrac{|V_{nk}|^2}{E_k^{(0)}-E_n^{(0)}} & \text{能量准确到2级的修正}\\ |\psi_k\rangle\approx|\psi_k^{(0)}\rangle+\sum\limits_{n\neq k}\dfrac{V_{nk}}{E_k^{(0)}-E_n^{(0)}}|\psi_n^{(0)}\rangle & \text{波函数准确到1级}\cdots\end{cases}$$

同时有波函数准确到2级修正:

$$|\psi_k\rangle\approx|\psi_k^{(0)}\rangle+\sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)}-E_n^{(0)}}|\psi_n^{(0)}\rangle+C_m^{(2)}|\psi_m^{(0)}\rangle$$

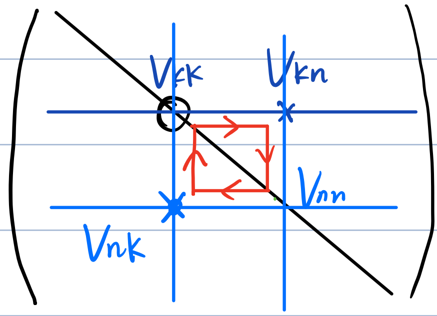
讨论:

i) 正交归一完备性(以1级近似为例)

$$\langle\psi_k|\psi_l\rangle=\delta_{kl}+\underbrace{\sum_{n\neq l,k}\frac{V_{ln}V_{nk}}{(E_k^{(0)}-E_n^{(0)})(E_l^{(0)}-E_n^{(0)})}}_{O(\lambda^2)}$$ 在λ的一阶精度下正交

同理: $\sum_k |\psi_k^{(1)}\rangle\langle\psi_k^{(1)}| = \hat I + O(\lambda^2)$

ii) 矩阵图像（在 $|\psi_n^{(0)}\rangle$ 的表像下）

$\hat V$ 

V_{kk}（对角元）为能量的1级修正.

在场论中，我们认为微扰是产生了图上红色箭头的虚过程，V_{kn} 与 V_{nk} 使 E_k 与 E_n 产生了耦合，一去一回有2级修正，注意修正 E_k，则2级修正中分母为 $E_k - E_n$ 不要记错

例 $\hat H = \underbrace{\frac{\hat p^2}{2m} + \frac12 m\omega^2\hat x^2}_{\hat H_0} + \underbrace{\frac12 m\omega^2\hat x^2\varepsilon}_{\hat V}$ 小量

求能量本征值精确到 ε 的二阶小量

解 $E_n^{(0)} = (n+\frac12)\hbar\omega$

$$E_n \approx E_n^{(0)} + \langle n|\hat V|n\rangle + \sum_{k\neq n}\frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$\hat x^2 = \frac{\hbar}{2m\omega}\left(\hat a^2 + (\hat a^+)^2 + \hat a\hat a^+ + \hat a^+\hat a\right)$$

$$\langle m|\hat x^2|n\rangle = \frac{\hbar}{2m\omega}\left(\sqrt{n(n-1)}\,\delta_{m,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + (n+1)\delta_{mn} + n\delta_{mn}\right)$$

$$\Rightarrow V_{nn} = \frac14(2n+1)\hbar\omega\varepsilon$$

$$V_{kn} = \frac14\hbar\omega\varepsilon\left(\sqrt{n(n-1)}\,\delta_{k,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{k,n+2}\right)$$

$$E_n \approx (n+\frac12)\hbar\omega + \frac14(2n+1)\hbar\omega\varepsilon - \underbrace{\frac1{32}\hbar\omega\varepsilon^2(n+2)(n+1)}_{\frac{\frac1{16}\hbar^2\omega^2\varepsilon^2}{-2\hbar\omega}(n+2)(n+1)}$$

$$+ \underbrace{\frac1{32}\hbar\omega\varepsilon^2 n(n-1)}_{\frac{\frac1{16}\hbar^2\omega^2\varepsilon^2}{2\hbar\omega}n(n-1)} \quad (n \geq 2)$$

$$|\psi_n\rangle \approx |n\rangle + \sum_{k\neq n} \frac{V_{kn}}{E_n^{(0)}-E_k^{(0)}} |k\rangle$$

$$= |n\rangle + \frac{1}{8}\varepsilon\left(\sqrt{n(n-1)}\,|n-2\rangle - \sqrt{(n+1)(n+2)}\,|n+2\rangle\right) \quad (n\geq 2)$$

$n=0 \Rightarrow$ $E_0 \approx \frac{1}{2}\hbar\omega + \frac{1}{4}\hbar\omega\varepsilon - \frac{1}{16}\hbar\omega\varepsilon^2$

$|\psi_0\rangle \approx |0\rangle - \frac{\sqrt{2}}{8}\varepsilon|2\rangle$

精确解:

$E = (n+\frac{1}{2})\sqrt{1+\varepsilon}\,\hbar\omega$

$= (n+\frac{1}{2})\hbar\omega\,(1+\frac{\varepsilon}{2} - \frac{\varepsilon^2}{8}+\cdots)$

b. 简并微扰论.

$\hat{H} = \hat{H}_0 + \hat{V}$ 其中 $\hat{H}_0$ 的本征态 $\{|\psi_{m\mu}^{(0)}\rangle, |\psi_n^{(0)}\rangle\}$

$\mu = 1,2\ldots g$ (简并度)

$$\begin{cases} \hat{H}_0|\psi_{m\mu}^{(0)}\rangle = E_m^{(0)}|\psi_{m\mu}^{(0)}\rangle \\ \hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \end{cases}$$

一般方法:

设 $|\psi\rangle = |\psi^{(0)}\rangle + \lambda|\psi^{(1)}\rangle$, $E_m = E_m^{(0)} + \lambda E_m^{(1)} + \cdots$

且 $|\psi^{(1)}\rangle$ 与整个简并子空间正交

$|\psi^{(0)}\rangle$ 由 $\{|\psi_{m\mu}^{(0)}\rangle\}$ 的线性叠加表示

考察 $\hat{H}|\psi\rangle = E|\psi\rangle$

λ 的1次项表达式

$$\hat{H}_0|\psi^{(1)}\rangle + \hat{V}|\psi^{(0)}\rangle = E_m^{(0)}|\psi^{(1)}\rangle + E_m^{(1)}|\psi^{(0)}\rangle$$

$$\Rightarrow \hat{H}_0|\psi^{(1)}\rangle + \hat{V}\sum_\mu C_{m\mu}^{(0)}|\psi_{m\mu}^{(0)}\rangle = E_m^{(0)}|\psi^{(1)}\rangle + E_m^{(1)}\sum_\mu C_{m\mu}^{(0)}|\psi_{m\mu}^{(0)}\rangle$$

两边左乘 $\langle\psi_{m\nu}^{(0)}|$

$$\Rightarrow \sum_\mu V_{m\nu,m\mu} C_{m\mu}^{(0)} = E_m^{(1)} C_{m\nu}^{(0)}$$

$$\Rightarrow \sum_\mu (V_{m\nu,m\mu} - E_m^{(1)}\delta_{\mu,\nu}) C_{m\mu}^{(0)} = 0$$

即在 $\{|\psi_{m\mu}^{(0)}\rangle\}$ 基下对角化 $\hat{V}$（简并子空间内）

本征态：简并子空间内的零级波函数

本征值：能量的一级修正.

如果对角化后简并消除，可以继续用利用非简并微扰论公式，求更高阶修正.

例：$\hat{H}$ 在 $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$ 下的矩阵表示为

$$\begin{pmatrix} E_1 & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_1 & E_1 & 0 \\ \varepsilon_2 & 0 & E_2 \end{pmatrix} \qquad |\varepsilon_1|, |\varepsilon_2| \ll |E_1|, |E_2|.$$

（认为 $\hat{H}_0 \to \begin{pmatrix} E_1 & & \\ & E_1 & \\ & & E_2 \end{pmatrix}$ $\hat{V} \to \begin{pmatrix} 0 & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_1 & 0 & 0 \\ \varepsilon_2 & 0 & 0 \end{pmatrix}$）

解：① 对角化 $\begin{pmatrix} 0 & \varepsilon_1 \\ \varepsilon_1 & 0 \end{pmatrix} \Rightarrow$ 本征值 $\pm\varepsilon_1$. 相应本征态

$$|\pm\rangle = \frac{\sqrt{2}}{2}(|\alpha\rangle \pm |\beta\rangle)$$

选取 $|+\rangle$ $|-\rangle$ $|\gamma\rangle$ 为基.

$$\hat{H}_0 \to \begin{pmatrix} E_1 & & \\ & E_1 & \\ & & E_2 \end{pmatrix} \qquad \hat{V} \to \begin{pmatrix} \varepsilon_1 & 0 & \boxed{a} \\ 0 & -\varepsilon_1 & \boxed{b} \\ \boxed{a} & \boxed{b} & 0 \end{pmatrix}$$

$$\boxed{a} = \langle + | \hat{V} | \gamma \rangle = \frac{\sqrt{2}}{2}(\langle \alpha | + \langle \beta |) \hat{V} | \gamma \rangle = \frac{\sqrt{2}}{2}\varepsilon_2$$

$$\boxed{b} = \langle - | \hat{V} | \gamma \rangle = \frac{\sqrt{2}}{2}(\langle \alpha | - \langle \beta |) \hat{V} | \gamma \rangle = \frac{\sqrt{2}}{2}\varepsilon_2$$

$$\hat{H} = \hat{H}_0 + \hat{V} \to \begin{pmatrix} E_1+\varepsilon_1 & 0 & \frac{\sqrt{2}}{2}\varepsilon_2 \\ 0 & E_1-\varepsilon_1 & \frac{\sqrt{2}}{2}\varepsilon_2 \\ \frac{\sqrt{2}}{2}\varepsilon_2 & \frac{\sqrt{2}}{2}\varepsilon_2 & E_2 \end{pmatrix}$$

则能量的修正后结果分别为（保留到二阶）

$$E_1 + \varepsilon_1 + \frac{\frac{1}{2}\varepsilon_2^2}{E_1+\varepsilon_1-E_2} \approx E_1+\varepsilon_1 + \frac{\frac{1}{2}\varepsilon_2^2}{E_1-E_2}$$

$$E_1 - \varepsilon_1 + \frac{\frac{1}{2}\varepsilon_2^2}{E_1-\varepsilon_1-E_2} \approx E_1-\varepsilon_1 + \frac{\frac{1}{2}\varepsilon_2^2}{E_1-E_2}$$

$$E_2 + \frac{\frac{1}{2}\varepsilon_2^2}{E_2-E_1} + \frac{\frac{1}{2}\varepsilon_2^2}{E_2-E_1} = E_2 + \frac{\varepsilon_2^2}{E_2-E_1}$$

用最初未做处理的矩阵计算结果 （结果自洽）

② "实际问题"的方法.

寻找算符 $\hat{A}$, 使 $[\hat{A}, \hat{H}_0] = [\hat{A}, \hat{V}] = 0$, 且 $\{\hat{H}_0, \hat{A}\}$ 的共同本征态在 $\hat{H}_0$ 的简并子空间中无简并(即 $\hat{A}$ 的本征值不同) 则这些本征态为合适的零级波函数, $\hat{V}$ 在这样的基下对角.

例 反常 Zeeman 效应 ⟶ 无相对论修正版.

$$\hat{H} = A\hat{L}\cdot\hat{S} + B(\hat{L}_z + 2\hat{S}_z)$$

在 $A \gg B$ 和 $B \gg A$ 的情况下，分别讨论体系能量的微扰展开到一级修正.

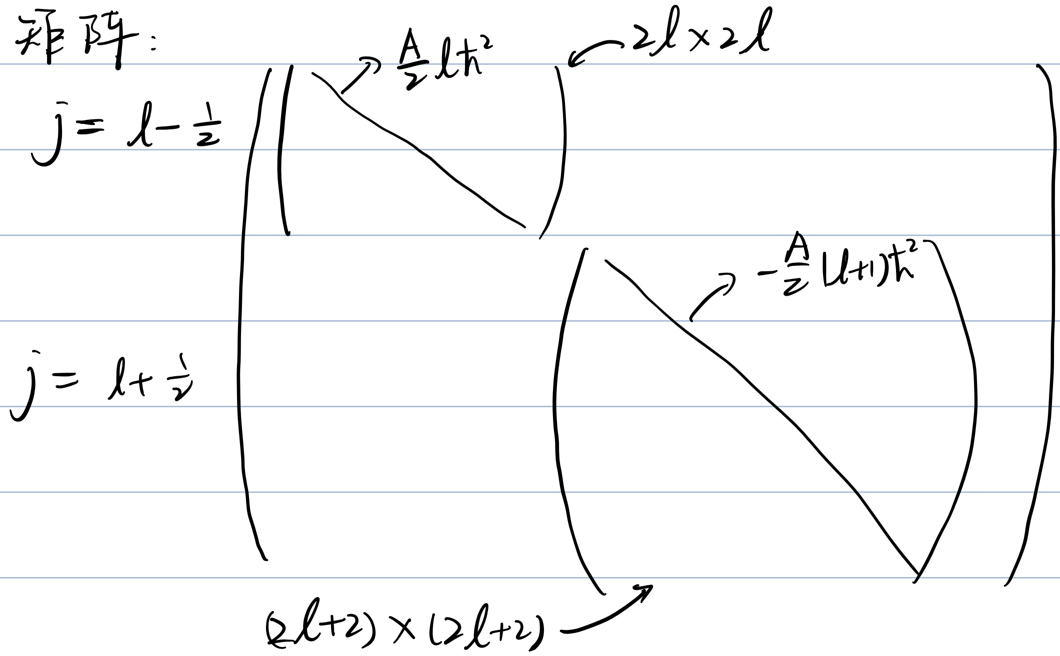
i) $A \gg B$. $\hat{H}_0 = A\hat{L}\cdot\hat{S}$ $\hat{V} = B(\hat{L}_z + 2\hat{S}_z)$

$$\hat{L}\cdot\hat{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \quad (\hat{J} = \hat{L} + \hat{S})$$

在 $\{|j, m_j\rangle\}$ 的基下

以 l, $s=\frac{1}{2}$ $J = l-\frac{1}{2}, l+\frac{1}{2}$ 为例

矩阵:



$$E_0 = \langle j\, m_j | \hat{H}_0 | j\, m_j\rangle = \frac{A}{2}[j(j+1) - l(l+1) - s(s+1)]\hbar^2$$

$$= \begin{cases} \frac{A}{2}l\hbar^2, & j = l-\frac{1}{2} \\ -\frac{A}{2}(l+1)\hbar^2, & j = l+\frac{1}{2} \end{cases}$$

$$\langle j' m_j' | \hat{V} | j\, m_j\rangle = B\langle j' m_j' | \hat{J}_z | j\, m_j\rangle + B\underbrace{\langle j' m_j' | \hat{S}_z | j\, m_j\rangle}_{\text{利用 C.G. 系数.}}$$

$$\hat{V} = B(\hat{L}_z + 2\hat{S}_z) = B(\hat{J}_z + \hat{S}_z)$$

如 $j=j_1+\frac12$

$$\begin{cases}\sqrt{j_1+m+\frac12}\,C_{-\frac12}=\sqrt{j_1-m+\frac12}\,C_{\frac12}\\ C_{-\frac12}^2+C_{\frac12}^2=1\end{cases}$$

$$\Rightarrow\begin{pmatrix}C_{-\frac12}\\C_{\frac12}\end{pmatrix}=\frac{1}{\sqrt{2j_1+1}}\begin{pmatrix}\sqrt{j_1-m+\frac12}\\\sqrt{j_1+m+\frac12}\end{pmatrix}=\frac{1}{\sqrt{2j}}\begin{pmatrix}\sqrt{j-m}\\\sqrt{j+m}\end{pmatrix}$$

即:

$$|j_1,\overset{j_2}{\tfrac12},j,m\rangle=\sqrt{\frac{j-m}{2j}}\,|j_1,\overset{m_1}{m+\tfrac12};\overset{j_2}{\tfrac12},\overset{m_2}{-\tfrac12}\rangle+\sqrt{\frac{j+m}{2j}}\,|j_1,\overset{m_1}{m-\tfrac12};\overset{j_2}{\tfrac12},\overset{m_2}{\tfrac12}\rangle$$

考试会给.

如 $j=j_1-\frac12$

$$\begin{cases}\sqrt{j_1-m+\frac12}\,C_{-\frac12}=-\sqrt{j_1+m+\frac12}\,C_{\frac12}\\ C_{\frac12}^2+C_{-\frac12}^2=1\end{cases}$$

$$\Rightarrow\begin{pmatrix}C_{-\frac12}\\C_{\frac12}\end{pmatrix}=\frac{1}{\sqrt{2j_1+1}}\begin{pmatrix}\sqrt{j_1+m+\frac12}\\-\sqrt{j_1-m+\frac12}\end{pmatrix}=\frac{1}{\sqrt{2j+2}}\begin{pmatrix}\sqrt{j+m+1}\\-\sqrt{j-m+1}\end{pmatrix}$$

即:

$$|j_1,\overset{j_2}{\tfrac12},j,m\rangle=\sqrt{\frac{j+m+1}{2j+2}}\,|j_1,\overset{m_1}{m+\tfrac12};\overset{j_2}{\tfrac12},\overset{m_2}{-\tfrac12}\rangle-\sqrt{\frac{j-m+1}{2j+2}}\,|j_1,\overset{m_1}{m-\tfrac12};\overset{j_2}{\tfrac12},\overset{m_2}{\tfrac12}\rangle$$

在同一个j的子空间内

$j=l+\frac12$

$$\langle j,m_j'|\,\hat S_z\,|j,m_j\rangle$$

$$=\left(\sqrt{\frac{j-m_j'}{2j}}\langle m_j'+\tfrac12,-\tfrac12|+\sqrt{\frac{j-m_j'}{2j}}\langle m_j'-\tfrac12,\tfrac12|\right)\hat S_z\left(\sqrt{\frac{j-m_j}{2j}}|m_j+\tfrac12,-\tfrac12\rangle+\sqrt{\frac{j-m_j}{2j}}|m_j-\tfrac12,\tfrac12\rangle\right)$$

$$=\frac12\hbar\left(\frac{j+m_j}{2j}-\frac{j-m_j}{2j}\right)\delta_{m_j,m_j'}$$

$$=\frac{m_j}{2j}\hbar\,\delta_{m_j m_j'}$$

同理: $j=l-\frac12$

$$\langle j,m_j'|\hat S_z|j,m_j\rangle=-\frac{m_j}{2(j+1)}\hbar.$$

$\hat V$的对角元:

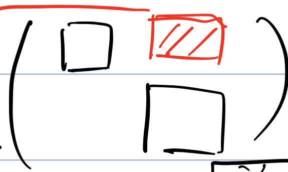
$j=l+\frac12$: $B\left(\frac{m_j}{2j}+m_j\right)\hbar$

$j=l-\frac{1}{2}$: $B\left(m_j-\frac{m_j}{2(j+1)}\right)\hbar$.

非对角元 $\sim\ S_{j,j\pm1}\ S_{m_j,m_j'}$

$\langle j'm_j'|\hat{S}_z|j\,m_j\rangle$ (二阶修正项)

$(j'=l-\frac{1}{2},\ j=l+\frac{1}{2})$



$$=-\frac{1}{2}\hbar\sqrt{\frac{j'+m_j+1}{2j'+2}}\sqrt{\frac{j-m_j}{2j}}-\frac{1}{2}\hbar\sqrt{\frac{j-m_j+1}{2j+2}}\sqrt{\frac{j+m_j}{2j}}$$

简并微扰一级修正

$j=l+\frac{1}{2}$

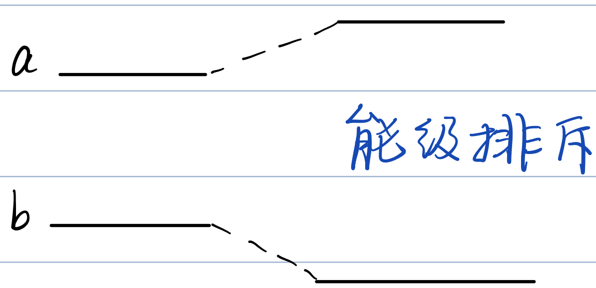
$$E_0+E_1=\frac{A}{2}l\hbar^2+B\left(\frac{m_j}{2j}+m_j\right)\hbar$$

$j=l-\frac{1}{2}$

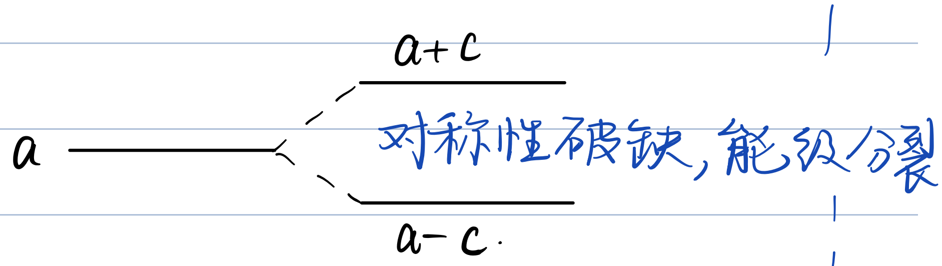
$$E_0+E_1=-\frac{A}{2}(l+1)\hbar^2+B\left(m_j-\frac{m_j}{2(j+1)}\right)\hbar.$$

图像上的理解:

$$\begin{pmatrix} a & c \\ c & b \end{pmatrix}\quad a\neq b\quad c\ll a,b$$



$$\begin{pmatrix} a & c \\ c & a \end{pmatrix}\quad c\ll a,b$$



继续关于 Zeeman 效应的讨论.

为什么我们选取耦合表象后会让 $\hat{J}_z$ 与 $\hat{S}_z$ 均为对角.

因为 $[\hat{J}_z, \hat{H}_0] = 0$. $[\hat{J}_z, \hat{V}] = 0$

因此 在 $|j, m_j\rangle$ 的表象下 $\hat{H}_0, \hat{V}$ 对角化

在 $A \gg B$ 的情况下:

简并微扰一级修正

$j = l + \frac{1}{2}$

$$E_0 + E_1 = \frac{A}{2} l \hbar^2 + B\left(\frac{m_j}{2j} + m_j\right)\hbar$$

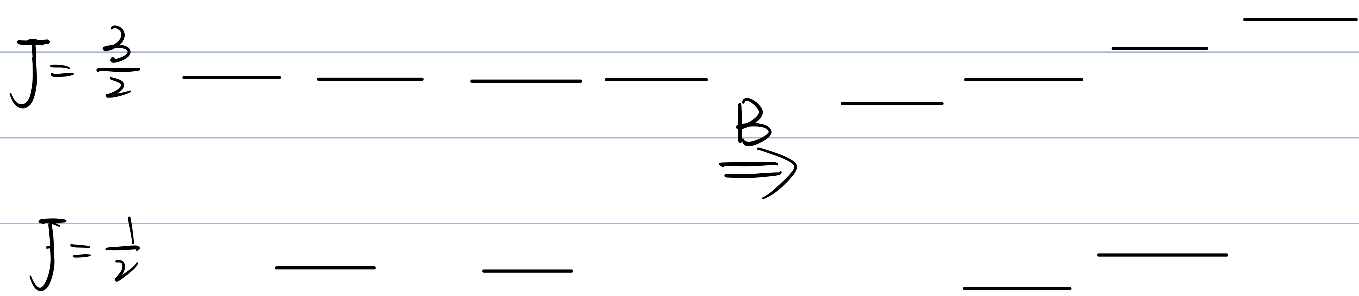
Lande 因子.

$j = l - \frac{1}{2}$

$$E_0 + E_1 = -\frac{A}{2}(l+1)\hbar^2 + B\left(m_j - \frac{m_j}{2(j+1)}\right)\hbar.$$

物理图像上考察能级

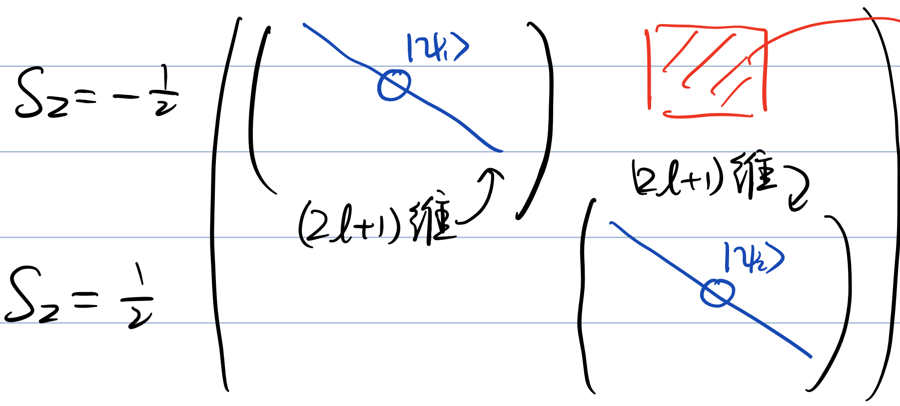
$l = 1.$



ii) $A \ll B$.

$\hat{H}_0 = B(\hat{L}_z + 2\hat{S}_z)$ $\hat{V} = A\hat{\vec{L}} \cdot \hat{\vec{S}}$

选则 $|l, m_l; S, S_z\rangle$ (非耦合表象基)



$m_l' + S_z' = m_l + S_z$

角动量守恒

可能存在 $|\psi_i\rangle$ $|\psi_j\rangle$

满足 $m_l' + 2S_z' = m_l + 2S_z$

但此处无耦合元, 因

$E_0 = \langle m_l\, S_z | \hat{H}_0 | m_l\, S_z \rangle$ 此不影响一阶修正.

$= B(m_l + 2S_z)\hbar$

$\hat{V}$ 的矩阵元.

$\langle m_l' S_z' | \hat{\vec{L}} \cdot \hat{\vec{S}} | m_l S_z \rangle$

(利用 $\hat{\vec{L}} \cdot \hat{\vec{S}} = \hat{l}_z \hat{S}_z + \frac{1}{2}(\hat{l}_+ \hat{S}_- + \hat{l}_- \hat{S}_+)$)

$= \langle m_l' S_z' | \hat{l}_z + \hat{S}_z + \frac{1}{2}(\hat{l}_+ \hat{S}_- + \hat{l}_- \hat{S}_+) | m_l S_z \rangle$

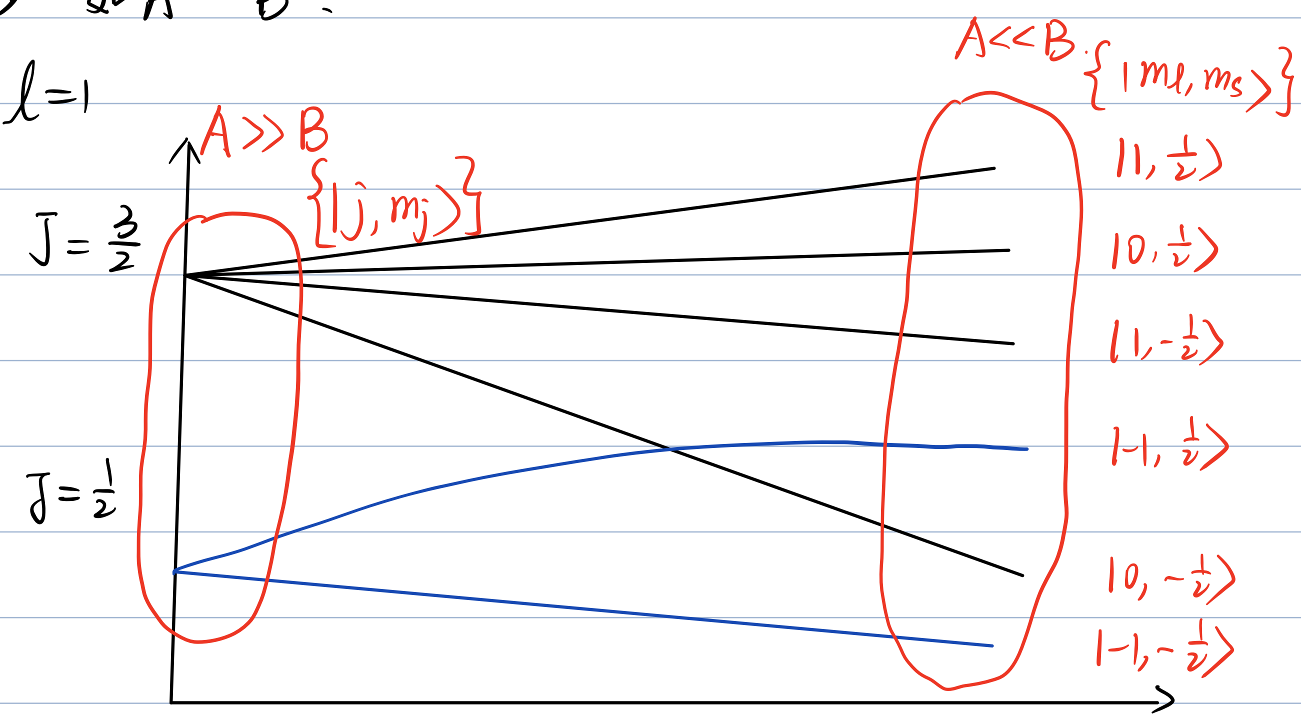
$= \underbrace{m_l S_z \hbar^2 \delta_{m_l' m_l} \delta_{S_z' S_z}}_{\text{对角元.}} + |\boxed{\ }|\, \delta_{S_z' S_z - 1}\, \delta_{m_l', m_l+1} + |\boxed{\ }|^* \delta_{S_z' S_z+1}\, \delta_{m_l', m_l - 1}$

$E_1 = \langle m_l S_z | A \hat{\vec{L}} \cdot \hat{\vec{S}} | m_l S_z \rangle = A m_l S_z \hbar^2.$

$E_0 = \langle m_l S_z | \hat{H}_0 | m_l S_z \rangle = B(m_l + 2S_z)\hbar.$

iii) 如 $A \sim B$?

$l = 1$



C. 微扰论在氢原子中的应用 (Griffiths P174)

零级近似 $\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$