quantum mechanics

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\text{五大公设}\begin{cases}
\text{波函数公设: 波函数完全描述粒子的状态} \\
\text{微观体系动力学演化公设: 状态波函数随空间和时间变化规律遵循薛定谔方程,} \\
\qquad\qquad\text{保持相干性且保持确定的因果性.} \\
\text{算符公设: 力学量用算符表示} \\
\text{测量公设: 观测值为本征值, 或者本征值的期望值.} \\
\text{全同性原理: 粒子的不可识别, 玻色子波函数满足交换对称性, 费米子满足交换反对称性}
\end{cases}
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\text{波函数性质}\begin{cases}
\text{单值, 连续, 有限} \\
\text{归一化} \\
\text{满足态叠加原理} \\
\text{相位不定性}
\end{cases}
$$

概率密度的连续性方程

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 \quad \rho = \psi^* \cdot \psi$$

$$\vec{j} = -\frac{i\hbar}{2m}(\psi^* \cdot \nabla\psi - \psi \cdot \nabla\psi^*) = \Re\left[\psi^*\left(-\frac{i\hbar\nabla}{m}\right)\psi\right]$$

$$i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

$$-i\hbar\frac{\partial}{\partial t}\psi^* = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V^*\psi^*$$

由连续性方程推出两个结论

1. 定态时, $\psi = \Psi(\vec{r}) \cdot A_0 \cdot e^{-\frac{i}{\hbar}Et} \Longrightarrow \vec{j} = 0$
2. 波函数在演化中保持归一化.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 \Longrightarrow$$

$$\int \frac{\partial \rho}{\partial t}\mathrm{d}\tau + \int \nabla \cdot \vec{j}\mathrm{d}\tau = 0 \Longrightarrow$$

$$\int \frac{\partial \rho}{\partial t}\mathrm{d}\tau = c$$

测不准原理的证明:

$$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}\left|\langle[A,B]\rangle\right|^2 \quad \Delta A = A - \langle A\rangle$$

1. Schwarz:
   set $|\lambda\rangle = |\alpha\rangle + \lambda\,|\beta\rangle$.

$$\langle\lambda|\lambda\rangle \geq 0 \implies \langle\alpha|\alpha\rangle + \lambda^*\langle\alpha|\beta\rangle + \lambda\langle\beta|\alpha\rangle + \lambda^*\lambda\langle\beta|\beta\rangle \geq 0$$

$$\begin{cases}\langle\alpha|\alpha\rangle + \lambda^*\langle\alpha|\beta\rangle + \lambda\langle\beta|\alpha\rangle + \lambda^*\lambda\langle\beta|\beta\rangle \geq 0 \\ \lambda = -\frac{\langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle}\end{cases} \implies \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\beta|\alpha\rangle|^2$$

$$\implies \langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq |\langle\Delta A\Delta B\rangle|^2$$

2. 厄密算符的本征值为实数, 反厄密算符的本征值为纯虚数.
   $A = A^\dagger \implies \langle a|\,A\,|a\rangle = (\langle a|\,A\,|a\rangle)^* \implies a = a^*$

$$\begin{cases}\Delta A\cdot\Delta B = \frac{1}{2}[\Delta A,\Delta B] + \frac{1}{2}[\Delta A,\Delta B]_+ \\ [\Delta A,\Delta B] = [A-\langle A\rangle, B-\langle B\rangle] = [A,B]\end{cases} \implies \Delta A\cdot\Delta B = \frac{1}{2}[A,B] + \frac{1}{2}[\Delta A,\Delta B]_+$$

$$\begin{cases}\langle\Delta A\cdot\Delta B\rangle = \frac{1}{2}\langle[A,B]\rangle + \frac{1}{2}\langle[\Delta A,\Delta B]_+\rangle \\ \langle[A,B]\rangle\text{实数}, \langle[\Delta A,\Delta B]_+\rangle\text{纯虚数}\end{cases} \implies |\langle\Delta A\cdot\Delta B\rangle|^2 = \frac{1}{4}\left|\langle[A,B]\rangle\right|^{+}\frac{1}{4}\left|\langle[\Delta A,\Delta B]_+\rangle\right|^2$$

$$\begin{cases}|\langle\Delta A\cdot\Delta B\rangle|^2 = \frac{1}{4}\left|\langle[A,B]\rangle\right|^{+}\frac{1}{4}\left|\langle[\Delta A,\Delta B]_+\rangle\right|^2 \\ \langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq |\langle\Delta A\Delta B\rangle|^2\end{cases} \implies \langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}\left|\langle[A,B]\rangle\right|^2 \quad \Delta A = A - \langle A\rangle$$

定态波函数的性质

定态波函数是量子微观体系的势函数不含时的波函数

$$i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \implies$$

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec r)T(t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec r)T(t) + V\Psi(\vec r)T(t) \implies$$

$$\begin{cases}i\hbar\frac{\partial}{\partial t}T(t) = ET(t) \\ -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec r) + V(\vec r)\Psi(\vec r) = E\Psi(\vec r)\end{cases} \implies$$

$$\psi(\vec r,t) = \Psi(\vec r)\cdot e^{-\frac{i}{\hbar}Et}$$

关于$T(t)$部分的性质

1. $\psi(\vec r,t) = \Psi(\vec r)\cdot A\cdot e^{-\frac{i}{\hbar}Et}$.
2. 概率密度ρ不随时间变化, $\frac{\partial\rho}{\partial t} = 0$, 概率流密度$\vec j = 0$

3. 任何不显含时的力学量平均值不随时间变化

4. 任何力学量的测量值的概率分布不随时间变化

关于$\Psi(\vec{r})$部分的性质

1. 若ψ是$\psi'' + \frac{2m}{\hbar^2}\left[E - V(\vec{r})\right]\psi = 0$的解, 则$\psi^*$也是该方程的解.

$$\begin{cases} \text{能级不简并, 意味着}\psi^* = c\psi, \implies \text{该}E\text{所对应的本征函数一定可取实函数} \\ \text{能级简并} \implies \text{可以找到一组完全基(基都是实函数)} \end{cases}$$

2. 若ψ是$\psi'' + \frac{2m}{\hbar^2}\left[E - V(\vec{r})\right]\psi = 0$的解, 则$\psi(-\vec{r})$也是该方程的解

$$\begin{cases} \text{能级不简并} \implies \text{该}E\text{对应的本征函数一定有确定宇称.} \\ \text{能级简并} \implies \text{可以找到一组完全基(基都有确定宇称)} \end{cases}$$

傅里叶变化

$$\psi(\vec{r}) = \frac{1}{\sqrt{2\pi}}\int \phi(\vec{p}) \cdot e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\mathrm{d}^3\vec{p}$$

$$\phi(\vec{p}) = \frac{1}{\sqrt{2\pi}}\int \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\mathrm{d}^3\vec{r}$$

一维无限深方势阱(一)

$$V(x) = \begin{cases} 0, & |x| < \frac{a}{2} \\ \infty, & |x| > \frac{a}{2} \end{cases}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$\psi_n = \begin{cases} \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x, n \neq 0, \text{偶数} \\ \sqrt{\frac{2}{a}}\cos\frac{n\pi}{a}x, n\text{奇数} \end{cases}$$

一维深方势阱(二)

$$V(x) = \begin{cases} 0, & 0 < x < a \\ \infty \end{cases}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$\psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x, n = 1, 2, 3\cdots$$

二维深方势阱

$$V(x,y) = \begin{cases} 0, & 0 < x < a, 0 < y < b \\ \infty \end{cases}$$

$$E_n = \frac{\pi^2\hbar^2}{2m}(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2})$$

$$\psi_{n_1,n_2} = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\sin\frac{n_1\pi}{a}x\sin\frac{n_2\pi}{b}y$$

三维深方势阱

$$V(x,y,z) = \begin{cases} 0, & 0<x<a, 0<y<b, 0<z<c \\ \infty \end{cases}$$

$$E_n = \frac{\pi^2\hbar^2}{2m}(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2})$$

$$\psi_{n_1,n_2} = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}\frac{2}{c}}\sin\frac{n_1\pi}{a}x\sin\frac{n_2\pi}{b}y\sin\frac{n_3\pi}{c}z$$

有限深方势阱

$$V(x) = \begin{cases} 0, & |x| < \frac{a}{2} \\ V_0, & |x| > \frac{a}{2} \end{cases}$$

1. $E < V_0$束缚态

$$\begin{cases} 阱外: \psi'' - \frac{2m}{\hbar^2}(V_0 - E)\psi = 0 \\ 阱内: \psi'' + \frac{2mE}{\hbar^2}\psi = 0 \end{cases}$$

$$\begin{cases} k_n \tan\frac{k_n a}{2} = \beta_n \\ (\frac{k_n a}{2})^2 + (\frac{k_n \beta_n}{2})^2 = \frac{ma^2}{2\hbar^2}V_0 \end{cases} \quad k_n^2 = \frac{2mE_n}{\hbar^2}, \beta_n^2 = \frac{2m}{\hbar}(V_0 - E_n), \quad n = 0, 2, 4\cdots$$

$$\begin{cases} k_n \cot\frac{k_n a}{2} = -\beta_n \\ (\frac{k_n a}{2})^2 + (\frac{k_n \beta_n}{2})^2 = \frac{ma^2}{2\hbar^2}V_0 \end{cases} \quad k_n^2 = \frac{2mE_n}{\hbar^2}, \beta_n^2 = \frac{2m}{\hbar}(V_0 - E_n), \quad n = 1, 2, 3\cdots$$

$$偶宇称\begin{cases} A\cos k_n x, & |x| < \frac{a}{2} \\ De^{-\beta_n x}, & x > \frac{a}{2} \\ De^{\beta_n x}, & x < -\frac{a}{2} \end{cases} \quad 奇宇称\begin{cases} A\sin k_n x, & |x| < \frac{a}{2} \\ De^{-\beta_n x}, & x > \frac{a}{2} \\ -De^{\beta_n x}, & x < -\frac{a}{2} \end{cases}$$

2. $E > V_0$非束缚态

$$\begin{cases} 阱外: \psi'' + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \\ 阱内: \psi'' + \frac{2mE}{\hbar^2}\psi = 0 \end{cases}$$

一维方势垒

1.

$$\begin{cases} \text{区域}I,III: \psi'' + \frac{2mE}{\hbar^2}\psi = 0 \\ \text{区域}II: \psi'' - \frac{2m}{\hbar^2}(V_0 - E)\psi = 0 \end{cases}$$

$$\begin{cases} \text{区域}I: \psi = e^{ik_n x} + Re^{-ik_n x} \quad k_n^2 = \frac{2mE_n}{\hbar^2} \\ \text{区域}II: \psi = C_1 e^{-i\kappa_n x} + C_2 e^{i\kappa_n x} \quad \kappa_n^2 = \frac{2m}{\hbar^2}(V_0 - E) \\ \text{区域}III: \psi = Se^{ikx} \quad k_n^2 = \frac{2mE_n}{\hbar^2} \end{cases}$$

2.

$\delta-$势阱

$$V(x) = -\gamma\delta(x) \begin{cases} -\gamma & x = 0 \\ 0, & x \neq 0 \end{cases}$$

$$-\frac{\hbar^2}{2m}\psi'' - \gamma\delta(x)\psi = E\psi \implies$$

$$\lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon} -\frac{\hbar^2}{2m}\psi''\mathrm{d}x - \lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon}\gamma\delta(x)\psi\mathrm{d}x = 0 \implies$$

$$\psi'(0+) - \psi'(0-) = \frac{2m\gamma}{\hbar^2}\psi(0)$$

1. 自由态, $\psi(0) = 0$
2. 束缚态, $\psi(0) = C_1$

$$\psi'' - \kappa\psi = 0, \quad \kappa^2 =$$

一维势垒
一维谐振子:

$$-\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}m\omega^2 x^2\psi = E\psi$$

令

$$\begin{cases} \xi = \alpha x = \sqrt{\frac{m\omega}{\hbar}}x \\ \lambda = \frac{2E}{\hbar\omega} \end{cases}$$

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

猜测解为$\psi = u(\xi)e^{-\frac{\xi^2}{2}}$, 将该解代入方程, 得到

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

这种形式的方程被称为Hermite方程, 用级数解方程得

$$C_{k+2} = \frac{2k + (1-\lambda)}{(k+2)(k+1)}C_k, k = 0, 1, 2, 3, \cdots$$

$$\begin{cases} C_2 = \frac{1-\lambda}{2}C_0 \\ C_3 = \frac{2+1-\lambda}{3\times 2}C_1 \\ C_4 = \frac{4+1-\lambda}{4\times 3}C_2 \\ \vdots \end{cases}$$

对于固定的$\lambda = \frac{2E}{\hbar\omega}$, 如果没有$k$, 使得$2k+1-\lambda=0$, 这个级数将不会截断.

只有当存在k, 使得$2k+1-\lambda=0$时, 这个级数才会截断, 所以可以取的能量值为

$$E_n = \frac{(2n+1)\hbar\omega}{2}$$

解为

$$\psi_n = N_n e^{-\frac{1}{2}\alpha^2x^2}H_n(\alpha x), \quad \alpha = \sqrt{\frac{m\omega}{\hbar}}, \quad \xi = \alpha x$$

$$N_n = \sqrt{\frac{\alpha}{\sqrt{\pi}\cdot 2^n\cdot n!}}$$

$$\psi_{n_x,n_y,n_z} = N_{n_x}\cdot N_{n_y}\cdot N_{n_z}\cdot H_{n_x}(\alpha x)H_{n_y}(\alpha y)\cdot H_{n_z}(\alpha z)e^{-\frac{1}{2}\alpha^2(x^2+y^2+z^2)}$$

$$E_{n_x,n_y,n_z} = (n_x+n_y+n_z+\frac{3}{2})\hbar\omega$$

厄密特多项式的一些小性质.

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

2. $$H_{2n}(\xi) - 2\xi H_n + 2nH_{n-1} = 0$$

3. $$\frac{\mathrm{d}H_n(\xi)}{\mathrm{d}\xi} = 2nH_{n-1}(\xi)$$

4. $$\int_{-\infty}^{\infty} H_m(\xi)H_n(\xi)e^{-\xi^2}\mathrm{d}\xi = \sqrt{pi}\cdot 2^n\cdot n!\cdot\delta_{mn}$$

5. $$H_n(\xi) = (-1)^n\cdot e^{\xi^2}\cdot\frac{\mathrm{d}^n}{\mathrm{d}\xi^n}(e^{-\xi^2})$$

$$H_n(-\xi) = (-1)^n\cdot H_n(\xi)$$

6.
$$\begin{cases} H_0(\xi)=1 \\ H_1(\xi)=2\xi \\ H_2(\xi)=4\xi^2-2 \\ H_3(\xi)=8\xi^3-12\xi \end{cases}$$

力学量算符的引入: 在求平均值的意义下, 力学量用算符来表示.

由于力学量算符的运算规则与矩阵的运算相同, 引入Hilbert 空间. (debatable)

实验可测的力学量对应的算符都是厄密算符.

一个算符$\hat{A}$的厄密共轭算符$\hat{A}^\dagger$满足$(\psi,\hat{A}^\dagger\psi)=(\hat{A}\psi,\psi) \iff (\psi,\hat{A}^\dagger\varphi)=(\hat{A}\psi,\varphi)$ 任何算符都可求其厄密共轭, 但是不是每一个算符都是厄密算符

一个算符$\hat{A}$是厄密算符的定义: 满足$\hat{A}^\dagger=\hat{A}$.

厄密算符的性质

1. 定义也是性质
$$\hat{A}^\dagger=\hat{A}$$

2. 在任何量子态下, 厄密算符的平均值必为实数.
$$\begin{aligned}\bar{\hat{A}}&=(\psi,\hat{A}\psi)=(\hat{A}^\dagger\psi,\psi)\\&=(\hat{A}\psi,\psi)\\&=(\psi,\hat{A}\psi)^*\end{aligned} \tag{1}$$
$$\implies \bar{\hat{A}}\text{是实数}$$

3. 在任何量子态下, 平均值都为实数的算符必为厄密算符.
$$(\psi,\hat{A}\psi)=(\psi,\hat{A}\psi)^* \implies (\hat{A}\psi,\psi)=(\psi,\hat{A}\psi)$$
$$\text{由算符的厄密共轭的定义}:(\hat{A}\psi,\psi)=(\psi,\hat{A}^\dagger\psi)$$
两相比较得$\hat{A}^\dagger=\hat{A}$

4. 本征函数正交归一完备
$$(\psi_m,\hat{A}\psi_n)=(\hat{A}^\dagger\psi_m,\psi_n)=(\hat{A}\psi_m,\psi_n)$$
$$A_n(\psi_m,\psi_n)=A_m^*(\psi_m,\psi_n)=A_m(\psi_m,\psi_n)$$
$$(A_n-A_m)(\psi_m,\psi_n)=0$$

算符对易的物理意义:

1. 若A,B有一组完备的共同本征矢, 则两个算符对易
2. 若两个算符对易, 有共同的完备的本征函数

力学量完全集

1. 定义: 为完全确定状态所需要的一组两两对易的力学量算符的最小集合.
2. 性质:
   (a) 其中力学量的个数往往等于体系的自由度
   (b) 其中所有的力学量具有共同的完备的本征函数

$$\hat{x},\hat{y},\hat{z}\text{两两对易}$$
$$\hat{p}_x,\hat{p}_y,\hat{p}_z\text{两两对易}$$
$$[\hat{x}_\alpha,\hat{p}_\beta]=i\hbar\delta_{\alpha\beta}$$

$$[A,BC]=[A,B]C+B[A,C]$$

$$[\hat{x},\hat{p}_x^n]=i\hbar n\cdot\hat{p}_x^{n-1}$$
$$[\hat{p}_x,\hat{x}^n]=-i\hbar\cdot n\cdot\hat{x}^{n-1}$$
$$[\hat{p}_x,f(\hat{x})]=-i\hbar\frac{\mathrm{d}f}{\mathrm{d}x}$$
$$[l_\alpha,l_\beta]=i\hbar\varepsilon_{\alpha\beta\gamma}\hat{l}_\gamma$$
$$[\hat{x}_\alpha,\hat{l}_\beta]=i\hbar\varepsilon_{\alpha\beta\gamma}\hat{x}_\gamma$$
$$[\hat{p}_\alpha,\hat{l}_\beta]=i\hbar\varepsilon_{\alpha\beta\gamma}\hat{p}_\gamma$$

$$\begin{cases}\hat{l}_x=y\hat{p}_x-z\hat{p}_y=i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta}+\cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\\\hat{l}_y=\hat{z}\hat{p}_x-\hat{x}\hat{p}_z=i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta}+\cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\\\hat{l}_z=\hat{x}\hat{p}_y-\hat{y}\hat{p}_x=-i\hbar\frac{\partial}{\partial\varphi}\end{cases}\quad\text{下标, 两个不是下标, xyz, yzx, zxy}$$

$$\left[\hat{l}_z,\hat{\vec{l}}^2=\hat{l}_x^2+\hat{l}_y^2+\hat{l}_z^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\right]=0$$

几个常见的力学量完全集

1. $\{\hat{p}_x,\hat{p}_y,\hat{p}_z\}$

$$\hat{p}\psi_p(\vec{r})=p\psi_p(\vec{r})\implies\psi_{p_x}(x)=A_x\cdot e^{-\frac{i}{\hbar}p_x\cdot x}$$

这三个力学量算符的共同本征函数为

$$\psi_p(\vec{r})=A_x\cdot A_y\cdot A_z\cdot e^{-\frac{i}{\hbar}(\vec{p}\cdot\vec{r})}$$

归一化该波函数,

$$
\begin{aligned}
&\int_{-\infty}^{+\infty} \psi_{p_x}(x)^* \cdot \psi_{p'_x}(x)\mathrm{d}x = \delta(p_x - p'_x) \\
\Longrightarrow &\int_{-\infty}^{+\infty} |A_x|^2 e^{-\frac{i}{\hbar}(p_x - p'_x)\cdot x}\mathrm{d}x = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i(p_x-p'_x)\cdot x}\mathrm{d}x \\
\Longrightarrow &\int_{-\infty}^{+\infty} |A_x|^2 e^{-\frac{i}{\hbar}(p_x - p'_x)\cdot x}\mathrm{d}x = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(p_x-p'_x)\cdot x}\mathrm{d}\frac{x}{\hbar} \\
\Longrightarrow &\int_{-\infty}^{+\infty} |A_x|^2 e^{-\frac{i}{\hbar}(p_x - p'_x)\cdot x}\mathrm{d}x = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(p_x-p'_x)\cdot x}\mathrm{d}x \\
\Longrightarrow &A_x = A_y = A_z = \frac{1}{\sqrt{2\pi\hbar}}
\end{aligned}
$$

2. $\{\hat{x}, \hat{y}, \hat{z}\}$.

$$\hat{x}\psi_r(\vec{r}) = r\psi_r(\vec{r}) \implies \psi_x(x) = \delta(x - x_0)$$

共同的本征波函数

$$\psi_r(\vec{r}) = \delta(x-x_0)\delta(y-y_0)\delta(z-z_0)$$

3. $\left\{\hat{l}_z, \hat{\vec{l}}^2\right\}$

$$\begin{cases} \hat{l}_z\psi = l_z\psi \\ \hat{l}_z = -i\hbar\frac{\partial}{\partial\varphi}\psi \end{cases} \implies \psi = Ce^{\frac{i}{\hbar}l_z\varphi}$$

$$\begin{cases} \text{周期性:}\psi(\varphi) = \psi(\varphi+2\pi) \implies l_z = m\hbar \quad m = 0,1,2\cdots \\ \text{归一化:}C = \frac{1}{\sqrt{2\pi}} \end{cases} \implies \psi = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \quad m = 0,1,2\cdots$$

$$\hat{\vec{l}}^2\psi = \vec{l}^2\psi$$

设$\psi = Y(\theta,\varphi)$, 特征值为$\lambda\hbar^2$.

$$\left[\frac{1}{\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = -\lambda Y(\theta,\varphi)$$

分离变量解这个方程, 设$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$

$$\frac{\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi)}{\Phi(\varphi)} = \frac{\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\Theta) + \lambda^2\sin^2\theta}{\Theta(\theta)}$$

由于我们的目的是找到共同本征波函数, 所以与一般的分离变量不同的是, 这里不随意设一个常数, 而是把由$\hat{l}_z$算出来的波函数带入左半边求常数, 得常数为上面的m^2.

所以右半边为

$$\frac{\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\Theta)+\lambda^2\sin^2\theta}{\Theta(\theta)}=m^2$$

$$\iff \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\Theta\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

解这个方程, 要花稍微多一点的功夫

(a) 变量代换$x=\cos\theta$

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

该方程被称为asscociated Legendre equation.

(b) 这个方程有两个奇点$x=\pm1$

(c) 为解这个方程, 首先讨论$m=0$的情况, 即

$$(1-x^2)\frac{\mathrm{d}^2\Theta}{\mathrm{d}x^2}-2x\frac{\mathrm{d}\Theta}{\mathrm{d}x}+\lambda\Theta=0$$

该方程被称为Legendre equation.
用级数来求这个方程的解,得到

$$C_{k+2}=\frac{k(k+1)-\lambda}{(k+1)(k+2)}C_k,\quad k=0,1,2\cdots$$

$$k\to\infty,\quad \frac{C_{k+2}}{C_k}=$$

反正最终得到关联勒让德方程的解

$$Y_{lm}(\theta,\varphi)=N_{lm}\cdot P_l^{|m|}(\cos\theta)\cdot e^{im\varphi}$$

$$N_m=\sqrt{\frac{(l-|m|)!(2l+1)}{4\pi\cdot(l+|m|)!}}$$

$$P_l^{|m|}(\xi)=(1-\xi^2)^{\frac{|m|}{2}}\cdot\frac{\mathrm{d}^{|m|}}{\mathrm{d}\xi^{|m|}}P_l(\xi)\quad P_l(\xi)=\frac{1}{2^l\cdot l!}\frac{\mathrm{d}^l}{\mathrm{d}\xi^l}(\xi^2-1)^l$$

$$P_l^{-|m|}(\xi)=(-1)^|m|\cdot\frac{(l-|m|)!}{(l+|m|)!}P_l^{|m|}(\xi)$$

$$Y_{0,0}=\frac{1}{\sqrt{4\pi}}$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}}\sin\theta\cdot e^{i\varphi} \quad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \quad Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\cdot e^{-i\varphi}$$

$$Y_{2,2} = -\sqrt{\frac{15}{32\pi}}\sin^{\theta}\cdot e^{2i\varphi} \quad Y_{2,1} = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cdot e^{i\varphi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

$$Y_{2,-2} = \sqrt{\frac{15}{32\pi}}\sin^{\theta}\cdot e^{-2i\varphi} \quad Y_{2,-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cdot e^{-i\varphi}$$

$$[\hat{F},\hat{G}] = i\hat{k} \implies \overline{(\hat{\Delta F})^2}\cdot\overline{(\hat{\Delta G})^2} \geq \frac{\bar{\hat{k}}^2}{4}$$

$$[\hat{x},\hat{p}_x] = i\hbar \implies \overline{(\hat{\Delta x})^2}\cdot\overline{(\hat{\Delta p_x})^2} \geq \frac{\hbar^2}{4}$$

$$[\hat{l}_x,\hat{l}_y] = i\hbar l_z \implies \overline{(\hat{\Delta l_x})^2}\cdot\overline{(\hat{\Delta l_y})^2} \geq \frac{\hbar^2}{4}\bar{\hat{l}_z}^2$$

薛定谔表象下: 力学量平均值的时间演化来自ψ

$$\frac{\mathrm{d}\langle\hat{A}\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle$$

$$\begin{aligned}
\frac{\mathrm{d}\langle\hat{A}\rangle}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}(\psi,\hat{A}\psi) \\
&= (\frac{\mathrm{d}}{\mathrm{d}t}\psi,\hat{A}\psi) + (\psi,\hat{A}\frac{\mathrm{d}}{\mathrm{d}t}\psi) \\
&= (\frac{\hat{H}}{i\hbar}\psi,\hat{A}\psi) + (\psi,\hat{A}\cdot\frac{\hat{H}}{i\hbar}\psi) \\
&= -\frac{1}{i\hbar}(\psi,\hat{H}\hat{A}\psi) + \frac{1}{i\hbar}(\psi,\hat{A}\hat{H}\psi) \\
&= \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle
\end{aligned}$$

海森堡表象下: 力学量平均值随时间的演化来自算符.

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{1}{i\hbar}[\hat{A},\hat{H}]$$

$$
\begin{aligned}
\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}(\hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{U}) \qquad \text{其中}\hat{U} = e^{-\frac{i}{\hbar}\hat{H}_0 \cdot t} \\
&= \frac{i}{\hbar}\hat{H}_0 \cdot \hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{U} - \frac{i}{\hbar}\hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{H}_0 \cdot \hat{U} \\
&= \frac{i}{\hbar}\hat{U}^\dagger \cdot \hat{H}_0 \cdot \hat{A}_0 \cdot \hat{U} - \frac{i}{\hbar}\hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{H}_0 \cdot \hat{U} \\
&= \frac{i}{\hbar}(\hat{U}^\dagger \cdot \hat{H}_0 \cdot \hat{U}) \cdot (\hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{U}) - \frac{i}{\hbar}(\hat{U}^\dagger \cdot \hat{A}_0 \cdot \hat{U}) \cdot (\hat{U}^\dagger \cdot \hat{H}_0 \cdot \hat{U}) \\
&= \frac{i}{\hbar}\hat{H} \cdot \hat{A} - \frac{i}{\hbar}\hat{A} \cdot \hat{H} \\
&= \frac{1}{i\hbar}[\hat{A}, \hat{H}]
\end{aligned}
$$

守恒量: 任意量子态下的平均值和观测值的概率不随时间改变. $\hat{A}$不显含时, 且$[\hat{A}, \hat{H}] = 0$

特点:

1. 系统在演化过程中, 守恒量的本征态和概率分布不变
2. 描述守恒量的量子数为好量子数
3. 若体系存在两个或两个以上的守恒量, 且彼此不对易, 则一般体系存在能级简并.

几个守恒及其对应的不变性

1. 空间平移不变性与动量守恒

   首先求平移算符, 由于平移算符要满足式子$D(\delta x)\psi(x) = \psi(x + \delta x)$.将右边泰勒展开, 得到平移算符的表达式为

   $$D(\delta x) = e^{\frac{i}{\hbar}\delta x \cdot p_x}, \quad D(\delta\vec{r}) = e^{\frac{i}{\hbar}\delta\vec{r} \cdot \vec{p}}$$

   在讨论平移不变性, 满足平移不变性的体系要满足$D(\delta\vec{r})\psi(\vec{r}) = C \cdot \psi(\vec{r})$

   $$\frac{i}{\hbar}\frac{\partial}{\partial t}\psi = \hat{H}\psi \implies \frac{i}{\hbar}\frac{\partial}{\partial t}(\hat{D}\psi) = \hat{H}(\hat{D})\psi \implies$$

   而本身将方程$\frac{i}{\hbar}\frac{\partial}{\partial t}\psi = \hat{H}\psi$同左乘算符$\hat{D}$得到

   $$\hat{D}\frac{i}{\hbar}\frac{\partial}{\partial t}\psi = \hat{D}\hat{H}\psi$$

   得到$[\hat{H}, \hat{D}] = 0$

   $$[\hat{H}, \hat{D}] = [\hat{H}, e^{\frac{i}{\hbar}\delta\vec{r} \cdot \vec{p}}] \implies [\hat{H}, \hat{P}] = 0$$

2. 空间转动不变性与角动量守恒

先讨论z轴旋转, 求z轴旋转算符的表达式, z轴旋转算符要满足$\hat{R}_z(\delta\varphi)\psi(r,\theta,\varphi) = \psi(r,\theta,\varphi+\delta\varphi)$, 推出$z$轴旋转算符的表达式为

$$\hat{R}_z(\delta\varphi) = e^{\frac{i}{\hbar}\delta\varphi\cdot l_z}$$

$$\hat{R}(\vec{n},\delta\varphi) = e^{\frac{i}{\hbar}\delta\varphi\cdot(\vec{l}\cdot\vec{n})}$$

求出表达式后, 空间旋转不变性要求体系有$[\hat{R}(\vec{n},\delta\varphi),\hat{H}] = 0$, 推出$[\hat{H},\hat{l}] = 0$, 角动量守恒.

3. 时间平移不变性与能量守恒

   时间平移算符即演化算符: $\hat{U}(\delta t) = e^{-\frac{i}{\hbar}\delta t\hat{H}}$

   满足时间平移的体系要满足$[\hat{U}(t),\hat{H}] = 0$, 推出$[\hat{H},\hat{H}] = 0$

4. 空间反射不变性与全同粒子波函数的交换对称性

   空间反射算符为$\hat{P}_{ij}$, 其满足$\hat{P}_{ij}\psi(\vec{r}) = \psi(-\vec{r})$.

   空间反射不变性要求体系满足$[\hat{P}_{ij},\hat{H}] = 0$, 推出交换对称性守恒.

投影算符: $\{|Q_n\rangle\langle Q_n|\}$, 作用到任一态矢$|\psi\rangle$. 相当于把$|\psi\rangle$投影到一个基矢$|Q_n\rangle$上.

$$|\psi\rangle = \sum_n |Q_n\rangle\left(\langle Q_n|\psi\rangle\right)$$

$$|\psi\rangle = \begin{pmatrix} \langle Q_1|\psi\rangle \\ \langle Q_2|\psi\rangle \\ \langle Q_3|\psi\rangle \\ \vdots \\ \langle Q_n|\psi\rangle \end{pmatrix} = \psi(\hat{F}) \quad \hat{F}\text{的基矢组为}\{|Q_n\rangle\}$$

矩阵元:

1. $\hat{L}$在$\hat{F}$的表象下, $L_{kn} = \langle Q_k|\hat{L}|Q_n\rangle$.
2. $\hat{F}$在$\hat{F}$表象下, $F_{kn} = \langle Q_k|\hat{F}|Q_n\rangle$. 将会对角阵.
3. 若$[\hat{L},\hat{F}] = 0$, 则$L_{kn} = \langle Q_k|\hat{L}|Q_n\rangle$将是对角阵.

平均值

1. 无表象

$$\bar{L} = \langle\psi|\hat{L}|\psi\rangle$$

2. 有表象

$$\begin{aligned}\bar{L} &= \langle\psi|\left(\sum_k |Q_k\rangle\langle Q_k|\right)\hat{L}\left(\sum_n |Q_n\rangle\langle Q_n|\right)|\psi\rangle \\ &= \sum_k\sum_n \left(\langle\psi|Q_k\rangle\right)\langle Q_k|\hat{L}|Q_n\rangle\left(\langle Q_n|\psi\rangle\right)\end{aligned}$$

本征方程:

1. 无表象
$$\hat{L}\,|\psi\rangle = \lambda\,|\psi\rangle$$

2. 有表象
$$\hat{L}\left(\sum_n |Q_n\rangle\langle Q_n|\right)|\psi\rangle = \lambda\left(\sum_n |Q_n\rangle\langle Q_n|\right)|\psi\rangle$$

上述方程左乘$\langle Q_k| \quad k=1,2,\cdots$,得到一系列方程

$$\sum_n \langle Q_k|\,\hat{L}\,|Q_n\rangle\langle Q_n|\psi\rangle = \lambda\sum_n \langle Q_k|Q_n\rangle\langle Q_n|\psi\rangle = \lambda\langle Q_k|\psi\rangle \quad k=1,2,3\cdots$$

即
$$\sum_n \langle Q_k|\,\hat{L}\,|Q_n\rangle\langle Q_n|\psi\rangle = \lambda\langle Q_k|\psi\rangle \quad k=1,2,3\cdots$$

定态薛定谔方程:

1. 无表象
$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}\,|\psi\rangle$$

2. 有表象
$$i\hbar\frac{\partial}{\partial t}\left(\sum_n |Q_n\rangle\langle Q_n|\right)|\psi\rangle = \hat{H}\left(\sum_n |Q_n\rangle\langle Q_n|\right)|\psi\rangle$$

上述方程左乘$\langle Q_k| \quad k=1,2,\cdots$,得到一系列方程

$$i\hbar\frac{\partial}{\partial t}\sum_n \langle Q_k|Q_n\rangle\langle Q_n|\psi\rangle = i\hbar\frac{\partial}{\partial t}\langle Q_k|\psi\rangle = \sum_n \langle Q_k|\,\hat{H}\,|Q_n\rangle\langle Q_n|\psi\rangle \quad k=1,2,3\cdots$$

即
$$i\hbar\frac{\partial}{\partial t}\langle Q_k|\psi\rangle = \sum_n \langle Q_k|\,\hat{H}\,|Q_n\rangle\langle Q_n|\psi\rangle \quad k=1,2,3\cdots$$

表象变换: 用幺正变换矩阵
幺正变换矩阵的性质:

1. 幺正性: $S^\dagger S = I$保内积
$$\psi^\dagger(\hat{F})\psi(\hat{F}) = \psi^\dagger(\hat{F})(S^\dagger S)\psi(\hat{F}) = \left(S\psi(\hat{F})\right)^\dagger\left(S\psi(\hat{F})\right) = \psi^\dagger(\hat{F}')\psi(\hat{F}')$$

即是
$$\psi^\dagger(\hat{F})\psi(\hat{F}) = \psi^\dagger(\hat{F}')\psi(\hat{F}')$$

2. 幺正变换不改变算符的本征值

$$
\begin{aligned}
\hat{L}\left|\psi\right\rangle = \lambda\left|\psi\right\rangle \implies \\
S\hat{L}S^{\dagger}\left|\psi\right\rangle = \lambda S\left|\psi\right\rangle \implies \\
\hat{L}'(S\left|\psi\right\rangle) = \lambda(S\left|\psi\right\rangle)
\end{aligned}
$$

3. 幺正变换不改变矩阵的迹

$$
\mathrm{Tr}(\hat{F}) = \sum(\text{本征值})
$$

4. 幺正变换不改变厄密矩阵的厄密性

5. 幺正变换的物理意义: 概率守恒

态矢作表象变换
已知两个表象$\hat{F} \sim \{Q_n\}$和$\hat{F}' \sim \{P_n\}$

$$
S_{\alpha\beta} = \langle P_\alpha | Q_\beta \rangle
$$

$$
\begin{aligned}
S_{\alpha\beta} &= \langle \text{后来表象的本征矢} | \text{开始表象的本征矢} \rangle \\
\left|\text{后来表象下的态矢}\right\rangle &= S\left|\text{开始表象的态矢}\right\rangle
\end{aligned}
$$

力学量作表象变换:
已知两个表象$\hat{F} \sim \{Q_n\}, \hat{F}' \sim \{P_n\}$. 可求

$$
S_{\alpha\beta} = \langle \text{后来表象的本征矢} | \text{开始表象的本征矢} \rangle
$$

$$
\begin{aligned}
[\text{后来表象下的矩阵}] &= S[\text{开始表象下的矩阵}]S^{\dagger} \\
[\text{开始表象下的矩阵}] &= S^{\dagger}[\text{后来表象下的矩阵}]S
\end{aligned}
$$

求坐标表象下$\hat{p}$的表达式$\langle x|\hat{p}$:

$$
\begin{aligned}
\langle x|\hat{p}\left|p\right\rangle &= p\langle x|p\rangle = p\psi_p(x) \\
&= p\left(\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p\cdot x}\right) \\
&= \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p\cdot x}\right) \\
&= \left(-i\hbar\frac{\partial}{\partial x}\right)(\langle x|p\rangle)
\end{aligned}
$$

随后将本征矢$|p\rangle$换成普通矢$|\psi\rangle$几乎一样的步骤

$$\begin{aligned}\langle x|\,\hat{p}\,|\psi\rangle &= \langle x|\,\hat{p}\int \mathrm{d}p\,|p\rangle\langle p|\psi\rangle \\ &= \int \mathrm{d}p\langle x|\,\hat{p}\,|p\rangle\langle p|\psi\rangle \\ &= \int \mathrm{d}p(-i\hbar\frac{\partial}{\partial x})\langle x|p\rangle\langle p|\psi\rangle \\ &= (-i\hbar\frac{\partial}{\partial x})\int \mathrm{d}p\langle x|p\rangle\langle p|\psi\rangle \\ &= (-i\hbar\frac{\partial}{\partial x})\langle x|\int \mathrm{d}p\,|p\rangle\langle p|\,|\psi\rangle \\ &= -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle\end{aligned}$$

对比可得$\langle x|\,\hat{p} = -i\hbar\frac{\partial}{\partial x}\langle x|$.
求动量表象下$\hat{x}$的表达式$\langle p|\,\hat{x}$:

$$\begin{aligned}\langle p|\,\hat{x}\,|x\rangle &= x\langle\rangle|xp \\ &= x\psi_x(p) \\ &= x(\frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}p\cdot x}\rangle \\ &= i\hbar\frac{\partial}{\partial p}\psi_x(p) \\ &= i\hbar\frac{\partial}{\partial p}\langle p|x\rangle\end{aligned}$$

随后将本征矢$|x\rangle$换成$|\psi\rangle$几乎一样的步骤:

$$\begin{aligned}\langle p|\,\hat{x}\,|\psi\rangle &= \langle p|\,\hat{x}\int \mathrm{d}x\,|x\rangle\langle x|\,|\psi\rangle \\ &= \int \mathrm{d}x\langle p|\,\hat{x}\,|x\rangle\langle x|\,|p\rangle \\ &= \int \mathrm{d}x\left(i\hbar\frac{\partial}{\partial p}\langle p|\,|x\rangle\right)\langle x|\,|\psi\rangle \\ &= i\hbar\frac{\partial}{\partial p}\langle p|\int \mathrm{d}x\,|x\rangle\langle x|\,|\psi\rangle \\ &= i\hbar\frac{\partial}{\partial p}\langle p|\psi\rangle\end{aligned}$$

对比得到$\langle p|\,\hat{x} = i\hbar\frac{\partial}{\partial p}\langle p|$
谐振子的升降算符法:

$$\hat{a}_- = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\omega\hbar}}\hat{p}_x$$

$$\hat{a}_+ = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\omega\hbar}}\hat{p}_x$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)$$

$$\hat{p}_x = i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a}_+ - \hat{a}_-)$$

$$\hat{H} = (\hat{a}_+\hat{a}_- + \frac{1}{2})\hbar\omega = (\hat{a}_-\hat{a}_+ - \frac{1}{2})\hbar\omega$$

$$[\hat{a}_-, \hat{a}_+] = 1$$

$$[\hat{a}_-, \hat{H}] = \hbar\omega\hat{a}$$

$$[\hat{a}_+, \hat{H}] = -\hbar\omega\hat{a}_+$$

$$\hat{a}_- \left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle$$
$$\hat{a}_+ \left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle$$

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

$$\hat{p}\left|n\right\rangle = i\sqrt{\frac{m\omega\hbar}{2}}\left(\sqrt{n+1}\left|n+1\right\rangle - \sqrt{n}\left|n-1\right\rangle\right)$$

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

$$\hat{x}^3\left|n\right\rangle = \left(\sqrt{\frac{\hbar}{2m\omega}}\right)^3\Big(\sqrt{(n+3)(n+2)(n+1)}\left|n+3\right\rangle + 3(n+1)\sqrt{n+1}\left|n+1\right\rangle + 2n\sqrt{n}\left|n-1\right\rangle + \sqrt{n(n-1)(n-2)}\left|n-3\right\rangle\Big)$$

$$\hat{p}^2\left|n\right\rangle = \left(i\sqrt{\frac{m\omega\hbar}{2}}\right)^2\Big(\sqrt{(n+2)(n+1)}\left|n+2\right\rangle - (2n+1)\left|n\right\rangle + \sqrt{n(n-1)}\left|n-2\right\rangle\Big)$$

$$\hat{p}^3 |n\rangle = \left(i\sqrt{\frac{m\omega\hbar}{2}}\right)^3 \Big(\sqrt{(n+3)(n+2)(n+1)}\,|n+3\rangle$$
$$- 3(n+1)\sqrt{n+1}\,|n+1\rangle + 3n\sqrt{n}\,|n-1\rangle - \sqrt{n(n-1)(n-2)}\,|n-3\rangle\Big)$$

中心力场: 中心力场对应着特殊的$\hat{H}$:

$$[\hat{H},\hat{H}]=0,\quad [\hat{\vec{l}}^2,\hat{H}]=0\quad [\hat{l}_x,\hat{H}]=0,[\hat{l}_y,\hat{H}]=0,\quad [\hat{l}_z,\hat{H}]=0$$

解方程

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi \implies$$
$$\nabla_r^2\psi + \frac{2m}{\hbar^2}(E-V(r))\psi = -\nabla_{\theta,\varphi}^2\psi$$
$$\frac{\{\nabla_r^2 + \frac{2m}{\hbar^2}(E-V(r))\}R(r)}{R(r)} = \frac{-\nabla_{\theta,\varphi}^2 Y(\theta,\varphi)}{Y(\theta,\varphi)} \implies$$
$$\frac{\{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr^2}{\hbar^2}[E-V(r)]\}R}{R} = l(l+1)$$

解这个方程, 首先换元$\chi = r\cdot R(r)$.

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2m}{\hbar^2}\left\{E - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right\}\chi = 0$$

中心场

$$V(r) = \begin{cases} 0, & 0<r<a \\ \infty, & r>a \end{cases}$$

$0<r<a$时, 方程为$V=0$

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2m}{\hbar^2}\left[E - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]\chi = 0$$

角向波函数

$$Y_{l,m_l}(\theta,\varphi) = C_{l,m_l}P_l^{m_l}(\cos\theta)e^{im\varphi}$$

where

$$P_l^{m_l}(\xi) = (1-\xi^2)^{\frac{|m_l|}{2}}\frac{\mathrm{d}^{|m_l|}}{\mathrm{d}\xi^{|m_l|}}P_l(\xi)$$
$$P_l(\xi) = \frac{1}{2^l\cdot l!}\frac{\mathrm{d}^l}{\mathrm{d}\xi^l}(\xi^2-1)^l$$
$$P_l^{-|m_l|} = (-1)^m\frac{(l-|m_l|)!}{(l+|m_l|)!}P_l^{|m_l|}(\xi)$$

$$C_{l,m_l} = \sqrt{\frac{(l-|m_l|)!(2l+1)}{(l+|m_l|)!4\pi}}$$

径向波函数

$$R_{n,l}(r) = N_{n,l}e^{-\frac{r}{2na_0}}\left(\frac{2r}{na_0}\right)^l F(-n+l+1, 2l+2, \frac{2r}{na_0})$$

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar n^2}$$

径向几率分布:

$$W_{n,l,m_l}(r)\mathrm{d}r = \int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}|R_{n,l}(r)Y_{l,m_l}(\theta,\varphi)|^2 r^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi$$

角向几率分布

$$W_{n,l,m}(\theta,\varphi)\mathrm{d}\Omega = |Y_{l,m}(\theta,\varphi)|^2\mathrm{d}\Omega\int_0^{\infty}|R_{n,l}(r)|^2 r^2\mathrm{d}r$$

电流分布和磁矩

$$j_r = -\frac{i\hbar}{2m_e}e\left(\psi^*\cdot\frac{\partial}{\partial r}\psi - \psi\cdot\frac{\partial}{\partial r}\psi^*\right) = 0$$

$$\begin{aligned}
j_\varphi &= -\frac{i\hbar}{2m_e}e\left(\psi^*\cdot\frac{1}{r\cdot\sin\theta}\frac{\partial}{\partial\varphi}\psi - \psi\cdot\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}\psi^*\right)\\
&= -\frac{ie\hbar}{2m_e}\cdot\frac{1}{r\sin\theta}\cdot(2im_l)|\psi_{n,l,m_l}|^2\\
&= -\frac{e\hbar m_l}{m_e\cdot r\sin\theta}
\end{aligned}$$

$$j_\theta = -\frac{i\hbar}{2m_e}e\left(\psi^*\frac{1}{r}\frac{\partial}{\partial\theta}\psi - \psi\frac{1}{r}\frac{\partial}{\partial\theta}\psi^*\right) = 0$$

$$a_0 = \frac{\hbar^2}{\mu_H e^2} \approx 0.529^{-10}\mathrm{m}$$

$$\mathrm{d}\mu_z = \frac{1}{c}S\mathrm{d}I = \frac{1}{c}\cdot\pi r^2\cdot\sin^2\theta\mathrm{d}I$$

$$\begin{aligned}
\mu_z &= \frac{1}{c}\int\pi r^2\sin^2\theta\cdot j_\varphi\mathrm{d}\sigma\\
&= -\frac{\hbar m_l e}{2c\mu_0}\int|\psi_{n,l,m_l}|^2\cdot 2\pi r\sin\theta\mathrm{d}\sigma\\
&= -\frac{\hbar m_l e}{2c\mu_0}\int|\psi_{n,l,m_l}|^2\cdot 2\pi r\sin\theta\cdot r\cdot\mathrm{d}\theta\mathrm{d}r\\
&= -\frac{\hbar m_l e}{2c\mu_0} = -\mu_B m_l \quad \mu_B = \frac{\hbar|e|}{2c\mu_0}
\end{aligned}$$

角动量的定义: $\hat{L}\times\hat{L}=i\hbar\hat{L}$(隐含性质 $[\hat{l}_\alpha,\hat{\vec{L}}^{\,2}]=0$)
升降算符:

$$\hat{J}_+=\hat{J}_x+i\hat{J}_y\quad \hat{J}_-=\hat{J}_x-i\hat{J}_y$$

$$\hat{J}_x=\frac{1}{2}(\hat{J}_++\hat{J}_-)\quad \hat{J}_y=\frac{i}{2}(\hat{J}_--\hat{J}_+)$$

矩阵表示

$$\langle j',m'|\,\hat{J}_z\,|j,m\rangle=m\hbar\delta_{j,j'}\delta_{m,m'}$$

$$\langle j',m'|\,\hat{J}^{\,2}\,|j,m\rangle=j(j+1)\hbar^2\delta_{j,j'}\delta_{m,m'}$$

$$\begin{aligned}\hat{J}_+\,|j,m\rangle&=\hbar\sqrt{(j+m+1)(j-m)}\,|j,m+1\rangle\\&=\hbar\sqrt{j(j+1)-m(m+1)}\,|j,m+1\rangle\end{aligned}$$

$$\begin{aligned}\hat{J}_-\,|j,m\rangle&=\hbar\sqrt{(j-m+1)(j+m)}\,|j,m-1\rangle\\&=\hbar\sqrt{j(j+1)-m(m-1)}\end{aligned}$$

$$\begin{aligned}\hat{J}_x\,|j,m\rangle=\frac{\hbar}{2}\Big(&\sqrt{(j+m+1)(j-m)}\,|j,m+1\rangle\\&+\sqrt{(j-m+1)(j+m)}\,|j,m-1\rangle\Big)\end{aligned}$$

$$\begin{aligned}\hat{J}_y\,|j,m\rangle=\frac{i\hbar}{2}\Big(&-\sqrt{(j+m+1)(j-m)}\,|j,m+1\rangle\\&+\sqrt{(j-m+1)(j+m)}\,|j,m-1\rangle\Big)\end{aligned}$$

$$[\hat{J}^2,f(\hat{J})]=0$$

$$[\hat{J}_z,\hat{J}_-]=-\hbar\hat{J}_-\quad [\hat{J}_z,\hat{J}_+]=\hbar\hat{J}_+$$

$$\hat{J}^2-\hat{J}_z+\hbar\hat{J}_z=\hat{J}_+\hat{J}_-\quad \hat{J}^2-\hat{J}_z^2-\hbar\hat{J}_Z=\hat{J}_-\hat{J}_+$$

$$\begin{aligned}\hat{J}_x^2\,|j,m\rangle=\left(\frac{\hbar}{2}\right)^2&\sqrt{(j+m+2)(j+m+1)(j-m)(j-m-1)}\,|j,m+2\rangle\\&+2(j^2-m^2+j)\,|j,m\rangle\\&+\sqrt{(j-m+2)(j-m+1)(j+m)(j+m-1)}\,|j,m-2\rangle\end{aligned}$$

$$
\begin{aligned}
\hat{J}_y^2 |j,m\rangle = \left(\frac{i\hbar}{2}\right)^2 & \sqrt{(j+m+2)(j+m+1)(j-m)(j-m-1)}\,|j,m+2\rangle \\
& -2(j^2-m^2+j)\,|j,m\rangle \\
& +\sqrt{(j-m+2)(j-m+1)(j+m)(j+m+1)}\,|j,m-2\rangle
\end{aligned}
$$

自旋角动量

1. 每个电子都有自旋角动量, 它在空间任何方向上的投影只能取两个数值
2. 每个电子都有自旋磁矩, 与自旋角动量的关系, $vec\mu_s = -\frac{e}{\mu c}\vec{s}$

$$\mu_{s_z} = \pm\frac{e\hbar}{2\mu c} = \pm\mu_B$$

自旋角动量算符

$$|s_x,+\rangle = \frac{1}{\sqrt{2}}\left(|s_z,+\rangle + |s_z,-\rangle\right)$$

$$|s_x,-\rangle = \frac{1}{\sqrt{2}}\left(|s_z,+\rangle - |s_z,-\rangle\right)$$

$$|s_y,+\rangle = \frac{1}{\sqrt{2}}\left(|s_z,+\rangle + i\,|s_z,-\rangle\right)$$

$$|s_y,+\rangle = \frac{1}{\sqrt{2}}\left(|s_z,+\rangle - i\,|s_z,-\rangle\right)$$

$$\hat{S} = \frac{\hbar}{2}\hat{\sigma}$$

$$[\hat{S}_i,\hat{S}_j] = i\hbar\epsilon_{ijk}\hat{s}_k$$

$$[\hat{S}_i,\hat{S}_j]_+ = \hbar\delta_{ij}$$

$$[\hat{\sigma}_\alpha,\hat{\sigma}_\beta] = 2i\epsilon_{\alpha\beta\gamma}\hat{\sigma}_\gamma$$

$$\hat{\sigma}_x^2 = \frac{4}{\hbar^2}\hat{S}_x^2 = 1 \quad \hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = 1$$

$$[\hat{\sigma}_\alpha,\hat{\sigma}_\beta]_+ = 2\delta_{\alpha\beta} \quad [\hat{\sigma}_\alpha,\hat{\sigma}_\beta] = 2i\varepsilon_{\alpha\beta\gamma}\hat{\sigma}_\gamma$$

$$\hat{\sigma}_x\left|\frac{1}{2}\right\rangle = \left|-\frac{1}{2}\right\rangle \quad \hat{\sigma}_x\left|-\frac{1}{2}\right\rangle = \left|\frac{1}{2}\right\rangle$$

$$\hat{\sigma}_y\left|\frac{1}{2}\right\rangle = i\left|-\frac{1}{2}\right\rangle \quad \hat{\sigma}_y\left|-\frac{1}{2}\right\rangle = -i\left|\frac{1}{2}\right\rangle$$

$$\hat{\sigma}_z\left|\frac{1}{2}\right\rangle=\left|\frac{1}{2}\right\rangle\quad\hat{\sigma}_z\left|-\frac{1}{2}\right\rangle=-\left|-\frac{1}{2}\right\rangle$$

$$\hat{\sigma}_\alpha\hat{\sigma}_\beta=\delta_{\alpha\beta}+i\varepsilon_{\alpha\beta\gamma}\hat{\sigma}_\gamma\quad\hat{\sigma}_\alpha\hat{\sigma}_\beta=-\hat{\sigma}_\beta\hat{\sigma}_\alpha$$

$$\hat{\sigma}_x=\begin{pmatrix}0&1\\1&0\end{pmatrix}\quad\lambda=1,\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix},\lambda=-1,\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

$$\hat{\sigma}_y=\begin{pmatrix}0&-i\\i&0\end{pmatrix}\quad\lambda=1,\frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix},\lambda=-1,\frac{1}{\sqrt{2}}\begin{pmatrix}-1\\i\end{pmatrix}$$

$$\hat{\sigma}_z=\begin{pmatrix}1&0\\0&-1\end{pmatrix}\quad\lambda=1,\begin{pmatrix}1\\0\end{pmatrix},\lambda=-1,\begin{pmatrix}0\\1\end{pmatrix}$$

$$R_x(\theta)=\begin{pmatrix}\cos\frac{\theta}{2}&-i\sin\frac{\theta}{2}\\-i\sin\frac{\theta}{2}&\cos\frac{\theta}{2}\end{pmatrix}$$

$$R_y(\theta)=\begin{pmatrix}\cos\frac{\theta}{2}&-\sin\frac{\theta}{2}\\\sin\frac{\theta}{2}&\cos\frac{\theta}{2}\end{pmatrix}$$

$$R_z(\theta)=\begin{pmatrix}e^{-\frac{i\theta}{2}}&0\\0&e^{\frac{i\theta}{2}}\end{pmatrix}$$

$$R(\varphi,\theta)=\begin{pmatrix}e^{\frac{i\varphi}{2}}\cos\frac{\theta}{2}&-e^{\frac{i\varphi}{2}}\sin\frac{\theta}{2}\\e^{-\frac{i\varphi}{2}}\sin\frac{\theta}{2}&e^{\frac{-i\varphi}{2}}\cos\frac{\theta}{2}\end{pmatrix}$$

角动量耦合

$$\begin{cases}\hat{J}_1\times\hat{J}_1=i\hbar\hat{J}_1\\\hat{J}_2\times\hat{J}_2=i\hbar\hat{J}_2\\{}[\hat{J}_1,\hat{J}_2]=0\end{cases}\implies\hat{J}=\hat{J}_1+\hat{J}_2\text{满足角动量的定义}$$

无耦合表象: $\left\{\hat{J}_1{}^2,\hat{J}_{1z},\hat{J}_2{}^2,\hat{J}_{2z}\right\}$, 基矢$|j_1,m_1,j_2,m_2\rangle$.

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

$$\hat{J}_{1z}\left|j_1,m_1,j_2,m_2\right\rangle=m_1\hbar\left|j_1,m_1,j_2,m_2\right\rangle$$

耦合表象: $\left\{\hat{J}^2,\hat{J}_z,\hat{J}_1^2,\hat{J}_2^2\right\}$, 基矢$|j_1,j_2,j,m\rangle$

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

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

CG系数特指由开始表象(耦合表象)转换为后来表象(无耦合表象)的变换矩阵的矩阵元.$\langle m_1,m_2|j,m\rangle$

计算CG系数的方法

1. $m_1+m_2\neq m$时,$\langle m_1,m_2|j,m\rangle=0$

$$\hat{J}_z=\hat{J}_{1z}+\hat{J}_{2z}$$

$$|j,m\rangle=\sum_{m_1,m_2}|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle$$

$$\begin{aligned}\hat{J}_z\,|j,m\rangle=&\sum_{m_1,m_2}\hat{J}_{1z}\,|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle\\&+\sum_{m_1,m_2}\hat{J}_{2z}\,|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle\implies\end{aligned}$$

$$\begin{aligned}m\hbar\,|j,m\rangle=&\sum_{m_1,m_2}m_1\hbar\,|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle\\&+\sum_{m_1,m_2}m_2\hbar\,|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle\implies\end{aligned}$$

$$|j,m\rangle=\sum_{m_1,m_2}\frac{m_1+m_2}{m}\,|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle$$

将这个式子和

$$|j,m\rangle=\sum_{m_1,m_2}|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle$$

可得出

$$m_1+m_2\neq m\implies\langle m_1,m_2|j,m\rangle=0$$

2. 用升降算符$\hat{J}_+=\hat{J}_{1+}+\hat{J}_{2+}$, $\hat{J}_-=\hat{J}_{1-}+\hat{J}_{2-}$. 和态矢的正交归一性求解其他位置.

具体CG系数的求解题目, 题目中会给出j_1,j_2的值.

1. j_1,j_2的值给出后, $m_1=-j_1,-j_1+1\dots j_1-1,j_1$, $m_2=-j_2,-j_2+1\dots j_2-1,j_2$
2. j_1,j_2的值给出后, $j=|j_1-j_2|\dots j_1+j_2$. 每一个j的取值, 都有一串m的取值.
3. 列出所有可能的$|j,m\rangle$和可能的$|m_1,m_2\rangle$.
4. 接下来就是计算$\langle m_1,m_2|j,m\rangle$.
5. 列出方程组 $|j,m\rangle=\sum_{m_1,m_2}|m_1,m_2\rangle\langle m_1,m_2|\,|j,m\rangle$.

6.

$$\begin{cases} m_1+m_2\neq m \implies \langle m_1,m_2|j,m\rangle = 0\\ |j=j_1+j_2, m=j_1+j_2\rangle = |m_1=j_1, m_2=j_2\rangle \\ |j=j_1+j_2, m=-(j_1+j_2)\rangle = |m_1=-j_1, m_2=-j_2\rangle \end{cases}$$

7. 利用上面的三个已知, 可简化方程组,

$$\begin{cases} \text{由上面已知式, 两边作用}\hat{J}_-\text{然后对比方程}\\ \text{利用正交归一性求其他系数} \end{cases}$$

电子的自旋$\hat{S}$和轨道耦合$\hat{L}$

$\left\{\hat{J}^2,\hat{L}^2,\hat{J}_z\right\}$的共同本征函数$\psi = C_1 Y_{l_1,m_{l_1}}\cdot\chi_{\frac{1}{2}} + C_2 Y_{l_2,m_{l_2}}\cdot\chi_{-\frac{1}{2}}$, $|l,m_l,m_s\rangle$.

$$\hat{J}^2 = \hat{L}^2+\hat{S}^2+2\hat{L}\cdot\hat{S}$$

设$\psi_{l,m_l,m_s} = aY_{l_1,m_{l_1}}\chi_{\frac{1}{2}}(S_z) + bY_{l_2,m_{l_2}}\chi_{-\frac{1}{2}}(S_z)$. 在$S_z$的表象下

$$\psi_{l,m_l,m_s} = \begin{pmatrix} aY_{l_1,m_{l_1}}\\ bY_{l_2,m_{l_2}}\end{pmatrix}$$

下面求本征值

$$\begin{aligned}\hat{l}^2\psi_{l,m_l,m_s} &= \begin{pmatrix}\hat{l}^2 & 0\\ 0 & \hat{l}^2\end{pmatrix}\begin{pmatrix} aY_{l_1,m_{l_1}}\\ bY_{l_2,m_{l_2}}\end{pmatrix} = \begin{pmatrix} a\hat{l}^2Y_{l_1,m_{l_1}}\\ b\hat{l}^2Y_{l_2,m_{l_2}}\end{pmatrix}\\ &= \begin{pmatrix} a\cdot l_1(l_1+1)\hbar^2 Y_{l_1,m_{l_1}}\\ b\cdot l_2(l_2+1)\hbar^2 Y_{l_2,m_{l_2}}\end{pmatrix}\end{aligned}$$

要想所设为$\hat{l}^2$的本征值, 必须有$l_1=l_2=l$.

$$\hat{l}^2\psi_{l,m_l,m_s} = l(l+1)\hbar^2\psi_{l,m_l,m_s}$$

$$\begin{aligned}\hat{J}_z\psi_{l,m_l,m_s} &= \begin{pmatrix}\hat{J}_z & 0\\ 0 & \hat{J}_z\end{pmatrix}\begin{pmatrix} aY_{l,m_l}\\ bY_{l,m_l'}\end{pmatrix}\\ &= \begin{pmatrix}\hat{l}_z+\hat{s}_z & 0\\ 0 & \hat{l}_z+\hat{s}_z\end{pmatrix}\begin{pmatrix} aY_{l,m_l}\\ bY_{l,m_l'}\end{pmatrix}\\ &= \begin{pmatrix} a(m_l\hbar+\frac{\hbar}{2})Y_{l,m_l}\\ b(m_l'-\frac{\hbar}{2})Y_{l,m_l'}\end{pmatrix}\end{aligned} \tag{2}$$

要想提出常数, 必须有$m_l+\frac{1}{2}=m_l'-\frac{1}{2}$.

$$\hat{J}^2\psi_{l,m_l,m_s} = \begin{pmatrix} \hat{l}^2+\hat{s}^2+2\hat{l}\cdot\hat{s} & 0 \\ 0 & \hat{l}^2+\hat{s}^2+2\hat{l}\cdot\hat{s} \end{pmatrix} \begin{pmatrix} aY_{l,m_l,m_s} \\ bY_{l,(m_l+1),m_s} \end{pmatrix} \tag{3}$$

$$\begin{aligned} \begin{pmatrix} \hat{l}\cdot\hat{s} & 0 \\ 0 & \hat{l}\cdot\hat{s} \end{pmatrix} &= \frac{\hbar}{2}\begin{pmatrix} l_x & 0 \\ 0 & l_x \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} l_y & 0 \\ 0 & l_y \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ &+ \frac{\hbar}{2}\begin{pmatrix} l_z & 0 \\ 0 & l_z \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= \frac{\hbar}{2}\begin{pmatrix} l_z & l_x - il_y \\ l_x + il_y & -l_z \end{pmatrix} \end{aligned} \tag{4}$$

$$\begin{aligned} \begin{pmatrix} \hat{l}\cdot\hat{s} & 0 \\ 0 & \hat{l}\cdot\hat{s} \end{pmatrix}\begin{pmatrix} aY_{l,m_l,m_s} \\ bY_{l,(m_l+1),m_s} \end{pmatrix} &= \frac{\hbar}{2}\begin{pmatrix} l_z & l_x - il_y \\ l_x + il_y & -l_z \end{pmatrix}\begin{pmatrix} aY_{l,m_l,m_s} \\ bY_{l,(m_l+1),m_s} \end{pmatrix} \\ &= \frac{\hbar}{2}\begin{pmatrix} \left[am_l\hbar + b\sqrt{l(l+1)-(m_l+1)m_l}\hbar\right]Y_{l,m_l,m_s} \\ \left[a\sqrt{l(l+1)-m_l(m_l+1)}\hbar - b(m_l+1)\hbar\right]Y_{l,m_l,m_s} \end{pmatrix} \end{aligned} \tag{5}$$

要能够提出常数, 必须有

$$\begin{cases} am_l\hbar + b\sqrt{l(l+1)-(m_l+1)m_l}\hbar = a\sqrt{l(l+1)-m_l(m_l+1)}\hbar - b(m_l+1)\hbar \\ a^2+b^2=1 \end{cases}$$

因此$\left\{\hat{J}^2,\hat{L}^2,\hat{J}_z\right\}$的共同本征函数$Y_{l,m_l,m_s} = aY_{l,m_l}\chi_{\frac{1}{2}} + bY_{l,(m_l+1)}\chi_{-\frac{1}{2}}$. 且其中的$a,b$可以用$l,m_l$来表示.

自旋与自旋耦合: 二电子自旋态 $\left\{\hat{\vec{S}},\hat{S}_z,\hat{S}^2\right\}$.

$$\begin{cases} \chi^S_{1,1} = \chi_{\frac{1}{2}}(s_{1z})\cdot\chi_{\frac{1}{2}}(s_{2z}) \\ \chi^S_{1,-1} = \chi_{-\frac{1}{2}}(s_{1z})\cdot\chi_{-\frac{1}{2}}(s_{2z}) \\ \chi^S_{1,0} = \frac{1}{\sqrt{2}}\left[\chi_{-\frac{1}{2}}(s_{1z})\cdot\chi_{\frac{1}{2}}(s_{2z}) + \chi_{\frac{1}{2}}(s_{1z})\cdot\chi_{-\frac{1}{2}}(s_{2z})\right] \\ \chi^A_{0,0} = \frac{1}{\sqrt{2}}\left[\chi_{\frac{1}{2}}(s_{1z})\cdot\chi_{-\frac{1}{2}}(s_{2z} - \chi_{-\frac{1}{2}}(s_{1z})\cdot\chi_{\frac{1}{2}}(s_{2z}))\right] \end{cases}$$

带电粒子在外场中的运动

$$\begin{cases} \hat{H} = \frac{1}{2m}(\hat{p} - \frac{q}{c}\hat{A})^2 + q\varphi \\ \vec{j} = -\frac{i\hbar}{2m}\left(\psi^*\cdot\nabla\psi - \psi\cdot\nabla\psi^*\right) - \frac{q}{mc}\vec{A}\psi^*\psi \end{cases}$$

其中

$$\begin{cases} \nabla\times\vec{A} = \vec{B} \\ \vec{E} = -\nabla\varphi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t} \end{cases}$$

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \implies$$
$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[\frac{1}{2m}(-i\hbar\nabla - \frac{q}{c}\vec{A})^2 + q\varphi\right]\psi(\vec{r},t)$$

用对称规范$\vec{A} = \frac{1}{2}\vec{B}\times\vec{r} = -\frac{1}{2}B\cdot y\vec{i} + \frac{1}{2}B\cdot x\vec{j}$,其中我们设$\vec{B} = B\cdot\vec{k}$.
这样薛定谔方程变为

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) &= \left\{\frac{1}{2m}\left[(p_x - \frac{q}{c}A_x)^2 + (p_y - \frac{q}{c}A_y)^2 + (p_z - \frac{q}{c}A_z)^2\right] + q\varphi\right\}\psi(\vec{r},t)\\
&= \left\{\frac{1}{2m}\left[(p_x - \frac{q}{c}A_x)^2 + (p_y - \frac{q}{c}A_y)^2 + p_z^2\right] + q\varphi\right\}\psi(\vec{r},t)\\
&= \left\{\frac{1}{2m}\left[\hat{p}^2 + \frac{q^2B^2}{4c^2}(\hat{x}^2 + \hat{y}^2) + \frac{qB}{c}(\hat{p}_x\hat{y} - \hat{p}_y\hat{x})\right] + q\varphi\right\}\psi(\vec{r},t)\\
&= \left\{\frac{1}{2m}\hat{p}^2 + q\varphi + \frac{q^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2) - \frac{qB}{2mc}\hat{l}_z\right\}\psi(\vec{r},t)
\end{aligned}$$

0 其中的顺磁项$-\frac{qB}{2mc}\hat{l}_z$. 如果令$\vec{\mu}_{l_z} = \frac{q}{2mc}\vec{l}_z$, 该项即为$-\vec{\mu}_{l_z}\cdot\vec{B}$.
反磁项$\frac{q^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2)$.

1. 赛曼效应: 轨道角动量和外磁场的耦合, m量子数的显现.

   氢原子: $\hat{H} = \frac{1}{2m}\hat{p}^2 + q\varphi + \frac{q^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2) - \frac{qB}{2mc}\hat{l}_z$. 其中$q = -e$, $\varphi = \frac{e}{r}$.
   根据原子的尺寸$x^2 + y^2 \sim 10^{-20}$m, 而最强磁场$B \sim 10$T.

   $$\frac{\frac{q^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2)}{-\frac{qB}{2mc}\hat{l}_z} \sim 10^{-5}$$

   从而忽略$\frac{q^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2)$.
   从而$\hat{H} = \frac{1}{2m}\hat{p}^2 + q\varphi - \frac{qB}{2mc}\hat{l}_z$.
   本征态为$\psi_{n,l,m_l} = R_{n,l}(r)Y_{l,m_l}(\theta,\varphi)$

   $$\hat{H}\psi_{n,l,m_l} = E_{n,l}\psi_{n,l,m_l} + \frac{eB}{2mc}m_l\hbar, m_l = -1, 0, 1$$

2. 精细结构: 电子自旋和轨道耦合, j量子数的显现(必须保证不加外磁场, 加外磁场会使这个耦合消失, 自旋是相对论效应)

   $$\hat{H} = \frac{1}{2m}\hat{p}^2 + q\varphi + f(r)\vec{s}\cdot\vec{l} = \frac{1}{2m}\hat{p}^2 + q\varphi + \left[\frac{1}{2m_ec^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{e}{r^2}\right)\right]\vec{s}\cdot\vec{l}$$

   $$\hat{T} = \frac{1}{2m_e}\hat{p}^2 = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{l}^2}{2m_er^2}$$
   $$\vec{l}\cdot\vec{s} = \frac{\hat{j}^2 - \hat{l}^2 - \hat{s}^2}{2}$$