第三章 量子力学中的力学量

§3.1 表示力学量的算符

算符是指作用在一个函数上得出另一个函数的运算符号。如 $\hat{O}u=v$，表示$\hat{O}$把函数u变成v，$\hat{O}$称为算符。算符有下述基本性质:

（1）算符相等

若两个算符$\hat{O}$、$\hat{U}$对任意函数u的运算结果都相同，即$\hat{O}u=\hat{U}u$，则算符$\hat{O}$和算符$\hat{U}$相等记为$\hat{O}=\hat{U}$。

（2）单位算符$\hat{I}$，作用到任意函数u上，u不变，即

$$\hat{I}u=u$$

（3）算符之和，对于任意函数u，$(\hat{O}+\hat{U})u=\hat{O}u+\hat{U}u=\hat{E}u$，则$\hat{O}+\hat{U}=\hat{E}$称为算符之和，满足交换和结合律。

（4）算符之积，对于任意函数u，$(\hat{O}\hat{U})u=\hat{O}(\hat{U}u)=\hat{E}u$，则$\hat{O}\hat{U}=\hat{E}$，与作用次序有关，一般不满足交换律，除非对易。

对易关系：若对于任意函数u，（$\hat{O}\hat{U}$）u＝（$\hat{U}\hat{O}$）u，则称 $\hat{O}$ 与 $\hat{U}$ 对易，反之不对易。若 $\hat{O}\hat{U}=-\hat{U}\hat{O}$，则称为反对易。

（5）逆算符

如果 $\hat{O}\hat{U}=I$，则称 $\hat{O}$ 、$\hat{U}$ 互为逆算符，记 $\hat{O}^{-1}=\hat{U}$， $\hat{U}^{-1}=\hat{O}$，且有 $\hat{U}\hat{O}=I$, $(\hat{O}\hat{U})^{-1}=\hat{U}^{-1}\hat{O}^{-1}$, 并非所有算符都存在逆算符，如投影算符不存在逆算符。

（6）算符的复共轭、转置和厄米

(a) 内积（标积）

$$(u,v)\equiv\int u^{*}v\,d\tau=\left(\int uv^{*}d\tau\right)^{*}=(v,u)^{*}$$

$$(u,v)\geq 0$$

$$(u,c_1v_1+c_2v_2)=c_1(u,v_1)+c_2(u,v_2)$$

(b) 复共轭算符，将原算符中复量换成共轭复量即可。

（c）转置算符

定义: $\int d\tau u^* \tilde{\hat{F}} v = \int d\tau v \hat{F} u^*$ 式中u，v为任意函数，即

$$(u, \tilde{\hat{F}} v) = (v^*, \hat{F} u^*)$$

性质:

(i) $\dfrac{\tilde{\partial}}{\partial x} = -\dfrac{\partial}{\partial x}$ (ii) $\tilde{p}_x = \dfrac{\hbar}{i}\dfrac{\tilde{\partial}}{\partial x} = -\dfrac{\hbar}{i}\dfrac{\partial}{\partial x} = -p_x$

(iii) $\widetilde{\hat{A}\hat{B}} = \tilde{\hat{B}}\tilde{\hat{A}}$

（d）厄密共轭

定义: $\int d\tau \psi^* \hat{O}^+ \phi = \int d\tau (\hat{O}\psi)^* \phi$ 式中φ，φ为任意函数，即

$(\psi, \hat{o}^+ \phi) = (\hat{o}\psi, \phi)$ 且有 $\hat{o}^+ = \widetilde{\hat{o}^*}$

证明: $(\psi, \phi) = (\hat{o}\psi, \phi) = (\phi, \hat{o}\psi)^* = (\phi^*, \hat{o}^* \psi^*) = (\psi, \widetilde{\hat{o}^*} \phi)$

（7）线性算符

$$\hat{O}(c_1\psi_1+c_2\psi_2)=c_1\hat{O}\psi_1+c_2\hat{O}\psi_2,$$

c_1, c_2 为任意常数，ψ_1, ψ_2 为任意函数

（8）算符的本征值与本征函数

$$\hat{F}\psi=\lambda\psi \qquad \hat{p}=-i\hbar\nabla \qquad \hat{r}=r \qquad \hat{H}=-\frac{\hbar^2}{2m}\nabla^2+U(r)$$

$$\hat{F}=\hat{F}(\hat{r},\hat{p})=\hat{F}(\hat{r},-i\hbar\nabla)$$

$$F(x)=\sum_{n=0}^{\infty}\frac{F^{(n)}(0)}{n!}x^n \longrightarrow F(\hat{U})=\sum_{n=0}^{\infty}\frac{F^{(n)}(0)}{n!}\hat{U}^n$$

$$e^{-\frac{i}{\hbar}\hat{H}t}=\sum_{n=0}^{\infty}\frac{1}{n!}[-\frac{i}{\hbar}\hat{H}t]^n$$

$$F(\hat{A},\hat{B})=\sum_{n,m=0}^{\infty}\frac{F^{(n,m)}(0,0)}{n!m!}\hat{A}^n\hat{B}^m \qquad F^{(n,m)}(x,y)=\frac{\partial^n}{\partial x^n}\frac{\partial^m}{\partial y^m}F(x,y)$$

$$\vec{L}=\vec{r}\times\vec{p} \longrightarrow \hat{\vec{L}}=\hat{\vec{r}}\times\hat{\vec{p}}=-i\hbar\vec{r}\times\nabla$$

如果算符 $\hat{F}$ 表示力学量F，那么当体系处于F的本征态 φ 时，力学量F有确定值，这个值就是 $\hat{F}$ 在 φ 态中的本征值。

厄米算符 $\int d\tau \psi^* \hat{O}\phi = \int d\tau (\hat{O}\psi)^* \phi$

$$\phi = \psi \quad \Big\downarrow \quad \hat{F}\psi = \lambda\psi$$

$$\lambda \int \psi^* \psi dx = \lambda^* \int \psi^* \psi dx$$

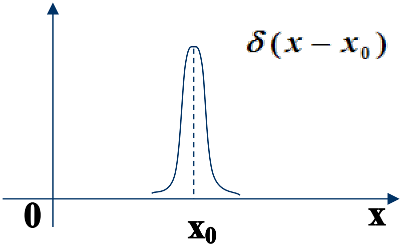
$$\Big\downarrow$$

$$\lambda = \lambda^*$$

表明：厄米算符本征值为实数。

量子力学中表示力学量的算符都是厄米算符，本征值为实数。如表示坐标的坐标算符、表示动量的动量算符，其本征值分别为坐标和动量，均为实数。

补充：狄拉克δ函数（分布）http://zh.wikipedia.org/wiki/狄拉克δ函数



$$\delta(x-x_0)=\begin{cases}0 & x\neq x_0\\ \infty & x=x_0\end{cases}$$

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon}\delta(x-x_0)dx=\int_{-\infty}^{\infty}\delta(x-x_0)dx=1\ (\varepsilon>0)$$

单位脉冲函数。通常用δ表示。在概念上，它是这么一个“函数”：在除了零以外的点都等于零，而其在整个定义域上的积分等于1。严格来说狄拉克δ函数不能算是一个函数，因为满足以上条件的函数是不存在的。但可以用分布的概念来解释，称为狄拉克δ分布，或δ分布

$$\delta(x-x_0)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ik(x-x_0)}dk$$

对任意连续函数 f(x)，在$x=x_0$附近

$$f(x)\delta(x-x_0)=f(x_0)\delta(x-x_0)$$

$k=p_x/\hbar$， $dk=dp_x/\hbar$

$$\int_{-\infty}^{\infty}f(x)\delta(x-x_0)dx=f(x_0)$$

$$\delta(x-x_0)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{\frac{i}{\hbar}p_x(x-x_0)}dp_x$$

$$\delta(-x)=\delta(x)$$

$$p_x\Leftrightarrow x，\ p_x'\Leftrightarrow x_0$$

$$\delta(ax)=\frac{1}{|a|}\delta(x)$$

$$\delta(p_x-p_x')=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{\frac{i}{\hbar}(p_x-p_x')x}dx$$

§ 3.2 动量算符和角动量算符

1.动量算符

本征方程

分量方程

$$\begin{cases} -i\hbar \frac{\partial}{\partial x}\psi_{\vec{p}}(\vec{r}) = \vec{p}_x\psi_{\vec{p}}(\vec{r}) \\ -i\hbar \frac{\partial}{\partial y}\psi_{\vec{p}}(\vec{r}) = \vec{p}_y\psi_{\vec{p}}(\vec{r}) \\ -i\hbar \frac{\partial}{\partial z}\psi_{\vec{p}}(\vec{r}) = \vec{p}_z\psi_{\vec{p}}(\vec{r}) \end{cases}$$

分离变量

$$\begin{cases} \frac{-i\hbar}{\psi(x)}\frac{d\psi(x)}{dx} = p_x \\ \frac{-i\hbar}{\psi(y)}\frac{d\psi(y)}{dy} = p_y \\ \frac{-i\hbar}{\psi(z)}\frac{d\psi(z)}{dz} = p_z \end{cases}$$

$$\begin{cases} \psi(x) = c_1 e^{\frac{i}{\hbar}p_x x} \equiv \psi_{p_x}(x) \\ \psi(y) = c_2 e^{\frac{i}{\hbar}p_y y} \equiv \psi_{p_y}(y) \\ \psi(z) = c_3 e^{\frac{i}{\hbar}p_z z} \equiv \psi_{p_z}(z) \end{cases}$$

$$\psi_{\vec{p}}(\vec{r}) = \psi(x)\psi(y)\psi(z)$$

$$= \psi_{p_x}(x)\psi_{p_y}(y)\psi_{p_z}(z)$$

$$= c_1 e^{\frac{i}{\hbar}p_x x} c_2 e^{\frac{i}{\hbar}p_y y} c_3 e^{\frac{i}{\hbar}p_z z}$$

$$= c e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

德布罗意波空间部分

$$\int_{-\infty}^{\infty} \psi^*_{\vec{p}'}(\vec{r})\psi_{\vec{p}}(\vec{r})d\tau$$

$$= |c|^2 \int_{-\infty}^{\infty} e^{-\frac{i}{\hbar}\vec{p}'\bullet\vec{r}} e^{\frac{i}{\hbar}\vec{p}\bullet\vec{r}} d\tau$$

$$= |c|^2 \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(\vec{p}-\vec{p}')\bullet\vec{r}} d\tau$$

$$= |c|^2 (2\pi\hbar)^3 \delta(\vec{p}-\vec{p}')$$

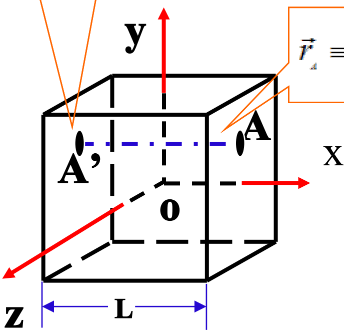
如果
$|c|^2(2\pi\hbar)^3=1$
则 $\psi_p(r)$归一化
为 δ 函数

由以上结果，动量的连续谱本征函数不能归一化到1而是δ函数是如果加上一些合适的边界条件，上述的归一化方法仍可适用，这种方法称为箱归一化。

周期性边界条件：A点的波函数与A’处具有相同的值。

$$\vec{r}_{A'} \equiv \left\{-\frac{L}{2}, y, z\right\}$$

$$\vec{r}_{A} \equiv \left\{\frac{L}{2}, y, z\right\}$$



$$ce^{\frac{i}{\hbar}[p_x\frac{L}{2}+p_y y+p_z z]} = ce^{\frac{i}{\hbar}[p_x\frac{-L}{2}+p_y y+p_z z]}$$

$$e^{\frac{i}{\hbar}[p_x L]} = 1$$

$$\frac{1}{\hbar} p_x L = 2\pi n_x \quad \Rightarrow \quad p_x = \frac{2\pi\hbar n_x}{L}$$

$$n_x = 0, \pm 1, \pm 2, \cdots$$

$$p_y = \frac{2\pi\hbar n_y}{L} \qquad p_z = \frac{2\pi\hbar n_z}{L}$$

$$n_y, n_z = 0, \pm 1, \pm 2, \cdots$$

在周期性边界条件下，
动量分量呈现分立谱

$$\psi_{\vec{p}}(\vec{r}) = ce^{\frac{i}{\hbar}\vec{p}\bullet\vec{r}}$$

$$\rightarrow \psi_{\vec{p}}(\vec{r}) = \psi_{n_x n_y n_z}$$

$$= ce^{\frac{i}{\hbar}[\frac{2\pi\hbar n_x}{L}x+\frac{2\pi\hbar n_y}{L}y+\frac{2\pi\hbar n_z}{L}z]}$$

$$\int\iint_{-L/2}^{L/2} \psi_{\vec{p}}{}^{*}\psi_{\vec{p}}\, d\tau = c^2\int\iint_{-L/2}^{L/2} d\tau = c^2L^3 = 1$$

$$\mathbf{c = L^{-3/2}}$$

$$\psi_{n_x n_y n_z} = \left(\frac{1}{L}\right)^{3/2} e^{\frac{i}{\hbar}\vec{p}\bullet\vec{r}}$$

$$= \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar}\vec{p}\bullet\vec{r}}$$

2.角动量算符

（1）表达式

经典力学的角动量

$$\vec{L} = \vec{r} \times \vec{p} \xrightarrow{\text{假定（2）}} \hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = -i\hbar\vec{r} \times \nabla$$

(1.1) 笛卡尔坐标系

$$\begin{cases} L_x = y\hat{p}_z - z\hat{p}_y = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \\ L_y = z\hat{p}_x - x\hat{p}_z = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \\ L_z = x\hat{p}_y - y\hat{p}_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \end{cases}$$

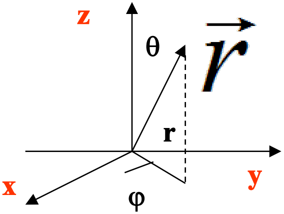
角动量平方算符

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= (y\hat{p}_z - z\hat{p}_y)^2 + (z\hat{p}_x - x\hat{p}_z)^2 + (x\hat{p}_y - y\hat{p}_x)^2$$

$$= -\hbar^2[(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})^2 + (z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})^2 + (x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})^2$$

笛卡尔坐标系下角动量平方算符存在交叉导数，难以求解，采用球极坐标。



(1.2) 球极坐标

两种坐标系的变换关系

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases} \qquad \begin{cases} r^2 = x^2 + y^2 + z^2 & (1) \\ \cos\theta = z/r & (2) \\ \tan\phi = y/x & (3) \end{cases}$$

r = r (x, y, z)
x = x (r, θ, ϕ)

对任意函数
f (r, θ, φ), 有

$$\frac{\partial f}{\partial x_i} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x_i} + \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial x_i} + \frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial x_i}$$

$$x_1, x_2, x_3 = x, y, z$$

对于 (1)

$$\begin{cases} \dfrac{\partial r}{\partial x} = \sin\theta\cos\phi \\ \dfrac{\partial r}{\partial y} = \sin\theta\sin\phi \\ \dfrac{\partial r}{\partial z} = \cos\theta \end{cases}$$

or

$$\begin{cases} \dfrac{\partial}{\partial x} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial x} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial x} + \dfrac{\partial}{\partial \phi}\dfrac{\partial \phi}{\partial x} \\ \dfrac{\partial}{\partial y} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial y} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial y} + \dfrac{\partial}{\partial \phi}\dfrac{\partial \phi}{\partial y} \\ \dfrac{\partial}{\partial z} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial z} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial z} + \dfrac{\partial}{\partial \phi}\dfrac{\partial \phi}{\partial z} \end{cases}$$

对于 (2)

$$\begin{cases} \dfrac{\partial \theta}{\partial x} = \dfrac{1}{r}\cos\theta\cos\phi \\ \dfrac{\partial \theta}{\partial y} = \dfrac{1}{r}\cos\theta\sin\phi \\ \dfrac{\partial \theta}{\partial z} = -\dfrac{1}{r}\sin\theta \end{cases}$$

对于 (3)

$$\begin{cases} \dfrac{\partial \phi}{\partial x} = -\dfrac{1}{r}\dfrac{\sin\phi}{\sin\theta} \\ \dfrac{\partial \phi}{\partial y} = \dfrac{1}{r}\dfrac{\cos\phi}{\sin\theta} \\ \dfrac{\partial \phi}{\partial z} = 0 \end{cases}$$

$$\begin{cases} \dfrac{\partial}{\partial x} = \sin\theta\cos\phi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\cos\phi\dfrac{\partial}{\partial\theta} - \dfrac{1}{r}\dfrac{\sin\phi}{\sin\theta}\dfrac{\partial}{\partial\phi} \\ \dfrac{\partial}{\partial y} = \sin\theta\sin\phi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\sin\phi\dfrac{\partial}{\partial\theta} + \dfrac{1}{r}\dfrac{\cos\phi}{\sin\theta}\dfrac{\partial}{\partial\phi} \\ \dfrac{\partial}{\partial z} = \cos\theta\dfrac{\partial}{\partial r} - \dfrac{1}{r}\sin\theta\dfrac{\partial}{\partial\theta} \end{cases}$$

$$\begin{cases} L_x = y\hat{p}_z - z\hat{p}_y = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \\ L_y = z\hat{p}_x - x\hat{p}_z = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \\ L_z = x\hat{p}_y - y\hat{p}_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \end{cases}$$

$$\begin{cases} \hat{L}_x = i\hbar[\sin\phi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\phi\dfrac{\partial}{\partial\phi}] \\ \hat{L}_y = -i\hbar[\cos\phi\dfrac{\partial}{\partial\theta} + \cot\theta\sin\phi\dfrac{\partial}{\partial\phi}] \\ \hat{L}_z = -i\hbar\dfrac{\partial}{\partial\phi} \end{cases}$$

$$\boxed{\hat{L}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]}$$

（2）本征方程

(2.1) L_z的本征方程

$$\hat{L}_z\psi(\phi) = -i\hbar\frac{d}{d\phi}\psi(\phi) = l_z\psi(\phi)$$

$$\psi(\phi) = ce^{\frac{i}{\hbar}l_z\phi}$$

$$\psi(\phi) = \psi(\phi + 2\pi)$$

$$ce^{\frac{i}{\hbar}l_z\phi} = ce^{\frac{i}{\hbar}l_z(\phi+2\pi)}$$

$$e^{\frac{i}{\hbar}l_z 2\pi} = \cos[2\pi l_z/\hbar] + i\sin[2\pi l_z/\hbar] = 1$$

$$\frac{2\pi l_z}{\hbar} = 2\pi m \qquad m = 0, \pm1, \pm2, \cdots \rightarrow l_z = m\hbar \qquad m = 0, \pm1, \pm2, \cdots$$

$$\int_0^{2\pi}|\psi|^2 d\phi = c^2\int_0^{2\pi}d\phi = 2\pi c^2 = 1$$

$$\rightarrow c = \frac{1}{\sqrt{2\pi}}$$

正交性：

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}$$

$$\frac{1}{2\pi}\int_0^{2\pi}e^{-im\phi}e^{in\phi}d\phi = 0 \qquad (n \neq m)$$

$$\frac{1}{2\pi}\int_0^{2\pi}e^{-im\phi}e^{in\phi}d\phi = \delta_{mn} \qquad \text{Kronecker}$$

(2.2) L^2的本征值

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

本征函数Y(θ,φ)是球谐函数

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

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

为使 Y(θ,φ)在θ变化的闭区域[0, π]上都是有限的，必须有

$\lambda = \ell(\ell+1),\ \ell = 0, 1, 2, \ldots$

$$Y_{lm}(\theta,\varphi)=(-1)^m N_{lm} P_l^m(\cos\theta)e^{im\varphi}$$

$$m=0,1,2,\cdots,l$$

$$Y_{lm}(\theta,\varphi)=(-1)^m Y_{l-m}^*(\theta,\varphi)$$

$$m=-1,-2,-3,\cdots,-l$$

$$\int_0^{2\pi}\int_0^{\pi} Y_{lm}^*(\theta,\varphi)Y_{lm}(\theta,\varphi)\sin\theta d\theta d\varphi=1 \longrightarrow N_{lm}=\sqrt{\frac{(l-m)!(2l+1)}{4\pi(l+m)!}}$$

正交归一条件：

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

(2.3) 简并

l表征角动量的大小，称为角量子数，**m** 称为磁量子数.

$$Y_{lm}(\theta,\varphi) = (-1)^m N_{lm} P_l^m(\cos\theta) e^{im\varphi} \quad m = 0,1,2,\cdots,l$$

$$Y_{lm}(\theta,\varphi) = (-1)^m Y_{l-m}^*(\theta,\varphi) \quad m = -1,-2,-3,\cdots,-l$$

m 可以取 (2 ℓ +1)个值, 即m=0, ± 1, ± 2, ± 3, ..., ± ℓ，所以，对应于一个角量子数ℓ，即L^2算符的一个本征值，有 (2ℓ +1)个磁量子数m，从而对应(2ℓ +1)个本征函数Y_{lm}，这种一个本征值有多个本征函数的情况称为简并，本征函数的数目称为简并度。一般称ℓ=0的态为s态，ℓ= 1,2,3,& 依次称为p,d,f,& 态。

§3.3 电子在库仑场中的运动

氢原子和类氢原子哈密顿算符

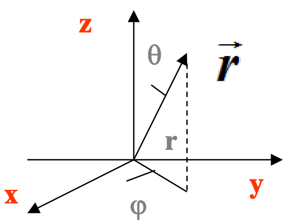
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze_s^2}{r}, \quad e_s = e(4\pi\varepsilon_0)^{-\frac{1}{2}}$$

H的本征方程写为

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze_s^2}{r})\ \psi = E\psi$$

球极坐标形式

$$-\frac{\hbar^2}{2m_e}(\frac{1}{r^2})\left[\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi - \frac{Ze_s^2}{r}\psi = E\psi$$



球极坐标

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

$$\left[-\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{\hat{L}^2}{2m_e r^2} - \frac{Ze_s^2}{r}\right]\psi = E\psi$$

分离变量法

$\psi(r, \theta, \varphi) = R(r)\, Y_{lm}(\theta, \varphi)$

$$\left[-\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2m_e r^2}-\frac{Ze_s^2}{r}\right]\psi = E\boxed{\psi}$$

$$\downarrow$$

$$\left[-\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2m_e r^2}-\frac{Ze_s^2}{r}\right]R(r)Y_{lm}(\vartheta,\phi) = E\boxed{R(r)Y_{lm}(\vartheta,\phi)}$$

$L^2 Y_{lm} = \ell(\ell+1)\hbar^2 Y_{lm}$

$$\downarrow$$

$$\left[-\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{l(l+1)\hbar^2}{2m_e r^2}-\frac{Ze_s^2}{r}\right]R = E\boxed{R}$$

令 $R(r) = u(r) / r$

$$\downarrow$$

$$V(r) = \frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{Ze_s^2}{r} \longrightarrow$$

$$\boxed{\frac{d^2u}{dr^2} + \left[\frac{2m_e}{\hbar^2}\left(E + \frac{Ze_s^2}{r}\right) - \frac{l(l+1)}{r^2}\right]\boxed{u} = 0}$$

$$\downarrow$$

$$\frac{d^2u}{dr^2} + \frac{2m_e}{\hbar^2}[E - V(r)]u = 0$$

E < 0，束缚态

$$\frac{d^2u}{dr^2} + \left[\frac{2m_e}{\hbar^2}\left(E + \frac{Ze_s^2}{r}\right) - \frac{l(l+1)}{r^2}\right]u = 0$$

$$u(r) \xrightarrow[r\to 0]{} 0$$

$$\alpha = \sqrt{\frac{8m_e|E|}{\hbar^2}}$$

$$\beta = \frac{2m_e Ze_s^2}{\alpha\hbar^2} = \frac{Ze_s^2}{\hbar}\sqrt{\frac{m_e}{2|E|}}$$

$$\frac{d^2u}{dr^2} + \left[\left(\frac{2m_eZe_s^2}{\hbar^2}\right)\frac{1}{r} - \frac{1}{4}\left(\frac{8m_e|E|}{\hbar^2}\right) - \frac{l(l+1)}{r^2}\right]u = 0$$

$$\frac{d^2u}{dr^2} + \left[\frac{\alpha\beta}{r} - \frac{\alpha^2}{4} - \frac{l(l+1)}{r^2}\right]u = 0$$

$$\rho = \alpha r$$

$$\frac{du}{dr} = \alpha\frac{du}{d\rho}$$

$$\frac{d^2u}{dr^2} = \alpha^2\frac{d^2u}{d\rho^2}$$

$$\frac{d^2u}{d\rho^2} + \left[\frac{\beta}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]u = 0$$

$\rho \to +\infty$

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0$$

$\rho \to +\infty$

波函数u有限

$$u_\infty = Ae^{-\rho/2} + A'e^{\rho/2} \Rightarrow u_\infty = Ae^{-\rho/2}$$

$$u = \boxed{f(\rho)e^{-\rho/2}}$$

$$\boxed{\frac{d^2f}{d\rho^2} - \frac{df}{d\rho} + \left[\frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]f = 0}$$

$$\frac{d^2u}{d\rho^2}+\left[\frac{\beta}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]u=0$$

ρ → 0

$$\frac{d^2u}{d\rho^2}-\frac{l(l+1)}{\rho^2}u=0 \Rightarrow k=l+1,-l$$

$$k=-l \quad (l=0,1,\ldots)$$

欧拉方程

$$u(\rho)=\rho^k$$

$$u(\rho)=\rho^k=\rho^{-l}=\frac{1}{\rho^l}$$

$k=-l$, ρ → 0，$u(\rho)$不趋于零，但 $k=l+1$满足条件

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

$$u=\rho^{l+1}e^{-\rho/2}f(\rho)$$

$$\frac{d^2u}{d\rho^2}+\left[\frac{\beta}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]u=0 \Rightarrow \rho\frac{d^2f}{d\rho^2}+(2l+2-\rho)\frac{df}{d\rho}-(l+1-\beta)f=0$$

合流超几何方程

$$z\frac{d^2y}{dz^2}+(c-z)\frac{dy}{dz}-ay=0$$

$$f(\rho)=F(l+1-\beta,2l+2,\rho)\xrightarrow[\rho\to\infty]{}e^{\rho}=e^{\alpha r}$$

$$u(r)=Ne^{-\frac{1}{2}\alpha r}r^{l+1}F(l+1-\beta,2l+2,\alpha r)\xrightarrow[r\to\infty]{}Ne^{\frac{1}{2}\alpha r}r^{l+1}\xrightarrow[r\to\infty]{}\infty$$

$$u(r)=Ne^{-\frac{1}{2}\alpha r}r^{l+1}F(l+1-\beta,2l+2,\alpha r)\xrightarrow[r\to\infty]{}Ne^{\frac{1}{2}\alpha r}r^{l+1}\xrightarrow[r\to\infty]{}\infty$$

$$l+1-\beta=-n_r,\ n_r=0,1,\ldots$$

$$F(l+1-\beta,2l+2,\alpha r)\qquad u(r)=Ne^{-\frac{1}{2}\alpha r}r^{l+1}F(l+1-\beta,2l+2,\alpha r)$$

合流超几何多项式

u(r)收敛，满足波函数有界条件

记 $\beta=l+1+n_r=n,\ l=0,1,\ldots,\ n=1,2,\ldots$

n_r称为径量子数，**n**称为总量子数或主量子数

$$\boxed{E_n=-\frac{m_eZ^2e_s^4}{2\hbar^2n^2}\qquad n=1,2,3\cdots}$$

$$\alpha=\sqrt{\frac{8m_e|E|}{\hbar^2}}=\sqrt{\frac{8m_e}{\hbar^2}\frac{m_eZ^2e_s^4}{2\hbar^2n^2}}=\frac{2Zm_ee_s^2}{n\hbar^2}=\frac{2Z}{na_0},\quad a_0=\frac{\hbar^2}{m_ee_s^2}$$

波尔半径

$$\Downarrow$$

$$\rho=\alpha r=\frac{2Z}{na_0}r$$

$$\Downarrow$$

径向波函数

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

$$\Downarrow$$

$$\int\psi_{nlm}^*\psi_{nlm}\,d\tau=\int_0^\infty R_{nl}^2(r)r^2dr\int Y_{lm}^*Y_{lm}\sin\theta d\theta d\varphi$$

$$=\int_0^\infty R_{nl}^2(r)r^2dr=1$$

$$\Downarrow$$

$$N_{nl}=\frac{2}{(2l+1)!}\sqrt{\frac{(n+l)!Z^3}{(n-l-1)!a_0^3}}$$

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-\frac{Z}{a0}r}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} (2 - \frac{Z}{a_0} r)e^{-\frac{Z}{2a0}r}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Z}{a_0\sqrt{3}} re^{-\frac{Z}{2a0}r}$$

$$R_{30}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} [2 - \frac{4Z}{3a_0} r + \frac{4}{27} (\frac{Z}{a_0} r)^2]e^{-\frac{Z}{3a0}r}$$

$$R_{31}(r) = \left(\frac{2Z}{a_0}\right)^{3/2} [\frac{2}{27\sqrt{3}} - \frac{Z}{81\sqrt{3}a_0} r] \frac{Z}{a_0} re^{-\frac{Z}{3a0}r}$$

$$R_{32}(r) = \left(\frac{2Z}{a_0}\right)^{3/2} \frac{1}{81\sqrt{15}} (\frac{Z}{a_0} r)^2 e^{-\frac{Z}{3a0}r}$$

（1）束缚态时的能量和定态波函数

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

$$l = 0,1,2,\cdots,n-1 \qquad m = 0,\pm1,\pm2,\cdots,\pm l$$

（2）能量简并

能量只和主量子数有关，本征波函数与n，ℓ，m 有关，所以能量有简并。

$$n = n_r + \ell + 1 \qquad \ell = 0,1,2,\ldots \qquad n_r = 0,1,2,\ldots$$

当 n确定后，ℓ的最大值可取为 n–1(ℓ=n-n_r-1=n-1， n_r=0)，且 m=0, ± 1, ± 2,...., ± ℓ，所以 E_n 的简并度为

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

基态 $\psi_{100} = R_{10}\, Y_{00}$没有简并

作业

3.1

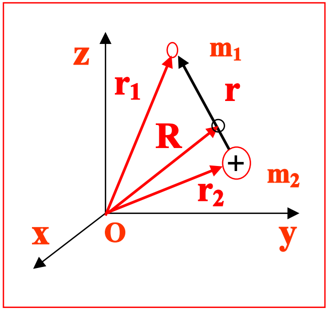
3.10

§ 3.4 氢原子

氢原子薛定谔方程

$$i\hbar\frac{\partial}{\partial t}\Psi(x_1,y_1,z_1;x_2,y_2,z_2;t)=[-\frac{\hbar^2}{2m_1}\nabla_1{}^2-\frac{\hbar^2}{2m_2}\nabla_2{}^2+U]\Psi(x_1,y_1,z_1;x_2,y_2,z_2;t)$$

或 $$i\hbar\frac{\partial}{\partial t}\Psi(r_1,r_2,t)=[-\frac{\hbar^2}{2m_1}\nabla_1{}^2-\frac{\hbar^2}{2m_2}\nabla_2{}^2+U]\Psi(r_1,r_2,t)$$



1-电子；2-核

$$\begin{cases} x = x_1 - x_2 \\ y = y_1 - y_2 \\ z = z_1 - z_2 \end{cases} \qquad \begin{cases} X = \dfrac{m_1x_1+m_2x_2}{m_1+m_2} \\ Y = \dfrac{m_1y_1+m_2y_2}{m_1+m_2} \\ Z = \dfrac{m_1z_1+m_2z_2}{m_1+m_2} \end{cases}$$

$$\frac{\partial}{\partial x_1}=\frac{\partial}{\partial X}\frac{\partial X}{\partial x_1}+\frac{\partial}{\partial x}\frac{\partial x}{\partial x_1}$$

$$=\frac{m_1}{m_1+m_2}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}$$

$$\Longrightarrow \begin{cases} \nabla_1=\dfrac{m_1}{m_1+m_2}\nabla_R+\nabla_r \\ \nabla_2=\dfrac{m_2}{m_1+m_2}\nabla_R-\nabla_r \end{cases}$$

体系哈密顿量

$$\hat{H} = -\frac{\hbar^2}{2m_1}\left(\frac{m_1}{m_1+m_2}\nabla_R + \nabla_r\right)^2 - \frac{\hbar^2}{2m_2}\left(\frac{m_2}{m_1+m_2}\nabla_R - \nabla_r\right)^2 + U$$

$$= -\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^{\ 2} - \frac{\hbar^2}{2m_\mu}\nabla_r^{\ 2} + U(r)$$

$m_\mu = m_1m_2 / (m_1+m_2)$
称为约化质量

薛定谔方程可写为

$$i\hbar\frac{\partial\Psi}{\partial t} = E_T\Psi = [-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^{\ 2} - \frac{\hbar^2}{2m_\mu}\nabla_r^{\ 2} + U(r)]\Psi$$

上式中不存在交叉求导项，波函数可以用分离变量来表达:

$$\Psi = \psi(\vec{r})\phi(\vec{R})\chi(t)$$

代入方程得 $i\hbar\frac{\partial\chi}{\partial t} = E_T\chi$ $\chi(t) = Ce^{-\frac{i}{\hbar}E_T t}$

和
$$\left[-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R{}^2-\frac{\hbar^2}{2m_\mu}\nabla_r{}^2+U(r)\right]\Psi=E_T\Psi$$

$$\left[-\frac{\hbar^2}{2(m_1+m_2)}\frac{1}{\phi}\nabla_R{}^2\phi\right]+\left[-\frac{\hbar^2}{2m_\mu}\frac{1}{\psi}\nabla_r{}^2\psi+U(r)\right]=E_T$$

$$\begin{cases}-\dfrac{\hbar^2}{2m_\mu}\nabla_r{}^2\psi(\vec{r})+U(r)\psi(\vec{r})=E\psi(\vec{r}) \\ -\dfrac{\hbar^2}{2(m_1+m_2)}\nabla_R{}^2\phi(\vec{R})=(E_T-E)\phi(\vec{R})\end{cases} \cdots\cdots\blacktriangleright\ E_n=-\frac{m_\mu e_s{}^4}{2\hbar^2n^2}=-\frac{e_s{}^4}{2a_\mu}\frac{1}{n^2}$$

$$n=1,2,3,\cdots$$

$$m_\mu=\frac{m_1m_2}{m_1+m_2}=\frac{m_1}{1+\dfrac{m_1}{m_2}}\approx m_1$$

$$\nu=\frac{1}{h}[E_n-E_m]=\frac{E_n-E_m}{2\pi\hbar}=\frac{m_\mu e_s{}^4}{4\pi\hbar^3}\left[\frac{1}{m^2}-\frac{1}{n^2}\right]$$

$$=R_HC\left[\frac{1}{m^2}-\frac{1}{n^2}\right]$$

$$E_1=-\frac{m_\mu e_s{}^4}{2\hbar^2}=-13.597\,\mathrm{eV}$$

$$R_H=\frac{m_\mu e_s{}^4}{4\pi\hbar^3C}\approx 1.097\times10^7\,m^{-1}$$

$$\approx-\frac{m_1e_s{}^4}{2\hbar^2}=-13.60\,\mathrm{eV}$$

氢原子波函数

$n=1$

$$R_{10}=\frac{2}{a_0^{3/2}}e^{-r/a_0}$$

$n=2$

$$R_{20}(r)=\left(\frac{1}{2a_0}\right)^{3/2}(2-\frac{1}{a_0}r)e^{-\frac{1}{2a_0}r}$$

$$R_{21}(r)=\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{a_0\sqrt{3}}re^{-\frac{1}{2a_0}r}$$

$n=3$

$$R_{30}(r)=\left(\frac{1}{3a_0}\right)^{3/2}[2-\frac{4}{3a_0}r+\frac{4}{27}(\frac{1}{a_0}r)^2]e^{-\frac{1}{3a_0}r}$$

$$R_{31}(r)=\left(\frac{2}{a_0}\right)^{3/2}[\frac{2}{27\sqrt{3}}-\frac{1}{81\sqrt{3}a_0}r]\frac{1}{a_0}re^{-\frac{1}{3a_0}r}$$

$$R_{31}(r)=\left(\frac{2}{a_0}\right)^{3/2}\frac{1}{81\sqrt{15}}(\frac{1}{a_0}r)^2e^{-\frac{1}{3a_0}r}$$

径向概率分布

$d\tau = r^2\sin\theta drd\theta d\varphi$

$$W_{nlm}(r,\theta,\varphi)d\tau$$
$$=|\psi_{nlm}(r,\theta,\varphi)|^2\ r^2\sin\theta drd\theta d\varphi$$

$$W_{nl}(r)dr=\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}|R_{nl}(r)Y_{lm}(\theta,\varphi)|^2\ r^2\sin\theta drd\theta d\varphi$$
$$=R_{nl}^{\ 2}(r)r^2dr\int_0^{2\pi}d\varphi\int_0^{\pi}|Y_{lm}(\theta,\varphi)|^2\sin\theta d\theta$$
$$=R_{nl}^{\ 2}(r)r^2dr$$

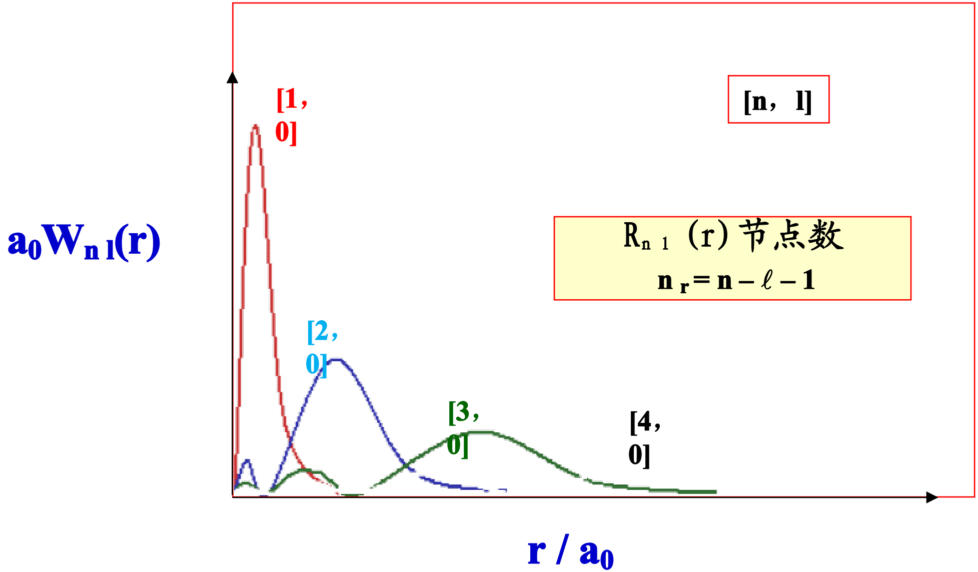
基态

$$W_{10}(r)=R_{10}^{\ 2}(r)r^2=\frac{4}{a_0^{\ 3}}r^2e^{-2r/a_0}$$

$$\frac{dW_{10}(r)}{dr}=\frac{4}{a_0^{\ 3}}(2r-\frac{2}{a_0}r^2)e^{-2r/a_0}$$

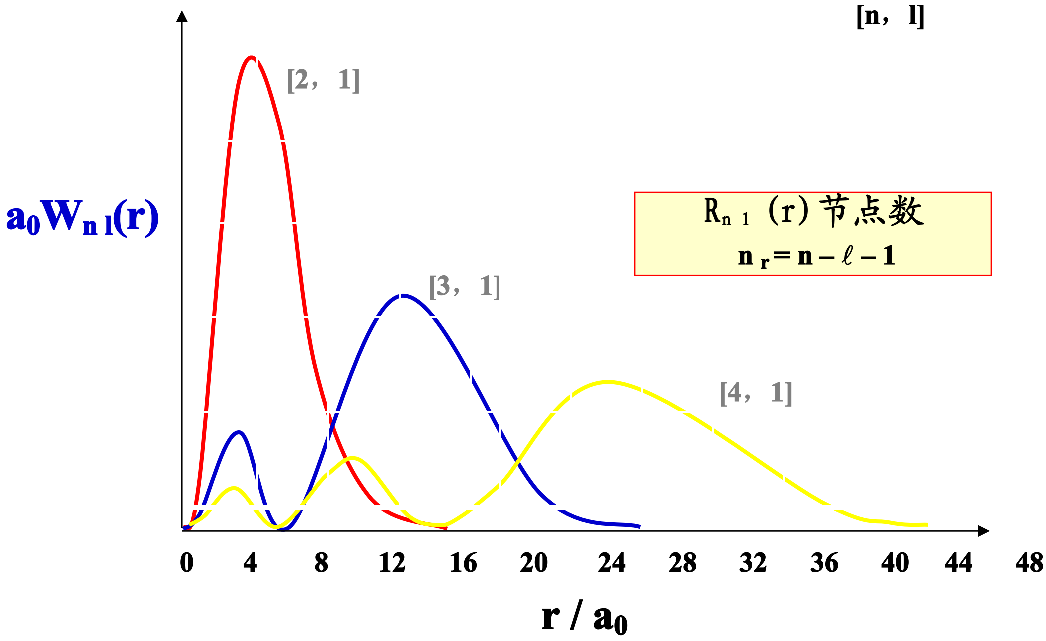
$$=\frac{8r}{a_0^{\ 4}}(a_0-r)e^{-2r/a_0}=0\rightarrow r=a_0$$

$W_{nl}(r) \sim r$



$$W_{10}(r) = R_{10}{}^2(r) r^2 = \frac{4}{a_0{}^3} r^2 e^{-2r/a_0}$$

$W_{nl}(r) \sim r$



$R_{nl}(r)$ 节点数

$n_r = n - \ell - 1$

角向概率分布

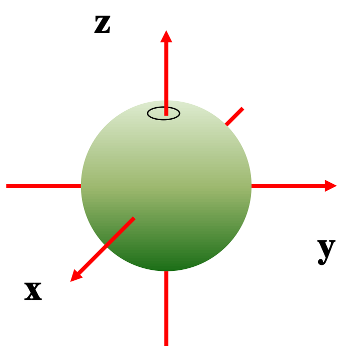
$$W_{nlm}(r,\theta,\varphi)d\tau = |\psi_{nlm}(r,\theta,\varphi)|^2\, r^2 dr \sin\theta d\theta d\varphi$$

在方向(θ ,φ)附近
立体角 **dΩ =sinθ dθ dφ**
内的概率

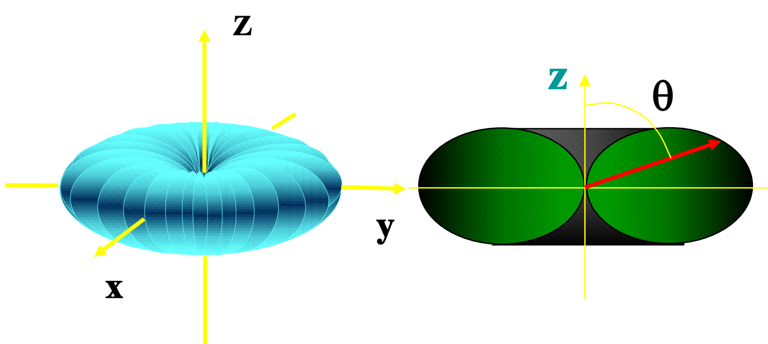
$$W_{lm}(\theta,\varphi)d\Omega = |Y_{lm}(\theta,\varphi)|^2\, d\Omega \int_0^\infty |R_{nl}(r) r^2 dr$$

$$= |Y_{lm}(\theta,\varphi)|^2\, d\Omega$$

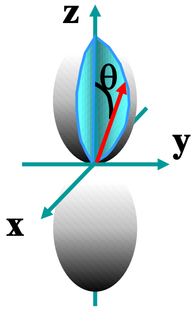
$$= N_{lm}^{\ 2}\, |P_l^m(\cos\theta)|^2\, d\Omega$$



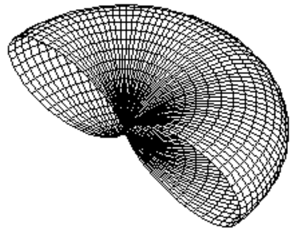
W00 = (1/4π)



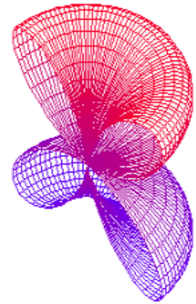
W1,±1 (θ) = (3/8 π)sin² θ



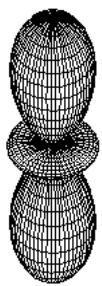
$W_{1,0}(\theta) = (3/4\,\pi)\cos^2\theta$



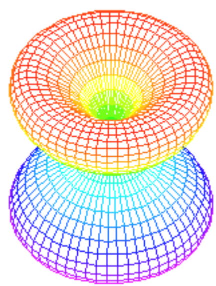
$W_{2,2}(\theta)$



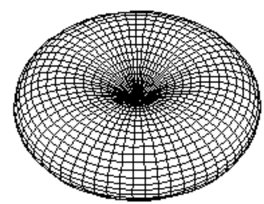
$W_{2,1}(\theta)$



$W_{2,0}(\theta)$



$W_{2,-1}(\theta)$



$W_{2,-2}(\theta)$

作业

3.2

§ 3.5 厄米算符本征函数的正交性

正交：$\int \phi_1 {}^* \phi_2 d\tau = 0$

定理：厄米算符的属于不同本征值的两个本征函数相互正交

证明：　已知　$\hat{F}\phi_n = F_n\phi_n$　$\hat{F}\phi_m = F_m\phi_m$

$$\int \phi_m {}^* \hat{F}\phi_n d\tau = \int (\hat{F}\phi_m)^* \phi_n d\tau \Leftarrow (\hat{F}\phi_m)^* = F_m\phi_m{}^* \Rightarrow \int (\hat{F}\phi_m)^* \phi_n d\tau = F_m \int \phi_m{}^* \phi_n d\tau$$

$$= F_n \int \phi_m{}^* \phi_n d\tau \Longrightarrow (F_m - F_n)\int \phi_m{}^* \phi_n d\tau = 0 \Longleftarrow$$

$$F_m \neq F_n \Rightarrow \boxed{\int \phi_m{}^* \phi_n d\tau = 0}$$

分立和连续谱正交归一表达式

分立谱
$$\begin{cases} \int \phi_n{}^* \phi_n d\tau = 1 \\ \int \phi_m{}^* \phi_n d\tau = 0 \end{cases}$$

$$\int \phi_m{}^* \phi_n d\tau = \delta_{mn}$$

连续谱
$$\int \phi_\lambda{}^* \phi_{\lambda'} d\tau = \delta(\lambda - \lambda')$$

正交归一函数系

上述的 ϕ_n 或 ϕ_λ 构成正交归一系

简并情形下的正交性

$$\hat{F}\phi_{ni} = F_n\phi_{ni},\ i = 1,2,\cdots,f$$

这些本征函数不一定正交，但可以将它们线性组合形成新的函数系，且满足正交归一条件

证明

如果新函数 ψ_{nj} 为 $\psi_{nj} = \sum_{i=1}^{f} A_{ji}\phi_{ni} \qquad j = 1,2,\cdots,f$

可以证明下述等式成立

$$\int \psi_{nj}{}^*\psi_{nj'}d\tau = \sum_{i=1}^{f}\sum_{i'=1}^{f} A_{ji}A_{j'i'}\int \phi_{ni}{}^*\phi_{ni'}d\tau = \delta_{jj'} \qquad j,j' = 1,2,\cdots,f$$

分两步证明：

（1） Ψ_{nj} 仍然是本征函数，本征值为 F_n

（2） 新函数满足正交归一条件

(1) Ψ nj 仍然是本征函数，本征值为 Fn

$$\hat{F}\psi_{nj} = \hat{F}\sum_{i=1}^{f} A_{ji}\phi_{ni}$$

$$= \sum_{i=1}^{f} A_{ji}\hat{F}\phi_{ni}$$

$$= F_n\sum_{i=1}^{f} A_{ji}\phi_{ni}$$

$$= F_n\psi_{nj}$$

（2） 新函数满足正交归一条件

只需要证明A_{ji}的数目， 即f^2比正交和归一条件建立的方程数目多

$$\psi_{nj} = \sum_{i=1}^{f} A_{ji}\phi_{ni} \qquad j = 1,2,\cdots,f$$

归一条件建立方程的数目为f，
正交条件建立方程的数目为 f(f−1)/2，
所以总数目为 f(f+1)/2

$$\int \psi_{nj}{}^{*}\psi_{nj'}d\tau = \delta_{jj'},\ j,j' = 1,2,\cdots,f$$

所以$f^2-f(f+1)/2=f(f-1)/2 \geqslant 0$，
新函数可以满足正交归一条件要求

结论：厄米算符的本征函数可以形成正交函数系

正交归一函数系的例子

（1）动量本征函数

（2）线性谐振子的能量本征函数

（3） 角动量算符的本征函数

1. L_z

2. L^2

（4） 氢原子的波函数

§3.6 算符与力学量的关系

（1） 力学量的可能值

根据量子力学假定，测量体系处于任意态时的任意力学量**F**的测量结果只能是该物理量所对应算符的本征函数的本征值之一λ**n**

$$\hat{F}\phi_n = \lambda_n \phi_n$$

先讨论一下本征函数的另一重要性质–完备系问题

(a) 力学量算符的本征函数组成完备系

a.1 函数系的完备性

如果任意函数ψ(x)可以用函数系$\phi_n(x)$ (n=1,2,...)展开

$$\psi(x) = \sum_n c_n \phi_n(x)$$

那么这个函数系φ**n(x)**是完备的

$$\Psi(\vec{r},t) = \int c(\vec{p},t)\psi_{\vec{p}}(\vec{r})d^3p$$

例如：动量本征函数构成完备系

或 $$\psi(\vec{r}) = \int c(\vec{p})\psi_{\vec{p}}(\vec{r})d^3p$$

a. 2. 力学量算符的本征函数组成完备系

I. 厄米算符的本征函数在某些条件下组成完备系

$$\hat{F}\phi_n = \lambda_n \phi_n \longrightarrow \psi(x) = \sum_n c_n \phi_n(x)$$

(II) 除了动量本征函数外，一些力学量的本征函数也可构成完备系，例如，

算符	本征函数系
L_Z	$\varphi_m(\varphi)=1/(2\pi)^{1/2}\exp[im\varphi]$
L^2, L_Z	$Y_{lm}(\theta, \varphi)$
无限深势能阱中粒子的能量	$\psi_n = (1/a)^{1/2}\sin[(n\pi(x+a)/2a)]$
线性谐振子的能量	$\psi_n(x) = N_n\exp[-\alpha^2x^2/2]H_n(\alpha x)$

量子力学中表示力学量的算符都是厄米算符，它们的本征函数组成完全系。

（b）力学量的可能值和相应的概率

由于φn(x)组成完备系，任意态可由它展开

$$\psi(x)=\sum_n c_n\phi_n(x)$$

系数 c_n独立于x

$$\int \phi_m^*(x)\psi(x)dx=\int \phi_m^*(x)\sum_n c_n\phi_n(x)dx$$

$$=\sum_n c_n\int \phi_m{}^*(x)\phi_n(x)dx$$

$$=\sum_n c_n\delta_{mn}=c_m$$

$$c_n=\int \phi_n^*(x)\psi(x)dx$$

可以证明如果φ(x)已经归一化，则 c_n也已经归一化

$$1=\int \psi^*(x)\psi(x)dx=\int\left[\sum_n c_n\phi_n\right]^*\left[\sum_m c_m\phi_m\right]dx=\sum_n\sum_m c_n{}^*c_m\int \phi_n^*\phi_m dx$$

$$=\sum_n\sum_m c_n{}^*c_m\delta_{nm}=\sum_n c_n{}^*c_n=\sum_n |c_n|^2$$

$$\psi(x)=\sum_n c_n\phi_n(x)$$

量子力学基本假定：表示力学量的算符都是厄米算符，它们的本征函数组成完全系，当体系处于波函数ψ(x)所描写的状态时，测量力学量F所得的数值，必定是其所对应算符的本征值之一，测得的概率是$|c_n|^2$.

这个假定的正确性，如同薛定谔方程一样，由整个理论与实验结果符合而得到验证。

按照由概率求平均值的法则，可以求得力学量F在ψ态中的平均值，为了与统计平均值区别，量子态的平均值称为期望值。例如，对长度x测量10次，4次结果是x_1，6次是x_2，则平均值是

$$\bar{x} = \frac{4x_1 + 6x_2}{10} = \tfrac{4}{10}x_1 + \tfrac{6}{10}x_2 = \omega_1 x_1 + \omega_2 x_2 = \sum_i \omega_i x_i$$

同上，测量力学量F处于任意态ψ的平均值可写为

$$\bar{F} = \sum_n |c_n|^2 \lambda_n \quad 或 \quad \bar{F} = \int \psi^*(x)\hat{F}\psi(x)dx$$

因为 $\bar{F} = \int \psi^*(x)\hat{F}\psi(x)dx = \int \left[\sum_n c_n\phi_n(x)\right]^* \hat{F}\sum_m c_m\phi_m(x)dx$

$$= \sum_n c_n^* \sum_m c_m \int \phi_n^*(x)\hat{F}\phi_m(x)dx = \sum_n \sum_m c_n^* c_m \lambda_m \int \phi_n^*(x)\phi_m(x)dx$$

$$= \sum_n \sum_m c_n^* c_m \lambda_m \delta_{nm} = \sum_n |c_n|^2 \lambda_n$$

如果波函数未归一化，则

$$\bar{F} = \frac{\sum_n |c_n|^2 \lambda_n}{\sum_n |c_n|^2} \qquad \bar{F} = \frac{\int \psi^*(x)\hat{F}\psi(x)dx}{\int \psi^*(x)\psi(x)dx}$$

例题：一空间转子处于如下状态

$$\Psi = \frac{1}{3} Y_{11}(\vartheta, \varphi) + \frac{2}{3} Y_{21}(\vartheta, \varphi)$$

求:

（1）Ψ 是否是 L^2的本征态?

（2）Ψ是否是 L_z的本征态?

（3）L^2的平均值是多少?

（4）L^2 和L_z 的可能值和相应概率是多少?

解:

(1)
$$\hat{L}^2 \Psi = \hat{L}^2 \left(\frac{1}{3} Y_{11}(\vartheta, \varphi) + \frac{2}{3} Y_{21}(\vartheta, \varphi) \right)$$
$$= \frac{1}{3}\left(1(1+1)\hbar^2 Y_{11}\right) + \frac{2}{3}\left(2(2+1)\hbar^2 Y_{21}\right)$$
$$= 2\hbar^2 \left(\frac{1}{3} Y_{11} + 2 Y_{21} \right) \neq \lambda \Psi$$

Ψ 不是L^2的本征态

(2) $$\hat{L}_z\Psi = \hat{L}_z\left(\frac{1}{3}Y_{11}(\vartheta,\varphi)+\frac{2}{3}Y_{21}(\vartheta,\varphi)\right)$$

$$=\frac{1}{3}\hbar Y_{11}+\frac{2}{3}\hbar Y_{21}$$

$$=\hbar\left(\frac{1}{3}Y_{11}+\frac{2}{3}Y_{21}\right) = \hbar\Psi$$

Ψ 是$\mathbf{L_z}$的本征态，本征值为$\hbar$.

（3）求L^2的平均值

方法 I $$\overline{F}=\int\psi^*(x)\hat{F}\psi(x)dx$$ (ψ 已经归一)

$$1=c^2\int\psi^*\psi d\Omega = c^2\int\left(\frac{1}{3}Y_{11}+\frac{2}{3}Y_{21}\right)^*\left(\frac{1}{3}Y_{11}+\frac{2}{3}Y_{21}\right)d\Omega$$

$$=c^2\int\left(\frac{1}{9}Y_{11}{}^*Y_{11}+\frac{4}{9}Y_{21}{}^*Y_{21}+\frac{2}{9}Y_{11}{}^*Y_{21}+\frac{2}{9}Y_{21}{}^*Y_{11}\right)d\Omega$$

$$=c^2\left(\frac{1}{9}+\frac{4}{9}\right)=\frac{5}{9}c^2 \quad\Rightarrow\quad c=\frac{3}{\sqrt{5}}$$

归一化波函数

$$\Psi = c\left(\frac{1}{3}Y_{11} + \frac{2}{3}Y_{21}\right) = \frac{3}{\sqrt{5}}\left(\frac{1}{3}Y_{11} + \frac{2}{3}Y_{21}\right) = \frac{1}{\sqrt{5}}(Y_{11} + 2Y_{21})$$

$$\overline{L^2} = \int \Psi^* \hat{L}^2 \Psi \, d\Omega = \int \frac{1}{\sqrt{5}}(Y_{11} + 2Y_{21})^* \hat{L}^2 \frac{1}{\sqrt{5}}(Y_{11} + 2Y_{21}) d\Omega$$

$$= \frac{1}{5}\int (Y_{11} + 2Y_{21})^* (2\hbar^2 Y_{11} + 6\hbar^2 2Y_{21}) d\Omega \quad = \frac{1}{5}\int \left(2\hbar^2 |Y_{11}|^2 + 24\hbar^2 |Y_{21}|^2\right) d\Omega$$

$$= \frac{1}{5}[2\hbar^2 + 24\hbar^2] = \frac{26}{5}\hbar^2$$

方法 II $\quad \overline{F} = \sum_n |c_n|^2 \lambda_n$

$$\Psi = \frac{1}{\sqrt{5}}(Y_{11} + 2Y_{21}) \qquad \overline{L^2} = \left|\frac{1}{\sqrt{5}}\right|^2 2\hbar^2 + \left|\frac{2}{\sqrt{5}}\right|^2 6\hbar^2 = \frac{26}{5}\hbar^2$$

(4) $\quad L^2 = \begin{cases} 2\hbar^2 \\ 6\hbar^2 \end{cases}$ 相应概率 $\begin{cases} \frac{1}{5} \\ \frac{4}{5} \end{cases}$

$L_z = \hbar$ 相应概率 1

作业

3.7

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§ 3.7 算符的对易关系 两力学量同时有确定值的条件 不确定关系

1.算符的对易关系

例如

$$\begin{cases} x \\ \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \end{cases}$$

不对易

证明：(1) $x\hat{p}_x\psi = x(-i\hbar \frac{\partial}{\partial x})\psi = -i\hbar x \frac{\partial}{\partial x}\psi$

(2) $\hat{p}_x x\psi = (-i\hbar \frac{\partial}{\partial x})x\psi = -i\hbar\psi - i\hbar x \frac{\partial}{\partial x}\psi$

所以 $x\hat{p}_x \neq \hat{p}_x x$

但（$x\hat{p}_x - \hat{p}_x x$）$\psi = i\hbar\psi$

且 ψ 是任意波函数

则 $x\hat{p}_x - \hat{p}_x x = i\hbar$

同理，

$$\begin{cases} y\hat{p}_y - \hat{p}_y y = i\hbar \\ z\hat{p}_z - \hat{p}_z z = i\hbar \end{cases}$$

但是

$$\begin{cases} x\hat{p}_y - \hat{p}_y x = 0 \\ x\hat{p}_z - \hat{p}_z x = 0 \end{cases} \quad \begin{cases} y\hat{p}_x - \hat{p}_x y = 0 \\ y\hat{p}_z - \hat{p}_z y = 0 \end{cases} \quad \begin{cases} z\hat{p}_x - \hat{p}_x z = 0 \\ z\hat{p}_y - \hat{p}_y z = 0 \end{cases}$$

$$\hat{p}_x\hat{p}_y - \hat{p}_y\hat{p}_x = 0 \quad \hat{p}_y\hat{p}_z - \hat{p}_z\hat{p}_y = 0 \quad \hat{p}_z\hat{p}_x - \hat{p}_x\hat{p}_z = 0$$

综上

$$x_\alpha \hat{p}_\beta - \hat{p}_\beta x_\alpha = i\hbar\delta_{\alpha\beta}$$

$$\hat{p}_\alpha \hat{p}_\beta - \hat{p}_\beta \hat{p}_\alpha = 0$$

$$\alpha, \beta = x, y, z$$

注意: Ô和Û对易， Û 和Ê对易， 并不意味着Ô和Ê一定对易， 例如

$(I)\ \hat{p}_x \leftrightarrow \hat{p}_y, \hat{p}_y \leftrightarrow x$，$\hat{p}_x$ 和 x不对易；

$(II)\ \hat{p}_x \leftrightarrow \hat{p}_y, \hat{p}_y \leftrightarrow z$，$\hat{p}_x$和 z对易

为了表达的简便，定义对易括号 **[Ô,Û] ≡ ÔÛ - ÛÔ** 则有

$$[x_\alpha, \hat{p}_\beta] = i\hbar\delta_{\alpha\beta}$$

$$\alpha, \beta = x, y, z$$

1) [Ô,Û] = - [Û,Ô]
2) [Ô,Û+Ê] = [Ô,Û] + [Ô, Ê]
3) [Ô,ÛÊ] = [Ô,Û]Ê+ Û[Ô,Ê]
4) [Ô,[Û,Ê]] + [Û,[Ê, Ô]] + [Ê,[Ô,Û]] = 0
(雅克比等式)

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

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

同理

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

或

$$[\hat{L}_\alpha, \hat{L}_\beta] = i\hbar \varepsilon_{\alpha\beta\gamma} \hat{L}_\gamma$$

$\varepsilon_{\alpha\beta\gamma} - Levi-Civita$ 标记

和

$$\varepsilon_{\alpha\beta\gamma} = -\varepsilon_{\beta\alpha\gamma} = -\varepsilon_{\alpha\gamma\beta}$$

$$\varepsilon_{123} = 1$$

这里 $\alpha,\ \beta,\ \gamma = 1,2,3$

或 x, y, z

则角动量算符可定义为

$$\hat{L} \times \hat{L} = i\hbar \hat{L}$$

2. 两力学量同时具有确定值的条件

定理：如果两个(或多个)算符有一组共同本征函数，且该组函数组成完全系，则这两个(或多个)算符彼此对易，反之亦然。

证明： 已知 $\begin{cases}\hat{F}\phi_n = F_n\phi_n \\ \hat{G}\phi_n = G_n\phi_n\end{cases} \quad n = 1,2,3,\cdots$

由于 ϕ_n c组成完备系，任意函数$\psi(x)$ 可展开成： $\psi(x) = \sum_n c_n\phi_n(x)$

则

$$(\hat{F}\hat{G} - \hat{G}\hat{F})\psi(x) = (\hat{F}\hat{G} - \hat{G}\hat{F})\sum_n c_n\phi_n$$

$$= \sum_n c_n(\hat{F}\hat{G} - \hat{G}\hat{F})\phi_n = \sum_n c_n(\hat{F}G_n - \hat{G}F_n)\phi_n$$

$$= \sum_n c_n(G_nF_n - F_nG_n)\phi_n = 0$$

由于 $\psi(x)$ 是任意函数，则 → $\hat{F}\hat{G} - \hat{G}\hat{F} = 0$

例 1：

$$\begin{cases} \hat{p}_x, \hat{p}_y, \hat{p}_z \text{ 对易;} \\ \text{共同本征函数组成完全系 } \psi_{\vec{p}}(\vec{r}) = \dfrac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{p}\bullet\vec{r}} \\ \text{三个算符有确定值 } p_x, p_y, p_z. \end{cases}$$

例 2：

$$\begin{cases} \text{氢原子:} \hat{H}, \hat{L}^2, \hat{L}_z \text{对易} \\ \text{共同完全函数系:} \psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\vartheta, \varphi) \\ \text{同时具有确定值:} E_n, l(l+1)\hbar^2, m\hbar. \end{cases}$$

例 3：

$$\begin{cases} \text{定轴转子}: \hat{H} = \dfrac{\hat{L}_z^{\,2}}{2I}, \hat{L}_z \text{ 对易}; \\ \text{共同完全系}: \Phi_m(\varphi) = \dfrac{1}{\sqrt{2\pi}} e^{im\varphi} \\ \text{同时确定值}: E_m = \dfrac{m^2\hbar^2}{2I}, m\hbar, (m = 0, \pm 1, \cdots). \end{cases}$$

例 **4**：

$$\begin{cases} \text{空间转子}: \hat{H} = \dfrac{\hat{L}^2}{2I}, \hat{L}^2, \hat{L}_z \text{ 对易}; \\ \text{共同完全系}: Y_{lm}(\vartheta, \varphi) \quad \begin{cases} l = 0,1,2,\cdots \\ m = 0, \pm 1, \cdots \pm l \end{cases} \\ \text{同时确定值}: E_l = \dfrac{l(l+1)\hbar^2}{2I}, l(l+1)\hbar^2, m\hbar. \end{cases}$$

力学量的完全集合

定义：

要完全确定体系所处的状态，需要有一组相互对易的力学量. 这 组完全确定体系状态的力学量，称为力学量的完全集合. 在完全集合中力学量的数目一般与体系自由度的数目相等。

例1： 三维空间中自由粒子的自由度是3，则需要三个力学量 $\hat{P}_x, \hat{P}_y, \hat{P}_z.$

例2： 氢原子中电子的自由度是3，需要三个力学量. $\hat{H}, \hat{L}^2, \hat{L}_z.$

例3： 线性谐振子只有1个自由度，需要一个力学量 $\hat{H}$

从对易关系看出，普朗克常数**h**在力学量的对易关系中占有重要的地位，标志着微观规律和宏观规律之间的差异。如果**h**在所讨论的问题中可以略去，则坐标和动量、角动量各分量之间都是对易的，这些力学量都同时具有确定值，微观规律就过渡到宏观规律。

两个算符不对易，不能同时具有确定值，现估计在同一个态中，两个不对易算符不确定程度之间的关系。

设 $\hat{F}\hat{G}-\hat{G}\hat{F}=i\hat{k}$ $\quad \Delta\hat{F}=\hat{F}-\overline{F} \quad \Delta\hat{G}=\hat{G}-\overline{G}$

k 是一个算符或普通的数

$$(\Delta\hat{F})^{+}=(\hat{F}-\overline{F})^{+}=\hat{F}^{+}-\overline{F}^{*}=\hat{F}-\overline{F}=\Delta\hat{F}$$

$$\boxed{I(\xi)=\int |\xi\Delta\hat{F}\psi-i\Delta\hat{G}\psi|^{2}d\tau \geq 0}$$

$$=\int [\xi\Delta\hat{F}\psi-i\Delta\hat{G}\psi]^{*}[\xi\Delta\hat{F}\psi-i\Delta\hat{G}\psi]d\tau$$

$$=\int [\xi(\Delta\hat{F}\psi)^{*}+i(\Delta\hat{G}\psi)^{*}][\xi\Delta\hat{F}\psi-i\Delta\hat{G}\psi]d\tau$$

$$=\xi^{2}\int (\Delta\hat{F}\psi)^{*}(\Delta\hat{F}\psi)d\tau-i\xi\int (\Delta\hat{F}\psi)^{*}(\Delta\hat{G}\psi)d\tau$$
$$+i\xi\int (\Delta\hat{G}\psi)^{*}(\Delta\hat{F}\psi)d\tau+\int (\Delta\hat{G}\psi)^{*}(\Delta\hat{G}\psi)d\tau$$

$$=\xi^{2}\int \psi^{*}\Delta\hat{F}(\Delta\hat{F}\psi)d\tau-i\xi\int \psi^{*}\Delta\hat{F}(\Delta\hat{G}\psi)d\tau$$
$$+i\xi\int \psi^{*}\Delta\hat{G}(\Delta\hat{F}\psi)d\tau+\int \psi^{*}\Delta\hat{G}(\Delta\hat{G}\psi)d\tau$$

$$=\xi^{2}\int \psi^{*}(\Delta\hat{F})^{2}\psi d\tau-i\xi\int \psi^{*}[\Delta\hat{F}\Delta\hat{G}-\Delta\hat{G}\Delta\hat{F}]\psi d\tau+\int \psi^{*}(\Delta\hat{G})^{2}\psi d\tau$$

$$I(\xi)=\xi^2\int\psi^*(\Delta\hat F)^2\psi d\tau-i\xi\int\psi^*\boxed{[\Delta\hat F\Delta\hat G-\Delta\hat G\Delta\hat F]}\psi d\tau+\int\psi^*(\Delta\hat G)^2\psi d\tau$$

$$\boxed{[\Delta\hat F\Delta\hat G-\Delta\hat G\Delta\hat F]\equiv[\Delta\hat F,\ \Delta\hat G]}=[\hat F-\overline{F},\ \hat G-\overline{G}]$$

$$=[\hat F-\overline{F},\ \hat G]-[\hat F-\overline{F},\ \overline{G}]=[\hat F,\ \hat G]-[\overline{F},\ \hat G]=[\hat F,\ \hat G]=i\hat k$$

所以 $I(\xi)=\xi^2\int\psi^*(\Delta\hat F)^2\psi d\tau-i\xi\int\psi^*[i\hat k]\psi d\tau+\int\psi^*(\Delta\hat G)^2\psi d\tau$

$$\boxed{I(\xi)=\xi^2\overline{(\Delta\hat F)^2}+\xi\overline{k}+\overline{(\Delta\hat G)^2}\geq 0}$$

对任意实数 ξ

和 $\overline{(\Delta\hat F)^2}\bullet\overline{(\Delta\hat G)^2}\geq\dfrac{(\overline{k})^2}{4}$

不确定关系

这里 $\overline{k}=\int\psi^*\hat k\psi d\tau$

均方差

$$\overline{(\Delta\hat F)^2}=\overline{(\hat F-\overline{F})^2}=\overline{\hat F^2-2\hat F\overline{F}+\overline{F}^2}$$

$$=\overline{F^2}-\overline{2\hat F\overline{F}}+\overline{\overline{F}^2}=\overline{F^2}-2\overline{F}\,\overline{F}+\overline{F}^2$$

$$=\overline{F^2}-\overline{F}^2$$

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

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

表明:

坐标和动量的均方差不能同时为零，一个小，则另一个大。

线性谐振子的零点能

线性谐振子的能量

$$E=\overline{H}=\frac{\overline{p^2}}{2\mu}+\frac{1}{2}\mu\omega^2\overline{x^2}$$

$$\begin{cases}\overline{(\Delta x)^2}=\overline{x^2}-\overline{x}^2\\ \overline{(\Delta p)^2}=\overline{p^2}-\overline{p}^2\end{cases} \Rightarrow \begin{cases}\overline{x^2}=\overline{(\Delta x)^2}+\overline{x}^2\\ \overline{p^2}=\overline{(\Delta p)^2}+\overline{p}^2\end{cases}$$

$$\overline{x}=\int_{-\infty}^{\infty}\psi_n^* x\psi_n dx=N_n^2\int_{-\infty}^{\infty}\underline{xe^{-\alpha^2x^2}H_n^2(\alpha x)}dx=0$$

奇函数

$$\overline{p}=\int_{-\infty}^{\infty}\psi_n^*\hat{p}\psi_n dx=-i\hbar\int_{-\infty}^{\infty}\psi_n^*\frac{\partial}{\partial x}\psi_n dx$$

$x=\infty$

$\psi_n=0$

$$=-i\hbar\psi_n^*\psi_n\Big|_{-\infty}^{\infty}+i\hbar\int_{-\infty}^{\infty}\psi_n\frac{\partial}{\partial x}\psi_n^* dx$$

$$=i\hbar\int_{-\infty}^{\infty}\psi_n\frac{\partial}{\partial x}\psi_n^* dx$$

ψ_n 是实函数

$$=i\hbar\int_{-\infty}^{\infty}\psi_n^*\frac{\partial}{\partial x}\psi_n dx$$

$$=-\overline{p} \qquad \therefore \overline{p}=0$$

所以 $\begin{cases}\overline{x^2}=\overline{(\Delta x)^2}\\ \overline{p^2}=\overline{(\Delta p)^2}\end{cases}$

$$E=\overline{H}=\frac{\overline{p^2}}{2\mu}+\frac{1}{2}\mu\omega^2\overline{x^2}=\frac{\overline{(\Delta p)^2}}{2\mu}+\frac{1}{2}\mu\omega^2\overline{(\Delta x)^2}$$

$$\because\ \overline{(\Delta x)^2}\bullet\overline{(\Delta p_x)^2}\geq\frac{\hbar^2}{4}\quad\therefore\overline{(\Delta p_x)^2}\geq\frac{\hbar^2}{4\overline{(\Delta x)^2}}$$

$$E=\frac{\overline{(\Delta p_x)^2}}{2\mu}+\frac{1}{2}\mu\omega^2\overline{(\Delta x)^2}\geq\frac{\hbar^2}{8\mu\overline{(\Delta x)^2}}++\frac{1}{2}\mu\omega^2\overline{(\Delta x)^2}$$

令 $\boldsymbol{y=\overline{(\Delta x)^2},\ E\geq E(y)=\frac{\hbar^2}{8\mu\overline{(\Delta x)^2}}+\frac{1}{2}\mu\omega^2\overline{(\Delta x)^2}=\frac{\hbar^2}{8\mu y}+\frac{1}{2}\mu\omega^2 y}$

$$\frac{\partial E(y)}{\partial y}=-\frac{\hbar^2}{8\mu y^2}+\frac{1}{2}\mu\omega^2=0,\ \frac{\partial^2 E}{\partial y^2}>0$$

$$\downarrow$$

$$y=\pm\frac{\hbar}{2\mu\omega}=\overline{(\Delta x)^2}\geq 0\ \rightarrow\ E_{\min}(y)=\frac{\hbar^2}{8\mu\left(\frac{\hbar}{2\mu\omega}\right)}+\frac{1}{2}\mu\omega^2\left(\frac{\hbar}{2\mu\omega}\right)=\frac{1}{2}\hbar\omega$$

$$\rightarrow\quad\because E\geq E(y)\geq E_{\min}(y)$$

$$\therefore E_{\min}=E_{\min}(y)=\frac{1}{2}\hbar\omega$$

角动量的不确定关系

$$\because [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \qquad \therefore \overline{(\Delta L_x)^2} \bullet \overline{(\Delta L_y)^2} \ge \frac{\hbar^2}{4} \overline{L_z}^2$$

$$\text{在}\hat{L}_z\text{的本征态,}\ \overline{(\Delta L_x)^2} \bullet \overline{(\Delta L_y)^2} \ge \frac{\hbar^2}{4}(m\hbar)^2 = \frac{1}{4} m^2 \hbar^4$$

例题：运用不确定关系证明在L_z的本征态Y_{lm}， $\langle L_x \rangle = \langle L_y \rangle = 0$

证明

$$\because [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \qquad \therefore \overline{(\Delta L_y)^2} \bullet \overline{(\Delta L_z)^2} \ge \frac{\hbar^2}{4} \overline{L_x}^2$$

在L_z的本征态Y_{lm} $\qquad \overline{(\Delta L_z)^2} = 0$

$$\overline{(\Delta L_y)^2} \bullet 0 \ge \frac{\hbar^2}{4} \overline{L_x}^2 \Rightarrow 0 \ge \frac{\hbar^2}{4} \overline{L_x}^2 \qquad \overline{L_x} = 0$$

$$\because [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

$$\therefore \overline{(\Delta L_z)^2} \bullet \overline{(\Delta L_x)^2} \ge \frac{\hbar^2}{4} \overline{L_y}^2 \rightarrow \qquad \overline{L_y} = 0$$

$$\left.\begin{matrix} \overline{L_x} = 0 \\ \overline{L_y} = 0 \end{matrix}\right\} \rightarrow \langle L_x \rangle = \langle L_y \rangle = 0$$

作业

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§3.8 力学量期望值随时间的变化 守恒定律

$$\overline{F}=\int\psi^*(x,t)\hat{F}\psi(x,t)dx$$

$$\frac{d\overline{F}}{dt}=\int\psi^*\frac{\partial\hat{F}}{\partial t}\psi dx+\int\frac{\partial\psi^*}{\partial t}\hat{F}\psi dx+\int\psi^*\hat{F}\frac{\partial\psi}{\partial t}dx$$

$$i\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi\Rightarrow\frac{\partial\Psi}{\partial t}=\frac{1}{i\hbar}\hat{H}\Psi\qquad\frac{\partial\Psi^*}{\partial t}=-\frac{1}{i\hbar}(\hat{H}\Psi)^*$$

$$\frac{d\overline{F}}{dt}=\int\psi^*\frac{\partial\hat{F}}{\partial t}\psi dx-\frac{1}{i\hbar}\int(\hat{H}\Psi)^*\hat{F}\psi dx+\frac{1}{i\hbar}\int\psi^*\hat{F}\hat{H}\Psi dx$$

$$=\int\psi^*\frac{\partial\hat{F}}{\partial t}\psi dx-\frac{1}{i\hbar}\int\Psi^*\hat{H}\hat{F}\psi dx+\frac{1}{i\hbar}\int\psi^*\hat{F}\hat{H}\Psi dx$$

$$=\int\psi^*\frac{\partial\hat{F}}{\partial t}\psi dx+\frac{1}{i\hbar}\int\psi^*(\hat{F}\hat{H}-\hat{H}\hat{F})\Psi dx$$

$$=\overline{\frac{\partial\hat{F}}{\partial t}}+\frac{1}{i\hbar}\overline{(\hat{F}\hat{H}-\hat{H}\hat{F})}=\overline{\frac{\partial\hat{F}}{\partial t}}+\frac{1}{i\hbar}\overline{[\hat{F},\hat{H}]}$$

如果F不显含时间，且与H对易，则有下式成立

$$\frac{d\overline{F}}{dt}=\overline{\frac{\partial\hat{F}}{\partial t}}+\frac{1}{i\hbar}\overline{[\hat{F},\hat{H}]}=\frac{1}{i\hbar}\overline{[\hat{F},\hat{H}]}=0$$

表明：F的**期望值**不随时间改变，称为运动恒量

运动恒量举例

（1）自由粒子的动量守恒-动量守恒定律

（2）中心力场中运动粒子的角动量守恒-角动量守恒定律

（3）哈密顿不显含时间的体系的能量守恒-能量守恒定律

（4）哈密顿对空间反演不变时的宇称守恒-宇称守恒定律

宇称算符

$$\hat{P}\psi(x,t)=\psi(-x,t)$$

$$\hat{P}^2\psi(x,t)=\hat{P}[\hat{P}\psi(x,t)]=\hat{P}\psi(-x,t)=\psi(x,t)$$

P^2的本征值是1，P的本征值是1（偶宇称）或-1（奇宇称）

$$\hat{P}\psi(x,t)=\lambda\psi(x,t)\quad \hat{P}^2\psi(x,t)=\lambda^2\psi(x,t)=\psi(x,t)$$

$$\lambda^2=1,\ \lambda=\pm 1$$

若对任意态 $\psi(x,t)$有$\hat{H}(x)\psi(x,t)=\phi(x,t)$

则$\hat{H}(-x)\psi(-x,t)=\phi(-x,t)$

$$\hat{P}\hat{H}(x)\psi(x,t)=\hat{P}\phi(x,t)=\phi(-x,t)$$

$$=\hat{H}(-x)\psi(-x,t)=\hat{H}(-x)\hat{P}\psi(x,t)$$

$$=\hat{H}(x)\hat{P}\psi(x,t)$$

这表示宇称是运动恒量 。同时表明，

若$\hat{H}(x)$在空间反演后保持不变 ，则$\hat{H}$与$\hat{P}$对易

它们有共同的本征函数 ，从而体系能量本征函 数可以有

确定的宇称，并且不随 时间改变

体系能量本征函数可以有确定的宇称，并且不随时间改变
这就是量子力学中的宇称守恒定律