量子力学与统计物理

Quantum mechanics and statistical physics

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第五章：求解定态薛定谔方程

第四讲：电子在库仑场中的运动

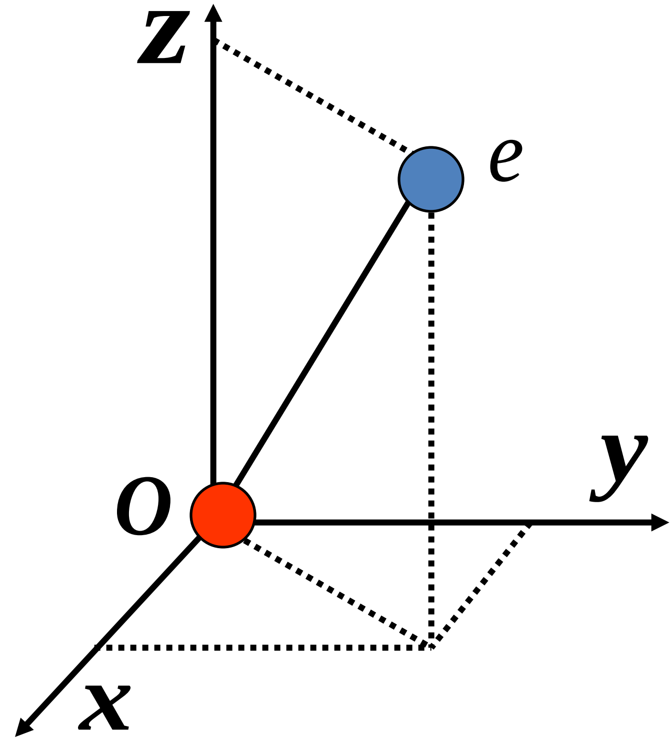
库仑势是一种有心势

物理学的几种有心势

物理学科	有心势
原子物理	库仑场 $-\frac{e_s^2}{r}$、屏蔽库仑场 $-\frac{e_s^2}{r}\left(1+\lambda\frac{a_0}{r}\right)$
原子核物理	各向同性谐振子场 $\frac{1}{2}Kr^2$、球方势阱、Woods-Saxon势
粒子物理	线性中心势 Ar、对数中心势 $V_0 \ln\frac{r}{r_0}$

1　库仑势能函数

$$V(r) = -\frac{Ze_s^2}{r}, \quad e_s = \frac{e}{\sqrt{4\pi\varepsilon_0}}$$



2　哈密顿量

$$H = \frac{p^2}{2m} + V(r) \Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze_s^2}{r}$$

势场具有球对称性，用球坐标系处理最方便。

3. 球坐标系下的哈密顿量

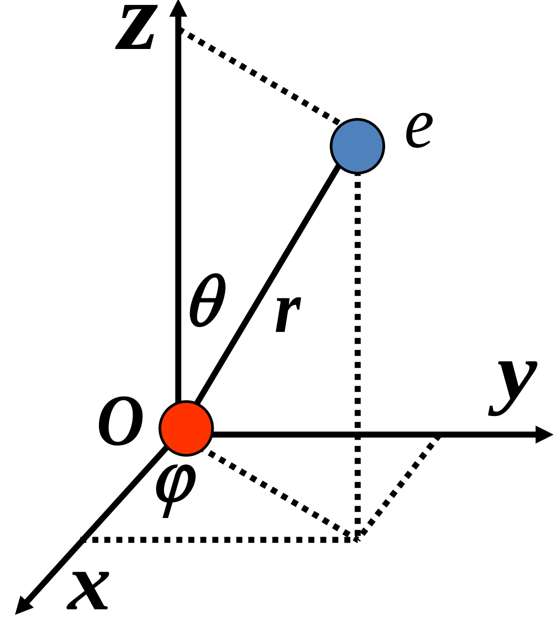
[方法1]

$$\hat{H}=\frac{\hat{\boldsymbol{p}}^2}{2\mu}+V(r),\ r=|\boldsymbol{r}|$$

$$\hat{\boldsymbol{p}}=\hat{\boldsymbol{p}}_r+\hat{\boldsymbol{p}}_\perp,\ \hat{\boldsymbol{p}}^2=\hat{\boldsymbol{p}}_r^2+\hat{\boldsymbol{p}}_\perp^2,$$

$$\hat{\boldsymbol{p}}_\perp=\frac{\boldsymbol{r}\times\hat{\boldsymbol{p}}}{r}=\frac{\hat{L}}{r},\ \hat{p}_\perp=|\hat{\boldsymbol{p}}_\perp|,$$

$$\hat{p}_r=|\hat{\boldsymbol{p}}_r|=\frac{1}{r}\boldsymbol{r}\cdot\hat{\boldsymbol{p}}$$



但这样的量子化有问题！所得的 $\hat{p}_r$ 不是厄密算符

采用Weyl量子化规则

$$\hat{p}_r = \frac{1}{r}\hat{\vec{r}}\cdot\hat{\vec{p}} \xrightarrow{\text{对称化}} \hat{p}_r = \frac{1}{2}\left(\frac{1}{r}\hat{\vec{r}}\cdot\hat{\vec{p}} + \hat{\vec{r}}\cdot\hat{\vec{p}}\frac{1}{r}\right) \Rightarrow$$

$$\hat{p}_r = \frac{1}{2}\left(\frac{x}{r}\hat{p}_x + \frac{y}{r}\hat{p}_y + \frac{z}{r}\hat{p}_z + \hat{p}_x\frac{x}{r} + \hat{p}_y\frac{y}{r} + \hat{p}_z\frac{z}{r}\right)$$

$$= \frac{1}{2}\left(\frac{x}{r}\hat{p}_x + \hat{p}_x\frac{x}{r}\right) + \frac{1}{2}\left(\frac{y}{r}\hat{p}_y + \hat{p}_y\frac{y}{r}\right) + \frac{1}{2}\left(\frac{z}{r}\hat{p}_z + +\hat{p}_z\frac{z}{r}\right),$$

$$x_1 = x,\ x_2 = y,\ x_3 = z,\ r = \sqrt{x_1^2 + x_2^2 + x_3^2} \Rightarrow \frac{\partial}{\partial x_i} = \frac{\partial r}{\partial x_i}\frac{\partial}{\partial r} = \frac{x_i}{r}\frac{\partial}{\partial r},\quad i = 1, 2, 3,$$

$$\hat{p}_{x_i} = -i\hbar\frac{\partial}{\partial x_i},\quad \left(\frac{x_i}{r}\hat{p}_{x_i} + \hat{p}_{x_i}\frac{x_i}{r}\right)\psi = -i\hbar\left(2\frac{x_i}{r}\frac{\partial}{\partial x_i} + \frac{1}{r} - \frac{x_i^2}{r^3}\right)\psi \Rightarrow$$

$$\frac{x}{r}\hat{p}_x + \hat{p}_x\frac{x}{r} = -i\hbar\left(2\frac{x}{r}\frac{\partial}{\partial x} + \frac{1}{r} - \frac{x^2}{r^3}\right) = -i\hbar\left(2\frac{x^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{r} - \frac{x^2}{r^3}\right),$$

$$\frac{y}{r}\hat{p}_y + \hat{p}_y\frac{y}{r} = -i\hbar\left(2\frac{y}{r}\frac{\partial}{\partial y} + \frac{1}{r} - \frac{y^2}{r^3}\right) = -i\hbar\left(2\frac{y^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{r} - \frac{y^2}{r^3}\right),$$

$$\frac{z}{r}\hat{p}_z + \hat{p}_z\frac{z}{r} = -i\hbar\left(2\frac{z}{r}\frac{\partial}{\partial z} + \frac{1}{r} - \frac{z^2}{r^3}\right) = -i\hbar\left(2\frac{z^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{r} - \frac{z^2}{r^3}\right),$$

$$\hat{p}_r = \frac{1}{2}(\frac{x}{r}\hat{p}_x + \hat{p}_x\frac{x}{r}) + \frac{1}{2}(\frac{y}{r}\hat{p}_y + \hat{p}_y\frac{y}{r}) + \frac{1}{2}(\frac{z}{r}\hat{p}_z + + \hat{p}_z\frac{z}{r})$$

$$= -\mathrm{i}\hbar(\frac{x^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{2r} - \frac{x^2}{2r^3} + \frac{y^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{2r} - \frac{y^2}{2r^3} + \frac{z^2}{r^2}\frac{\partial}{\partial r} + \frac{1}{2r} - \frac{z^2}{2r^3})$$

$$= -\mathrm{i}\hbar(\frac{x^2+y^2+z^2}{r^2}\frac{\partial}{\partial r} + \frac{3}{2r} - \frac{x^2+y^2+z^2}{2r^3}) = -\mathrm{i}\hbar(\frac{\partial}{\partial r} + \frac{1}{r}),$$

$$\hat{p}_r^2 = -\hbar^2(\frac{\partial}{\partial r} + \frac{1}{r})(\frac{\partial}{\partial r} + \frac{1}{r}) = -\hbar^2(\frac{\partial}{\partial r}\frac{\partial}{\partial r} + \frac{\partial}{\partial r}\frac{1}{r} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2})$$

$$= -\hbar^2(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) = -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}),$$

$$\hat{p}_\perp = \hat{L}/r, \quad \hat{p}_\perp^2 = \hat{L}^2/r^2,$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + V(r) = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{p}_\perp^2}{2\mu} + V(r) \Rightarrow$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{\hat{L}^2}{2\mu r^2} + V(r)$$

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

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

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2}{r^2\hbar^2} = -\frac{1}{\hbar^2}\left(p_r^2 + p_\perp^2\right)$$

$$\hat{p}^2 = -\hbar^2\nabla^2 = p_r^2 + p_\perp^2$$

$$= -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{r^2} \Rightarrow$$

$$\frac{\hat{p}^2}{2\mu} = -\frac{\hbar^2\nabla^2}{2\mu} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2}$$

$$= \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2}$$

4. 球坐标系下的薛定谔方程

$$\hat{H}=-\frac{\hbar^2\nabla^2}{2\mu}+V(r)=\frac{\hat{p}_r^2}{2\mu}+\frac{\hat{L}^2}{2\mu r^2}+V(r)$$

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)$$

能量本征方程： $\hat{H}\psi_{nlm}=E\psi_{nlm}\Rightarrow$

$$[\frac{\hat{p}_r^2}{2\mu}+\frac{\hat{L}^2}{2\mu r^2}+V(r)]R_{nl}(r)Y_{lm}(\theta,\varphi)=ER_{nl}(r)Y_{lm}(\theta,\varphi)$$

$$\because\ \hat{L}^2Y_{lm}(\theta,\varphi)=l(l+1)\hbar^2Y_{lm}(\theta,\varphi)\Rightarrow$$

$$[\frac{\hat{p}_r^2}{2\mu}+\frac{l(l+1)\hbar^2}{2\mu r^2}+V(r)]R_{nl}(r)Y_{lm}(\theta,\varphi)=ER_{nl}(r)Y_{lm}(\theta,\varphi)$$

$\Rightarrow$ 径向薛定谔方程

$$[\frac{\hat{p}_r^2}{2\mu}+\frac{\hbar^2}{2\mu r^2}l(l+1)+V(r)]R_{nl}(r)=ER_{nl}(r)$$

$$[\frac{\hat{p}_r^2}{2\mu}+\frac{\hbar^2}{2\mu r^2}l(l+1)+V(r)]R_{nl}(r)=ER_{nl}(r)$$

$$\frac{\hat{p}_r^2}{2\mu}=-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}),\ V(r)=-\frac{Ze_s^{\ 2}}{r},\ e_s=\frac{e}{\sqrt{4\pi\varepsilon_0}}\Rightarrow$$

$$[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})+\frac{\hbar^2}{2\mu r^2}l(l+1)-\frac{Ze_s^{\ 2}}{r}]R_{nl}(r)=ER_{nl}(r)$$

$$\xrightarrow{\text{改记为}R(r)}[\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})-\frac{\hbar^2}{2\mu r^2}l(l+1)+E+\frac{Ze_s^{\ 2}}{r}]R(r)=0$$

整理后的径向薛定谔方程

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}[r^2\frac{\mathrm{d}}{\mathrm{d}r}R(r)]+[\frac{2\mu}{\hbar^2}(E+\frac{Ze_s^{\ 2}}{r})-\frac{l(l+1)}{r^2}]R(r)=0,\quad (1)$$

5. 解径向薛定谔方程

1) 我们先简化它，令 $R(r)=u(r)/r$ ，代入

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}[r^2\frac{\mathrm{d}}{\mathrm{d}r}R(r)]+[\frac{2\mu}{\hbar^2}(E+\frac{Ze_s{}^2}{r})-\frac{l(l+1)}{r^2}]R(r)=0, \quad (1)$$

得：

$$\frac{\mathrm{d}^2u(r)}{\mathrm{d}r^2}+[\frac{2\mu}{\hbar^2}(E+\frac{Ze_s{}^2}{r})-\frac{l(l+1)}{r^2}]u(r)=0, \quad (2)$$

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

这里，我们主要研究电子在库仑场中，所以，只考虑 $E<0$ 的情况。

令 $$\alpha=\sqrt{\frac{8\mu|E|}{\hbar^2}},\ \lambda=\frac{2\mu Ze_s^{\ 2}}{\alpha\hbar^2}=\frac{Ze_s^{\ 2}}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

$$\rho=\alpha r$$

径向方程可改写为：

$$\frac{d^2u(\rho)}{d\rho^2}+[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}]u(\rho)=0,\ (3)$$

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

2）先研究它的渐进行为(1)，当 $\rho = \alpha r \to \infty$ 时，方程变为

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

它的一般解为 $u(\rho) = A\exp(-\rho/2) + B\exp(\rho/2)$

在渐近条件 $\rho \to \infty$ 下的合理解为：

$$u(\rho) = A\exp(-\rho/2) \to u(\rho) = F(\rho)\exp(-\rho/2)$$

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

渐近行为（2），当 $\rho=\alpha r\to 0$ 时，方程变为

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2}-\frac{l(l+1)}{\rho^2}u=0\Rightarrow \text{一般解 } u(\rho)=C\rho^{l+1}+D\rho^{-l}$$

在渐近条件$\rho\to 0$下的合理解为：$u(\rho)=C\rho^{l+1}$

综合两渐近行为，有： $u(\rho)=F(\rho)\rho^{l+1}\exp(-\rho/2)$

代回原方程，并化简，得

$$[\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2}+(2l+2-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho}-(l+1-\lambda)]F(\rho)=0$$

$$[\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2}+(2l+2-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho}-(l+1-\lambda)]F(\rho)=0$$

3) 级数法求解，令 $F(\rho)=\sum_{j=0}^{\infty}c_j\rho^j$

代回，得：

$$\rho\sum_j c_j j(j-1)\rho^{j-2}+\sum_j(2l+2-\rho)c_j j\rho^{j-1}-\sum_j(l+1-\lambda)c_j\rho^j=0$$

整理后，得：

$$\sum_j[c_j j(j-1)+c_j j(2l+2)]\rho^{j-1}-\sum_j[c_j j+c_j(l+1-\lambda)]\rho^j=0$$

$$\Rightarrow\sum_i c_i i(2l+2+i-1)\rho^{i-1}-\sum_j c_j(l+1+j-\lambda)\rho^j=0$$

$$\sum_i c_i i(2l+2+i-1)\rho^{i-1} - \sum_j c_j (l+1+j-\lambda)\rho^j = 0 \xrightarrow{i=j+1}$$

$$\sum_j [c_{j+1}(j+1)(2l+2+j) - c_j(l+1+j-\lambda)]\rho^j = 0 \Rightarrow$$

$$c_{j+1}(j+1)(2l+2+j) - c_j(l+1+j-\lambda) = 0$$

$$\Downarrow$$

$$c_{j+1} = \frac{(j+l+1-\lambda)}{(j+1)(j+2l+2)} c_j$$

$$\frac{c_{j+1}}{c_j} = \frac{(j+l+1-\lambda)}{(j+1)(j+2l+2)} \xrightarrow{j\to\infty} \frac{1}{j+1}$$

与 e^{ρ} 的渐进行为相同

$$e^{\rho}=\sum_j d_j \rho^j=\sum_j \frac{\rho^j}{j!}\Rightarrow \frac{d_{j+1}}{d_j}=\frac{1}{j+1}$$

这样的话：当$j\to\infty$

$$R=\alpha u(\rho)/\rho=\alpha\rho^l\exp(-\rho/2)F(\rho)$$

$$\to R=\alpha\rho^l\exp(\rho/2)\to\infty$$

即R也趋于无穷大！因此级数只能是有限项，才能保证

R有限：设最高次为 $j=j_r$，有 $c_{j_r+i}=0,\ (i\geq 1)$

$$c_{j_r+1}=\frac{(j_r+l+1-\lambda)}{(j_r+1)(j_r+2l+2)}c_{j_r}=0\Rightarrow \lambda=j_r+l+1$$

令： $\lambda = j_r + l + 1 = n$

j_r 称为径向量子数，

l 为角量子数

n 称为总量子数。

$$j_r = n - (l+1) \geq 0$$

$$\Rightarrow l = 0,\ 1,\ 2, \ldots,\ (n-1)$$

由：

$$n = \lambda = \frac{Ze_s^{\ 2}}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}$$

得：

$$E_n = -\frac{\mu Z^2 e_s^{\ 4}}{2\hbar^2 n^2} = -\frac{Z^2 e_s^{\ 2}}{2n^2 a_0}$$

$$a_0 = \frac{\hbar^2}{\mu e_s^{\ 2}},\quad e_s = \frac{e}{\sqrt{4\pi\varepsilon_0}}$$

中心力场中的束缚态，能量和角动量都是分立的

4) 继续求波函数…

将 $\lambda = n$ 代回 $$c_{j+1} = \frac{(j+l+1-\lambda)}{(j+1)(j+2l+2)} c_j$$

说明所有的系数都可用 c_0 表示出，则得：

$$F(\rho) = \sum_{j=0}^{\infty} c_j \rho^j = -c_0 \frac{(2l+1)!(n-l-1)!}{[(n+l)!]^2} \rho^{l+1} L_{n+l}^{2l+1}(\rho)$$

式中：$L_{n+l}^{2l+1}(\rho)$ 是缔合拉盖多项式

$$L_{n+l}^{2l+1}(\rho) = \sum_{j=0}^{n-l-1} (-1)^{j+1} \frac{[(n+l)!]^2 \rho^j}{(n-l-1-j)!(2l+1+j)!\, j!}$$

合并得解：$\{\rho=\alpha r,\ \alpha=\sqrt{8\mu|E|/\hbar^2},\ E_n=-\frac{Z^2e_s^2}{2n^2a_0},\ a_0=\frac{\hbar^2}{\mu e_s^2}\}$

$$F(\rho)=\sum_{j=0}^{\infty}c_j\rho^j=-c_0\frac{(2l+1)!(n-l-1)!}{[(n+l)!]^2}\rho^{l+1}L_{n+l}^{2l+1}(\rho)$$

缔合拉盖多项式

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

$$R(r)=\frac{\alpha}{\rho}u(\rho)=\alpha\exp(-\rho/2)\rho^{l}F(\rho)\xrightarrow{\text{改回}R_{nl}(r)}$$

归一化系数

$$R_{nl}(r)=N_{nl}\exp(-Zr/na_0)\left(\frac{2Zr}{na_0}\right)^{l}L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

$$R_{nl}(r) = N_{nl}\exp(-Zr/na_0)(\frac{2Zr}{na_0})^l L_{n+l}^{2l+1}(\frac{2Zr}{na_0})$$

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

求归一化系数……

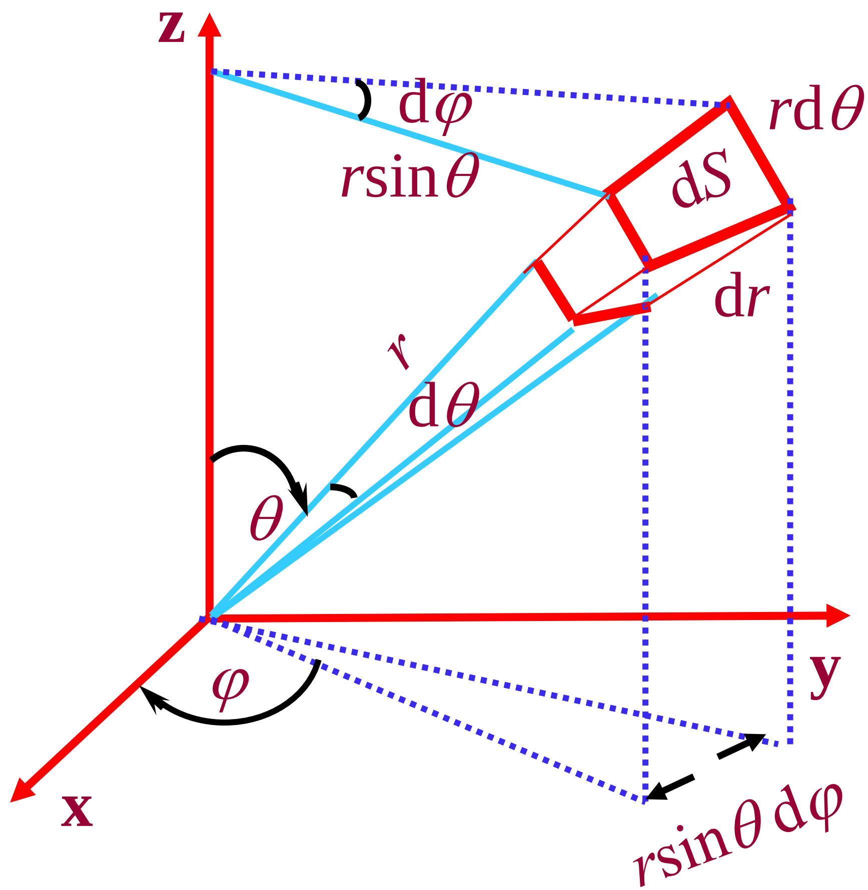
$$\int \left|\psi_{nlm}(r,\theta,\phi)\right|^2 \mathrm{d}\tau = 1$$

$$\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y\mathrm{d}z = r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi$$

附：数学基础回顾

$$d\tau = dxdydz$$

体积元在球坐标系下几何描述



$$dS = (rd\theta)\cdot(r\sin\theta d\varphi) = r^2\sin\theta d\theta d\varphi$$

$$d\tau = dS\cdot dr = r^2\sin\theta dr d\theta d\varphi$$

以上就是球坐标系下的积分元

$$1=\int\left|\psi_{nlm}(r,\theta,\varphi)\right|^2\mathrm{d}\tau=\int\left|\psi_{nlm}(r,\theta,\varphi)\right|^2 r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi$$

$$=\int\left|R_{nl}(r)\right|^2 r^2\mathrm{d}r\ \int\left|Y_{lm}(\theta,\varphi)\right|^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi$$

$$=\underbrace{\int\left|R_{nl}(r)\right|^2 r^2\mathrm{d}r}_{\text{径向}}\ \underbrace{\int\left|Y_{lm}(\theta,\varphi)\right|^2\mathrm{d}\Omega}_{\text{角向}}$$

$\Rightarrow$

$$1=\int\left|R_{nl}(r)\right|^2 r^2\mathrm{d}r$$

$$=\int\left|N_{nl}\exp(-Zr/na_0)\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)\right|^2 r^2\mathrm{d}r$$

$\Rightarrow$

$$N_{nl}=-\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

最终解：

$$\boxed{R_{nl}(r) = N_{nl}\exp\left(-\frac{Zr}{na_0}\right)\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)}$$

$$\boxed{\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)}$$

式中：

N_{nl} 是归一化常数

a_0 是第一玻尔半径

$L_{n+l}^{2l+1}(\rho)$ 是缔合拉盖尔多项式

$Y_{lm}(\theta,\varphi)$ 是球谐函数

备用公式

$$N_{nl} = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}, \quad a_0 = \frac{\hbar^2}{\mu e_s^{\ 2}}$$

$$L_{n+l}^{2l+1}(\rho) = \sum_{j=0}^{n-l-1} (-1)^{j+1} \frac{[(n+l)!]^2 \rho^j}{(n-l-1-j)!(2l+1+j)!\, j!}$$

$$L_{n+l}^{2l+1}(\rho) = \frac{1}{(n+l)!} e^{\rho} \rho^{-(2l+1)} \frac{\mathrm{d}^{n+l}}{\mathrm{d}\rho^{n+l}} (e^{-\rho} \rho^{n+l+2l+1})$$

$$Y_{lm}(\theta,\varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos\theta) \Phi_m(\varphi)$$

$$P_l^m(\cos\theta) = (-1)^{l+m} \frac{1}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi}} \frac{(l+m)!}{(l-m)!} \frac{1}{\sin^m\theta} \left(\frac{\mathrm{d}}{\mathrm{d}\cos\theta}\right)^{l-m} \sin^{2l}\theta$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} \exp(\mathrm{i}m\varphi)$$

几个径向和角向波函数

$$\boxed{\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)}$$

$$R_{10}=(Z/a_0)^{3/2}2\exp(-Zr/a_0)$$

$$R_{20}=(Z/2a_0)^{3/2}(2-Zr/a_0)\exp(-Zr/2a_0)$$

$$R_{21}=(Z/2a_0)^{3/2}(Zr/a_0\sqrt{3})\exp(-Zr/2a_0)$$

$$R_{30}=(\frac{Z}{3a_0})^{3/2}[2-\frac{4Zr}{3a_0}+\frac{4}{27}(\frac{Zr}{a_0})^2]\exp(-\frac{Zr}{3a_0})$$

$$R_{31}=(\frac{2Z}{a_0})^{3/2}(\frac{2}{27\sqrt{3}}-\frac{Zr}{81a_0\sqrt{3}})\frac{Zr}{a_0}\exp(-\frac{Zr}{3a_0})$$

$$R_{32}=(\frac{2Z}{a_0})^{3/2}(\frac{1}{81\sqrt{15}})(\frac{Zr}{a_0})^2\exp(-\frac{Zr}{3a_0})$$

$$Y_{00}=\frac{1}{\sqrt{4\pi}},\quad Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{20}=\sqrt{\frac{15}{16\pi}}(3\cos^2\theta-1)$$

$$Y_{1\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\varphi)$$

$$Y_{2\pm1}=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\exp(\pm i\varphi)$$

$$Y_{2\pm2}=\mp\sqrt{\frac{15}{32\pi}}\sin^2\theta\exp(\pm i2\varphi)$$

6 小结：电子在库仑场中运动

$$\hat{H}\psi_{nlm}(r,\theta,\varphi)=E_n\psi_{nlm}(r,\theta,\varphi)$$

能量本征值与本征函数

$$E_n=-\frac{\mu Z^2e_s^4}{2n^2\hbar^2}=-\frac{Z^2e_s^2}{2a_0}\frac{1}{n^2}=E_1\frac{1}{n^2},\ a_0=\frac{\hbar^2}{\mu e_s^2}$$

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)=R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

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

$$l=0,1,2,\cdots,n-1$$

$$m=0,\pm1,\pm2,\cdots,\pm l$$

7. 讨论

电子自旋与自旋投影：$S^2 = \frac{3}{4}\hbar^2,\ S_z = \pm\frac{1}{2}\hbar$

(1) 四个量子数

主量子数（决定不同能级）

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

$$E_n = -\frac{\mu Z^2 e_s^4}{2\hbar^2}\frac{1}{n^2} = E_1\frac{1}{n^2}$$

角量子数（决定角动量大小）

$$l = 0,\ 1,\ 2,\ \ldots,\ (n-1)$$

$$L^2 = l(l+1)\hbar^2$$

磁量子数（决定角动量方向）

$$m = 0,\ \pm 1,\ \pm 2,\ \ldots,\ \pm l$$

$$L_z = m\hbar$$

自旋角量子数与自旋磁量子数

$$l_s = 0,\ 1/2,\ 1,\ 3/2,\ \ldots,$$

$$-l_s \le m_s \le l_s$$

$$S^2 = l_s(l_s+1)\hbar^2,\ S_z = m_s\hbar$$

电子：$l_s = 1/2,\ m_s = \pm 1/2$

能量本征值： $E_n = -\dfrac{\mu Z^2 e_s^4}{2\hbar^2 n^2}$

确定能量的大小

$\hat{L}^2$本征值：

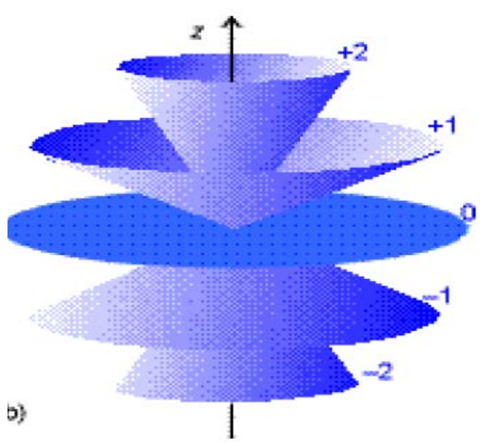
$$l(l+1)\hbar^2, l = 1,2,\ldots$$

确定了角动量的大小

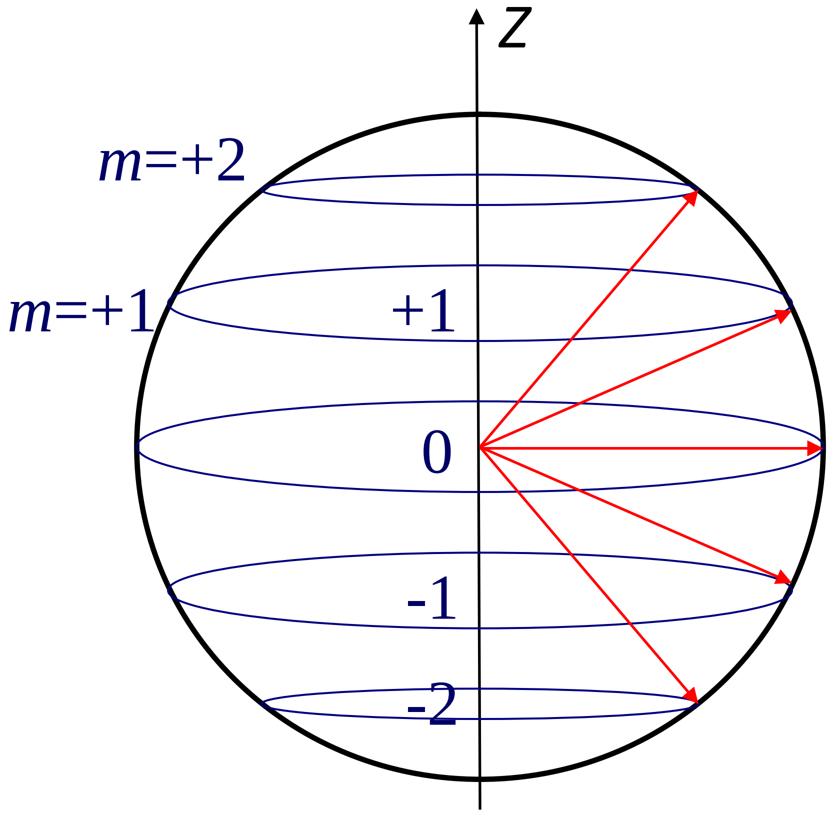
$\hat{L}_z$本征值：

$$L_z = m\hbar, m = 0,\pm 1,\pm 2,\ldots \pm l$$

确定了角动量的方向



$$\boxed{|L| = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar,\ (l = 2)}$$



角动量大小量子化

角动量空间取向量子化

(2) 能级简并度

$$\hat{H}\psi_{nlm} = E_n\psi_{nlm}, \quad \psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

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

$$l = 0,\ 1,\ 2, \cdots,\ n-1$$

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

角动量平方 L^2 是 $2l+1$ 度简并 $\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi)$

能级 E_n 是 n^2 度简并 $\sum_{l=0}^{n-1}(2l+1) = n^2$

若考虑自旋，电子能级 E_n 是 $2n^2$ 度简并的

例 . 一质量为μ的粒子处于中心势场中，若t=0时其状态波函数为：

$$\psi(r,\theta,\varphi,t_0) = R(r)\Theta(\theta)\cos^2\varphi$$

求t时刻的L_z测量值的可能值、概率及平均值

解：

$$\psi(r,\theta,\varphi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}m\varphi)$$

$$\Phi(\varphi) = \cos^2\varphi = \frac{1}{2}(1+\cos 2\varphi)$$

$$= \frac{1}{2} + \frac{1}{4}[\exp(2\mathrm{i}\varphi) + \exp(-2\mathrm{i}\varphi)]$$

$$= \frac{\sqrt{2\pi}}{2}\Phi_0(\varphi) + \frac{\sqrt{2\pi}}{4}\Phi_2(\varphi) + \frac{\sqrt{2\pi}}{4}\Phi_{-2}(\varphi)$$

$$\Phi(\varphi,t)=\frac{\sqrt{2\pi}}{2}\Phi_0(\varphi)+\frac{\sqrt{2\pi}}{4}\Phi_2(\varphi)+\frac{\sqrt{2\pi}}{4}\Phi_{-2}(\varphi)$$

$$=[\frac{\sqrt{2\pi}}{2}\Phi_0(\varphi)+\frac{\sqrt{2\pi}}{4}\Phi_2(\varphi)+\frac{\sqrt{2\pi}}{4}\Phi_{-2}(\varphi)]\exp(-\mathrm{i}\,Et/\hbar)$$

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}m\varphi),\ \ m=0,\ 2,\ -2$$

L_z 测量的可能值： $L_z=m\hbar=0,\ 2\hbar,\ -2\hbar$

对应概率：

$$\frac{\pi}{2}+\frac{\pi}{8}+\frac{\pi}{8}=\frac{3\pi}{4}\Rightarrow p_1=\frac{\pi/2}{3\pi/4}=\frac{2}{3},\ p_2=p_2=\frac{\pi/8}{3\pi/4}=\frac{1}{6}$$

L_z 平均值： $\frac{2}{3}\times 0+\frac{1}{6}\times 2\hbar+\frac{1}{6}\times(-2\hbar)=0$

作业　1.求粒子处于如下中心势场中的运动

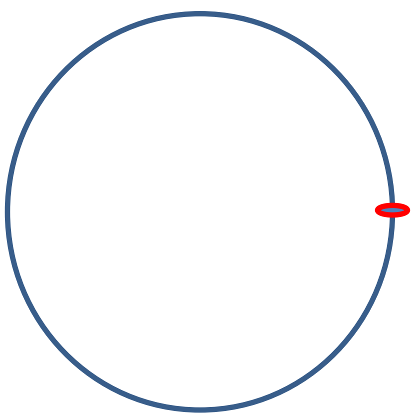
$$V(r) = kr, \quad (k > 0)$$

能级和波函数

作业　2.一质量为**μ**的量子环被束缚在半径为**r**的环上运动，

（1）求能级和波函数

（2）若**t=0**时处于 $\Phi(\theta, t_0) = \cos^2\theta$ 的态，求**t**时刻的波函数及其能量时的可能值



（选）.碱金属原子中的价电子相当于处于如下中心势场中

$$V(r)=-\frac{e^2}{r}-\lambda\frac{e^2a_0}{r^2},\quad (0<\lambda\ll 1)$$

求其能级和波函数

期末加5分

（选）.求粒子处于如下中心势场中的运动时的能级

$$V(r)=\frac{1}{2}kr^2+DL^2,\quad (k>0)$$

方式L为角动量

期末加5分

附录 1 . 证明如下对易关系

$$\left[r, \hat{p}_r\right] = i\hbar$$

$$\left[r, \hat{p}_r\right]\psi = -i\hbar(\mathrm{r}\frac{\partial}{\partial r}\psi - \frac{\partial}{\partial r}(\mathrm{r}\psi))$$

$$= -i\hbar(-\psi\frac{\partial}{\partial r}\mathrm{r})$$

$$= i\hbar\psi$$

附录2：证明 $\frac{1}{r}\frac{d^2(rR)}{dr^2}=\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr})$

证：$\frac{1}{r}\frac{d^2(rR)}{dr^2}=\frac{1}{r}\frac{d}{dr}(rR)'=\frac{1}{r}\frac{d}{dr}[R+rR']=\frac{1}{r}[R'+R'+rR'']=\frac{1}{r}[2R'+rR'']$

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr})=\frac{1}{r^2}[2rR'+r^2R'']=\frac{1}{r}[2R'+rR'']$$

$\therefore$ 得证

附录3：一维谐振子处在基态 $\psi(x)=\sqrt{\frac{\alpha}{\pi}}e^{-\frac{\alpha^2x^2}{2}}$，求

(1)势能的平均值 $\bar{u}=\frac{1}{2}\mu\omega^2\overline{x^2}$ (2)动能的平均值 $\bar{T}=\frac{\overline{p^2}}{2\mu}$

(3)动量的几率分布函数

解:(1) $\overline{F}=\int\psi^*(x)\hat{F}\psi^*(x)dx$

$$\therefore \overline{x^2} = \frac{\alpha}{\pi^{1/2}} \int_{-\infty}^{\infty} x^2 e^{-\alpha^2 x^2} dx = \frac{2\alpha}{\pi^{1/2}} \int_{0}^{\infty} x^2 e^{-\alpha^2 x^2} dx$$

由积分公式$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{(2n-1)!!}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$

代入上式中：$n = 1, a = \alpha^2$，有$\overline{x^2} = \frac{2\alpha}{\pi^{1/2}} \frac{(2-1)!!}{2^2 (\alpha^2)^1} \sqrt{\frac{\pi}{\alpha^2}} = \frac{1}{2\alpha^2}$

$$\therefore \overline{u} = \frac{1}{2} \mu \omega^2 \overline{x^2} = \frac{1}{2} \mu \omega^2 \frac{1}{2\alpha^2} = \frac{\hbar \omega}{4}$$

(2)平均动能 $\overline{T} = \frac{\overline{p^2}}{2\mu}$

$$\overline{P^2} = \int_{-\infty}^{\infty} \psi^*(x) \hat{P}^2 \psi(x) dx = \int_{-\infty}^{\infty} \frac{\alpha}{\sqrt{\pi}} e^{-\frac{\alpha^2 x^2}{2}} (-i\hbar \frac{d}{dx})^2 e^{-\frac{\alpha^2 x^2}{2}} dx$$

$$= -\frac{\alpha \hbar^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2 x^2}{2}} \frac{d^2}{dx^2} e^{-\frac{\alpha^2 x^2}{2}} dx = -\frac{\alpha \hbar^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} -\alpha^2 (1 - \alpha^2 x^2) e^{-\alpha^2 x^2} dx$$

$$= -\frac{\alpha^3 \hbar^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} (\alpha^2 x^2 - 1) e^{-\alpha^2 x^2} dx = -\frac{2\alpha^3 \hbar^2}{\sqrt{\pi}} \int_{0}^{\infty} (\alpha^2 x^2 - 1) e^{-\alpha^2 x^2} dx$$

利用利用积分公式$\int_0^{\infty} e^{-ax^2}dx=\frac{1}{2}\sqrt{\frac{\pi}{a}}$和 $\int_0^{\infty} x^{2n}e^{-ax^2}dx=\frac{(2n-1)!!}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$

$$\overline{P^2}=-\frac{2\alpha^3\hbar^2}{\sqrt{\pi}}[\alpha^2\frac{1!!}{2^2\alpha^2}\sqrt{\frac{\pi}{\alpha^2}}-\frac{1}{2}\sqrt{\frac{\pi}{\alpha^2}}]=-\frac{\alpha^2\hbar^2}{2}$$

$$\therefore \overline{T}=\frac{\overline{P^2}}{2\mu}=\frac{1}{4\mu}\alpha^2\hbar^2=\frac{\hbar^2}{4\mu}\frac{\mu\omega}{\hbar}=\frac{\hbar\omega}{4}$$

$\hat{P}$ 的厄米性，又解：

$$\overline{P^2}=\int_{-\infty}^{\infty}\psi_n^*(x)\hat{P}^2\psi_n(x)dx=\overline{P^2}=\int_{-\infty}^{\infty}(\hat{P}\psi_n)^*(\hat{P}\psi_n)dx\sqrt{a^2+b^2}$$

$$=\int_{-\infty}^{\infty}\hat{P}^*\psi_n{}^*(\hat{P}\psi_n)dx=\alpha^2\hbar^2\int[\sqrt{\frac{n}{2}}\psi_{n-1}-\sqrt{\frac{n+1}{2}}\psi_{n+1}][\sqrt{\frac{n}{2}}\psi_{n-1}-\sqrt{\frac{n+1}{2}}\psi_{n+1}]dx$$

$$\overset{n=0}{=}\frac{\alpha^2\hbar^2}{2}\int_{-\infty}^{\infty}|\psi_1|^2dx=\frac{\alpha^2\hbar^2}{2}$$

(3) $\psi(x)$可用动量本征函数$\psi_p(x)$来展开：$\psi(x)=\int c(p)\psi_p(x)dp$

$$\therefore c(p)=\int\psi_p^*(x)\psi(x)dx=\frac{1}{(2\pi\hbar)^{1/2}}\int e^{-\frac{i}{\hbar}px}\sqrt{\frac{\alpha}{\pi^{1/2}}}e^{-\frac{\alpha^2x^2}{2}}dx$$

$$=\frac{1}{(2\pi\hbar)^{1/2}}\sqrt{\frac{\alpha}{\pi^{1/2}}}\int e^{-\frac{i}{\hbar}px-\frac{\alpha^2x^2}{2}}dx=\frac{1}{(2\pi\hbar)^{1/2}}\sqrt{\frac{\alpha}{\pi^{1/2}}}\int e^{-\frac{\alpha^2}{2}(x^2+\frac{2}{\alpha^2}\frac{i}{\hbar}p)}dx$$

$$=\frac{1}{(2\pi\hbar)^{1/2}}\sqrt{\frac{\alpha}{\pi^{1/2}}}\int e^{-\frac{\alpha^2}{2}(x+\frac{i}{\hbar}\frac{p}{\alpha^2})^2-\frac{p^2}{2\hbar^2\alpha^2}}dx=\frac{1}{(2\pi\hbar)^{1/2}}\sqrt{\frac{\alpha}{\pi^{1/2}}}e^{-\frac{p^2}{2\hbar^2\alpha^2}}\int e^{-\frac{\alpha^2}{2}(x+\frac{i}{\hbar}\frac{p}{\alpha^2})^2}dx$$

$$=\frac{1}{(2\pi\hbar)^{1/2}}\sqrt{\frac{\alpha}{\pi^{1/2}}}e^{-\frac{p^2}{2\hbar^2\alpha^2}}\sqrt{\frac{\pi}{\alpha^2/2}}=\frac{1}{(\pi^{1/2}\hbar\alpha)^{1/2}}e^{-\frac{p^2}{2\hbar^2\alpha^2}}$$

动量几率密度(动量取值在p附近单位动量区间的几率密度)：

$$|c(p)|^2=\frac{1}{\pi^{1/2}\hbar\alpha}e^{-\frac{p^2}{\hbar^2\alpha^2}}=e^{-\frac{p^2}{\hbar^2\alpha^2}}\cdot\frac{1}{\pi^{1/2}\hbar}\sqrt{\frac{\hbar}{\mu\omega}}$$

$$=\frac{1}{\pi^{1/2}}\frac{e^{-\frac{p^2}{\hbar^2\alpha^2}}}{(\mu\omega\hbar)^{1/2}}=\frac{\beta}{\pi^{1/2}}e^{-\beta p^2}$$

实际上，$c(p)$ 就是以p为变量的谐振子的波函数 $\psi_0(p)$

又解，利用 $|c(p)|^2$ 求 $\overline{P^2}$ 和 $\overline{T}$（平均动能）

$$\overline{P^2} = \int_{-\infty}^{\infty} c_p^* \hat{p}^2 c_p dp = \int_{-\infty}^{\infty} |c_p|^2 p^2 dp = \frac{\beta}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\beta^2 p^2} p^2 dp$$

$$= \frac{\beta}{\sqrt{\pi}} \frac{1}{2\beta^2} \sqrt{\frac{\pi}{\beta^2}} = \frac{1}{2\beta^2}$$

$$\therefore \overline{T} = \frac{\overline{P^2}}{2\mu} = \frac{1}{4\mu\beta^2} = \frac{\mu\omega\hbar}{4\mu} = \frac{\omega\hbar}{4}$$