

第6章：中心力场

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- ☐ 角动量守恒 → 径向方程
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- ☐ 三维谐振子
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中心力场问题的一般表述

中心力场：力作用线过某点，场（势能）关于某一点对称

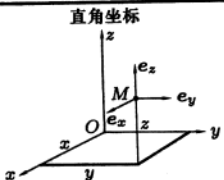
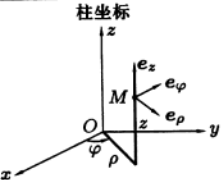
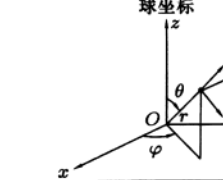
$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r)$$

关于原点对称：

✍ 球坐标系 (r, θ, φ)

$$\begin{cases} x = r \sin \theta \cos \varphi \\ y = r \sin \theta \sin \varphi \\ z = r \cos \theta \end{cases} \quad \begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \theta = \arctan \left(\frac{\sqrt{x^2 + y^2}}{z} \right) \\ \varphi = \arctan \left(\frac{y}{x} \right) \end{cases}$$

坐标系

	直角坐标	柱坐标	球坐标
定义	 $U = U(x, y, z)$ $\mathbf{A} = A_x \mathbf{e}_x + A_y \mathbf{e}_y + A_z \mathbf{e}_z$ $A_x = A_x(x, y, z)$ $A_y = A_y(x, y, z)$ $A_z = A_z(x, y, z)$	 $U = U(\rho, \varphi, z)$ $\mathbf{A} = A_\rho \mathbf{e}_\rho + A_\varphi \mathbf{e}_\varphi + A_z \mathbf{e}_z$ $A_\rho = A_x \cos \varphi + A_y \sin \varphi$ $A_\varphi = -A_x \sin \varphi + A_y \cos \varphi$	 $U = U(r, \theta, \varphi)$ $\mathbf{A} = A_r \mathbf{e}_r + A_\theta \mathbf{e}_\theta + A_\varphi \mathbf{e}_\varphi$ $A_r = A_\rho \sin \theta + A_z \cos \theta$ $A_\theta = A_\rho \cos \theta - A_z \sin \theta$ $A_\varphi = -A_x \sin \varphi + A_y \cos \varphi$
梯度	$\nabla U = (\partial U / \partial x) \mathbf{e}_x + (\partial U / \partial y) \mathbf{e}_y + (\partial U / \partial z) \mathbf{e}_z$	$(\nabla U)_\rho = \partial U / \partial \rho$ $(\nabla U)_\varphi = [\partial U / \partial \varphi] / \rho$ $(\nabla U)_z = \partial U / \partial z$	$(\nabla U)_r = \partial U / \partial r$ $(\nabla U)_\theta = [\partial U / \partial \theta] / r$ $(\nabla U)_\varphi = [\partial U / \partial \varphi] / (r \sin \theta)$
拉普拉斯算符	$\Delta U = \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2}$	$\Delta U = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial U}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 U}{\partial \varphi^2} + \frac{\partial^2 U}{\partial z^2}$	$\Delta U = \frac{1}{r} \frac{\partial^2}{\partial r^2} (rU) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial U}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 U}{\partial \varphi^2}$
散度	$\nabla \cdot \mathbf{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$	$\nabla \cdot \mathbf{A} = \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho A_\rho) + \frac{1}{\rho} \frac{\partial A_\varphi}{\partial \varphi} + \frac{\partial A_z}{\partial z}$	$\nabla \cdot \mathbf{A} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 A_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta A_\theta) + \frac{1}{r \sin \theta} \frac{\partial A_\varphi}{\partial \varphi}$
旋度	$\nabla \times \mathbf{A} = (\partial A_z / \partial y - \partial A_y / \partial z) \mathbf{e}_x + (\partial A_x / \partial z - \partial A_z / \partial x) \mathbf{e}_y + (\partial A_y / \partial x - \partial A_x / \partial y) \mathbf{e}_z$	$(\nabla \times \mathbf{A})_\rho = (\partial A_z / \partial \varphi) / \rho - \partial A_\varphi / \partial z$ $(\nabla \times \mathbf{A})_\varphi = \partial A_\rho / \partial z - \partial A_z / \partial \rho$ $(\nabla \times \mathbf{A})_z = [\partial (\rho A_\varphi) / \partial \rho - \partial A_\rho / \partial \varphi] / \rho$	$(\nabla \times \mathbf{A})_r = [\partial (\sin \theta A_\varphi) / \partial \theta - \partial A_\theta / \partial \varphi] / (r \sin \theta)$ $(\nabla \times \mathbf{A})_\theta = [\partial A_r / \partial \varphi - \sin \theta \partial (r A_\varphi) / \partial r] / (r \sin \theta)$ $(\nabla \times \mathbf{A})_\varphi = [\partial (r A_\theta) / \partial r - \partial A_r / \partial \theta] / r$

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

角度部分（角动量）：

$$\begin{cases} \hat{l}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{l}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{l}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases} \quad \begin{cases} \hat{l}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{l}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{l}_z = -i\hbar\frac{\partial}{\partial\varphi} \end{cases}$$

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

径向部分（径向动量）：

$$\begin{aligned} \hat{p}_r &= -i\hbar\left(\frac{1}{r} + \frac{\partial}{\partial r}\right) \\ \hat{H} &= -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{L}^2}{2mr^2} + V(r) \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} + V(r) \\ &= \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} + V(r) \end{aligned}$$

✍ 空间旋转不变 → 角动量守恒 $[\hat{l}, \hat{H}] = 0$

守恒量完全集 $\{\hat{H}, \hat{l}^2, \hat{l}_z\}$. 所以 \hat{l}^2 和 \hat{l}_z 的共同本征态 $Y_l^m(\theta, \varphi)$

$$\hat{l}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m$$

$$\hat{l}_z Y_l^m = m\hbar Y_l^m$$

$$l = 0, 1, 2, \dots$$

$$|m| \leq l, \text{ 即 } m = -l, -l+1, \dots, l-1, l$$

也是 \hat{H} 的本征态，但缺少径向自由度。于是三维问题的本征问题，可以通过分离变量求解：

将本征函数分解为径向部分和角度部分

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

$$\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi)$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{L}^2}{2mr^2} + V(r)\right]R(r)Y_l^m(\theta, \phi) = ER(r)Y_l^m(\theta, \phi)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l(l+1)}{2mr^2} + V(r)\right]R(r)Y_l^m(\theta, \phi) = ER(r)Y_l^m(\theta, \phi)$$

同除以 $Y_l^m(\theta, \phi)$ ，可得径向方程

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l(l+1)}{2mr^2} + V(r)\right]R_l(r) = ER_l(r)$$

所以对于给定 l ，只需要求解径向方程就能确定能量 E 。即

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}[rR_l(r)] + \left[\frac{2m}{\hbar^2}(E - V) - \frac{l(l+1)}{r^2}\right]R_l(r) = 0$$

或

$$R_l''(r) + \frac{2}{r} R_l'(r) + \left[\frac{2m}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] R_l(r) = 0$$

做变量代换 $R_l(r) = \chi(r)/r$, 则径向方程变为

$$\chi_l'' + \left[\frac{2m}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] \chi_l = 0$$

- ☐ 对于束缚态能量量子化, 将出现径向量子数 $n_r, n_r = 0, 1, 2, \dots$,
- ☐ 轨道角动量量子数 $l = 0, 1, 2, \dots$ s, p, d, f, ...
- ☐ E 只依赖 n_r 和 l , 不依赖磁量子数 m , 所以中心力场能级一般是 $2l + 1$ 重简并的

★ 三维中心力场问题求解小结

守恒量完全集 $\{\hat{H}, \hat{l}^2, \hat{l}_z\}$

将本征函数分解为径向部分和角度部分

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi)$$

角度方程

$$\hat{l}^2 Y_l^m = l(l+1) \hbar^2 Y_l^m$$

$$\hat{l}_z Y_l^m = m \hbar Y_l^m$$

$$l = 0, 1, 2, \dots$$

$$|m| \leq l, \text{ 即 } m = -l, -l+1, \dots, l-1, l$$

径向方程

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{2mr^2} + V(r) \right] R_l(r) = E R_l(r)$$

变量代换 $R_l(r) = \chi(r)/r$

$$\chi_l'' + \left[\frac{2m}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] \chi_l = 0$$

边界条件: $\chi_l(r) \xrightarrow{r \rightarrow \infty} 0, \chi_l(0) = 0$ (因为 $R_l(r)$ 在 0 点有限)

本征态 $R_{n_r l}(r), n_r = 0, 1, 2, \dots$,

☐ s 态 (s 波) 情况

$$\chi_l'' + \left[\frac{2m}{\hbar^2} (E - V) \right] \chi_l = 0$$

与一维定态问题类似, 但注意边界条件不同。

☐ 中心力场在 $r \rightarrow 0$ 邻域内的行为

假设 $\chi_l \xrightarrow{r \rightarrow 0} r^s$, 则有

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

即

$$[s(s-1) - l(l+1)] + \frac{2m}{\hbar^2} (E - V) r^2 = 0$$

若 $r^2 V \xrightarrow{r \rightarrow 0} 0$, 则要求

$$s(s-1) - l(l+1) = 0$$

即 $s = -l \text{ or } l+1$

又, $\chi_l(0) = 0$

所以 $s = l + 1$, 即

$$\lim_{r \rightarrow 0} R_l(r) \approx r^l$$

满足 $r^2 V \xrightarrow{r \rightarrow 0} 0$ 的势

- 库仑势 $V \propto r^{-1}$
- 线性中心势 $V \propto r$
- 对数中心势 $V \propto \ln r$
- 谐振子势 $V \propto r^2$
- 汤川势 $V \propto r^{-1} e^{-\alpha r}$

★ 两体问题化为单体问题

中心力场往往是两体问题。比如两个质量分别为 m_1 和 m_2 的粒子, 坐标为 \mathbf{r}_1 和 \mathbf{r}_2 。

？ 如果相互作用 $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ 只依赖二者之间的距离, 是否可以化成中心力场问题

这个二粒子的能量本征方程为

$$\left[-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2) = E_T \Psi(\mathbf{r}_1, \mathbf{r}_2)$$

引进质心坐标 \mathbf{R} 及相对坐标 \mathbf{r} 为

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad \mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

由此可得

$$\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 = \frac{1}{M} \nabla_R^2 + \frac{1}{\mu} \nabla^2$$

$$M = m_1 + m_2 \quad (\text{总质量})$$

$$\mu = m_1 m_2 / (m_1 + m_2) \quad (\text{约化质量})$$

$$\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

于是有

$$\left[-\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi = E_T \Psi$$

于是可以把质心运动与相对运动分离变量

$$\Psi = \phi(\mathbf{R}) \psi(\mathbf{r})$$

质心方程

$$-\frac{\hbar^2}{2M} \nabla_R^2 \phi(\mathbf{R}) = E_C \phi(\mathbf{R})$$

相对运动方程

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \psi(\mathbf{r}) = (E_T - E_C) \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

与前面的中心力场方程相一致。例如在原子物理中, 我们研究氢原子中电子的运动, 可以将原子核看作静止来研究电子的绕核运动。所需要做的改变就是将电子质量变为约化

质量 $\mu = Mm/(m + M)$

例：无限深球方势阱

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

s态 ($l = 0$)

$$\chi_l'' + \left[\frac{2m}{\hbar^2} (E - V) \right] \chi_l = 0$$

$$\chi_l'' + k^2 \chi_l = 0 \quad (r \leq a)$$

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (E > 0)$$

$$\text{边界条件+连续性条件: } \begin{cases} \chi(0) = 0 \\ \chi(a) = 0 \end{cases}$$

于是有量子化条件

$$ka = (n_r + 1)\pi, n_r = 0, 1, 2, 3, \dots$$

$$\text{能量本征值: } E_n = \frac{(n_r + 1)^2 \pi^2 \hbar^2}{2\mu a^2}$$

$$\text{本征波函数: } \psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{(n_r + 1)\pi x}{a}$$

$l \neq 0$

$$R_l'' + \frac{2}{r} R_l' + \left[k^2 - \frac{l(l+1)}{r^2} \right] R_l = 0 \quad (r < a) \quad (6.2.10)$$

而在边界上要求

$$R_l(r) \big|_{r=a} = 0 \quad (6.2.11)$$

引进无量纲变数

$$\rho = kr \quad (6.2.12)$$

则式(6.2.10)化为

$$\frac{d^2 R_l}{d\rho^2} + \frac{2}{\rho} \frac{dR_l}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2} \right] R_l = 0 \quad (6.2.13)$$

这就是球 Bessel 方程. 令

$$R_l = u_l(\rho) / \sqrt{\rho} \quad (6.2.14)$$

经过计算, 可求出 u_l 满足下列方程:

$$u_l'' + \frac{1}{\rho} u_l' + \left[1 - \frac{(l+1/2)^2}{\rho^2} \right] u_l = 0 \quad (6.2.15)$$

这正是半奇数 $(l+1/2)$ 阶 Bessel 方程 ($l=0, 1, 2, \dots$), 它的两个线性无关解可以表示为

$$J_{l+1/2}(\rho), \quad J_{-l-1/2}(\rho)$$

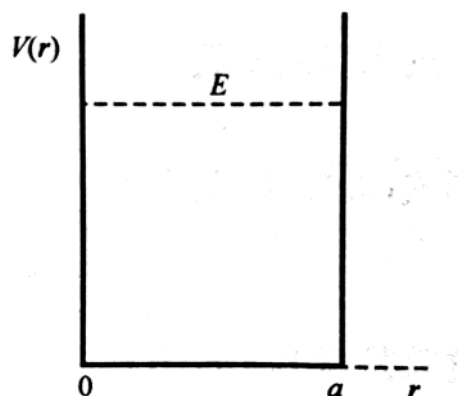
所以径向波函数的两个解是

$$R_l \propto \frac{1}{\sqrt{\rho}} J_{l+1/2}(\rho), \quad \frac{1}{\sqrt{\rho}} J_{-l-1/2}(\rho)$$

例：三维各向同性谐振子

$$V(r) = \frac{1}{2} K r^2 = \frac{1}{2} \mu \omega^2 r^2, \quad \omega = \sqrt{K/\mu}$$

$$R_l''(r) + \frac{2}{r} R_l'(r) + \left[\frac{2\mu}{\hbar^2} \left(E - \frac{1}{2} \mu \omega^2 r^2 \right) - \frac{l(l+1)}{r^2} \right] R_l(r) = 0$$



先分析渐近行为再求解

1. $r \rightarrow 0$

$$R_l''(r) + \frac{2}{r} R_l'(r) - \frac{l(l+1)}{r^2} R_l(r) = 0$$

$$R_l(r) \propto r^l$$

2. $r \rightarrow \infty$

$$R_l''(r) + \frac{\mu^2 \omega^2 r^2}{\hbar^2} R_l(r) = 0$$

$$R_l(r) \propto e^{\pm \frac{\alpha^2 r^2}{2}} \quad \left(\alpha = \sqrt{\mu \omega / \hbar} \right)$$

$$R_l(r) \xrightarrow{r \rightarrow \infty} 0 \Rightarrow R_l(r) \propto e^{-\frac{\alpha^2 r^2}{2}}$$

再利用渐近解构造解为

$$R_l(r) \propto r^l e^{-\frac{\alpha^2 r^2}{2}} u_l(r)$$

则

$$u_l'' + \frac{2}{r} (l+1 - r^2) u_l' + [2E - (2l+3)] u_l = 0$$

再令

$$\xi = r^2$$

方程(6.3.10)化为

$$\xi \frac{d^2 u_l}{d\xi^2} + \left[\left(l + \frac{3}{2} \right) - \xi \right] \frac{du_l}{d\xi} + \left(\frac{E}{2} - \frac{l+3/2}{2} \right) u_l = 0$$

这正是合流超几何方程

$$u_l \propto F(\alpha, \gamma, \xi)$$

$$E = 2n_r + l + 3/2$$

$$E = (2n_r + l + 3/2) \hbar \omega$$

$$N = 2n_r + l$$

$$E = E_N = (N + 3/2) \hbar \omega$$

$$N = 0, 1, 2, \dots$$

直角坐标系解法

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{1}{2} \mu^2 \omega^2 r^2 = H_x + H_y + H_z$$

$$H_x = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \mu \omega^2 x^2$$

守恒量完全集 $(\hat{H}_x, \hat{H}_y, \hat{H}_z)$

$$\Phi_{n_x n_y n_z}(x, y, z) = \varphi_{n_x}(x) \varphi_{n_y}(y) \varphi_{n_z}(z)$$

$$n_x, n_y, n_z = 0, 1, 2, \dots$$

$$E_{n_x, n_y, n_z} = \left(n_x + \frac{1}{2}\right)\hbar\omega + \left(n_y + \frac{1}{2}\right)\hbar\omega + \left(n_z + \frac{1}{2}\right)\hbar\omega = (N + 3/2)\hbar\omega$$

★ 氢原子

$$V = -\frac{e^2}{4\pi\epsilon_0 r}$$

分离变量： $\psi(r, \theta, \phi) = R_l(r)Y_l^m(\theta, \phi)$

径向：

$$\chi_l'' + \left[\frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] \chi_l = 0$$

角向 (球谐函数, spherical harmonic function)：

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

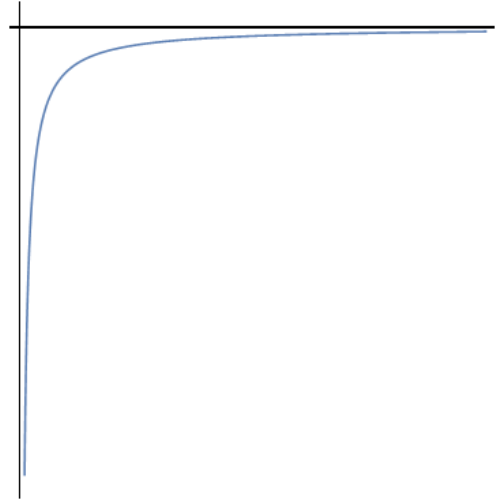
$$Y_l^{m*} = (-1)^m Y_l^{-m}$$

$$\hat{L}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m$$

$$\hat{L}_z Y_l^m = m\hbar Y_l^m$$

$$l = 0, 1, 2, \dots$$

$$|m| \leq l, \text{ 即 } m = -l, -l+1, \dots, l-1, l$$



✍ 径向一维问题

$$\frac{d^2 \chi_l}{dr^2} + \left[\frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] \chi_l = 0$$

1. 首先改写方程形式, 定义参数

$$k = \sqrt{\frac{-2\mu E}{\hbar^2}}$$

$$\Rightarrow \frac{d^2 \chi_l}{dr^2} + \left[-k^2 + \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 r} - \frac{l(l+1)}{r^2} \right] \chi_l = 0$$

$$\rho = kr, \rho_0 = \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 k}$$

$$\Rightarrow \frac{d^2 \chi_l}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] \chi_l$$

2. 考查两个奇点的渐进行为

■ $r \rightarrow 0$

$$\chi_l'' = \frac{l(l+1)}{\rho^2} \chi_l$$

$$\chi_l \sim r^{l+1}, r^{-l} \quad \chi_l(0) = 0 \Rightarrow \chi_l \sim \rho^{l+1}$$

■ $r \rightarrow \infty$

$$\chi_l'' = \chi_l$$

$$\chi_l \sim e^{-\rho}, e^{\rho} \quad \chi_l(\infty) = 0 \Rightarrow \chi_l \sim e^{-\rho}$$

3. 通过渐进解构造解的形式

$$\chi_l = \rho^{l+1} e^{-\rho} u_l(\rho)$$

$$\Rightarrow \rho u_l'' + 2(l+1-\rho)u_l + [\rho_0 - 2(l+1)]u_l = 0$$

4. 求解方程得到能量本征值

假设 u_l 可以写成 ρ 的幂级数的形式

$$u_l = \sum_{j=0}^{\infty} c_j \rho^j$$

代入方程可得

$$u'_l = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=1}^{\infty} (j+1) c_{j+1} \rho^j = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$u''_l = \sum_{j=0}^{\infty} j(j-1) c_j \rho^{j-2} = \sum_{j=1}^{\infty} (j+1) j c_{j+1} \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) j c_{j+1} \rho^{j-1}$$

$$\sum_{j=0}^{\infty} (j+1) j c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$\sum_{j=0}^{\infty} \{ (j+1) j c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(l+1)] c_j \} \rho^j = 0$$

于是有

$$(j+1) j c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(l+1)] c_j = 0$$

即

$$c_{j+1} = \frac{[2(l+j+1) - \rho_0]}{(j+1)(j+2l+2)} c_j$$

考虑高幂次情况 (j 很大)

$$c_{j+1} \approx \frac{2j}{(j+1)j} c_j = \frac{2}{j+1} c_j$$

假定这个式子是严格成立的, 则有

$$c_{j+1} = \frac{2}{j+1} c_j = \frac{4}{(j+1)j} c_{j-1} = \cdots \frac{2^j}{j!} c_0$$

于是有

$$u_l = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

$$\Rightarrow \chi_l = \rho^{l+1} e^{-\rho} u_l(\rho) = c_0 \rho^{l+1} e^{\rho}$$

与边界条件 $\chi_l(\infty) = 0$ 矛盾!

所以, 不能所有的 c_j 都存在, 求和必需中断成一个多项式, 才能避免这一情况发生, 假设不为0的最大幂次为 j_{max} , 则有

$$2(l + j_{max} + 1) - \rho_0 = 0$$

$$\text{令 } j_{max} = n_r, n = n_r + l + 1, n_r = 0, 1, 2, \dots$$

则有

$$\rho_0 = \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 k} = \frac{\frac{\mu e^2}{2\pi\epsilon_0 \hbar^2}}{\sqrt{\frac{-2\mu E}{\hbar^2}}} = 2n$$

由此可得

$$E_n = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 \cdot 2\hbar^2} \cdot \frac{1}{n^2} = -\frac{e^2 \hbar^2}{2ma^2} \cdot \frac{1}{n^2} = -13.6 \times \frac{1}{n^2} \text{ (eV)}$$

其中

$$a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \text{ \AA}$$

为玻尔半径。如果定义 $n = 1, 2, 3 \dots$ 为主量子数, 那么轨道角动量量子数 $l = 0, 1, \dots, n - 1$

此外,

$$\rho = \frac{r}{an}$$

5. 能量本征函数

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$$R_{nl}(r) = \frac{\chi_l}{r} = \frac{1}{r} \rho^{l+1} e^{-\rho} u_l(\rho) = \frac{1}{r} \rho^{l+1} e^{-\rho} \sum_{j=0}^n c_j \rho^j$$

$$\Rightarrow R_l(r) = \frac{1}{r} \left(\frac{r}{an} \right)^{l+1} e^{-r/(na)} \sum_{j=0}^{n-l-1} c_j \left(\frac{r}{an} \right)^j$$

$$c_{j+1} = \frac{[2(l+j+1) - \rho_0]}{(j+1)(j+2l+2)} c_j = \frac{[2(l+j+1-n)]}{(j+1)(j+2l+2)} c_j$$

基态波函数 ($n = 1$)

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi)$$

$$R_{10} = \frac{c_0}{a} e^{-r/a}$$

$$(R_{10}, R_{10}) = \int_0^\infty \frac{|c_0|^2}{a^2} e^{-2r/a} r^2 dr = \frac{|c_0|^2 a^2}{4} = 1$$

归一化可得 $c_0 = 2/\sqrt{a}$, 又 $Y_0^0 = 1/\sqrt{4\pi}$, 所以氢原子基态波函数为

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

由递推公式

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

第一激发态

■ ($n = 2, l = 0$)情况

$$c_1 = -c_0, c_2 = 0$$

$$R_{20} = \frac{1}{r} \left(\frac{r}{2a} \right) e^{-r/(2a)} \sum_{j=0}^1 c_j \left(\frac{r}{2a} \right)^j = \frac{c_0}{2a} \left(1 - \frac{r}{2a} \right) e^{-r/(2a)}$$

■ ($n = 2, l = 1$)情况

$$c_1 = 0$$

$$R_{20} = \frac{1}{r} \left(\frac{r}{2a} \right)^2 e^{-r/(2a)} \sum_{j=0}^0 c_j \left(\frac{r}{2a} \right)^j = \frac{c_0}{4a^2} r e^{-r/(2a)}$$

由递推公式

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

可知,

$$u_l(\rho) = \sum_{j=0}^n c_j \rho^j = L_{n-l-1}^{2l+1}(2\rho)$$

是关联拉盖尔(Laguerre)多项式

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x)$$

q阶拉盖尔多项式 $L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$

最终我们得到了氢原子的能量本征函数

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

对应能量本征值

$$E_n = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 \cdot 2\hbar^2} \cdot \frac{1}{n^2} = -\frac{e^2 \hbar^2}{2ma^2} \cdot \frac{1}{n^2}$$

$$n = 1, 2, 3 \dots, l = 0, 1, \dots, n-1$$

波函数正交归一性

$$(\psi_{nlm}, \psi_{n'l'm'}) = \int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta dr d\theta d\varphi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

关于氢原子能谱的讨论

- **能级简并度**：能量本征值只与主量子数 n 有关，与轨道角动量量子数 l ($= 0, 1, \dots, n-1$) 和磁量子数 m ($= -l, -l+1, \dots, l$) 无关。因此简并度为

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

- **Rydberg公式**

$$\tilde{\nu} = \frac{E_n - E_m}{hc} = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

$$\text{Rydberg常数} : R = \frac{2\pi^2 e^4 m}{(4\pi\epsilon_0)^2 \cdot ch^3}$$

★ 类氢离子

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 \cdot 2\hbar^2} \cdot \frac{1}{n^2} = -\frac{e^2 \hbar^2}{2ma^2} \cdot \frac{Z^2}{n^2}$$

本征函数性质

$$n = 1 (\text{基态}), R_{10} = \frac{2}{a^{3/2}} \exp(-r/a)$$

$$n = 2, \quad R_{20} = \frac{1}{\sqrt{2} a^{3/2}} \left(1 - \frac{r}{2a} \right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{2\sqrt{6} a^{3/2}} \frac{r}{a} \exp(-r/2a) \quad (6.4.34)$$

$$n = 3, \quad R_{30} = \frac{2}{3\sqrt{3} a^{3/2}} \left[1 - \frac{2r}{3a} + \frac{2}{27} \left(\frac{r}{a} \right)^2 \right] \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6} a^{3/2}} \frac{r}{a} \left(1 - \frac{r}{6a} \right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30} a^{3/2}} \left(\frac{r}{a} \right)^2 \exp(-r/3a)$$

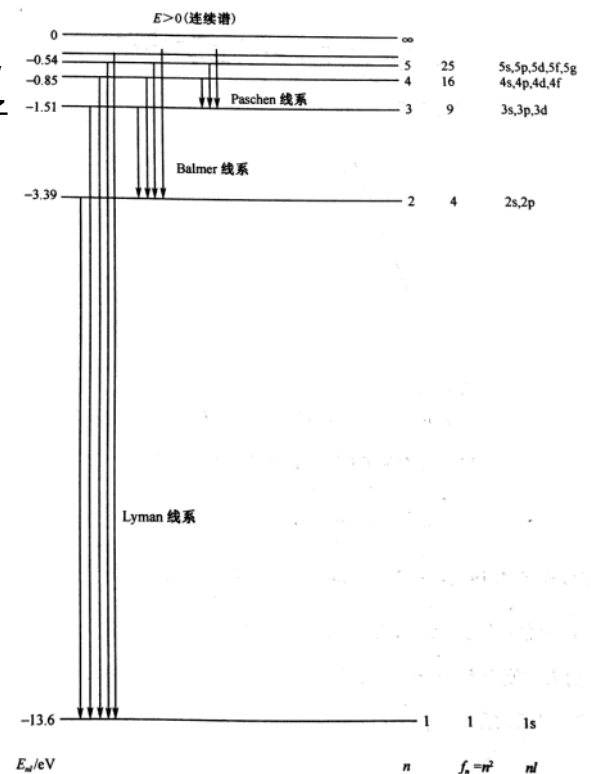


表 6.2 类氢离子径向波函数(原子单位)

n	l	n_r	光谱符号(nl)	$R_{nl}(r)$
1	0	0	1s	$2Z^{3/2}e^{-Zr}$
2	0	1	2s	$\frac{1}{\sqrt{2}}Z^{3/2}(1-Zr/2)e^{-Zr/2}$
	1	0	2p	$\frac{1}{2\sqrt{6}}Z^{5/2}re^{-Zr/2}$
3	0	2	3s	$\frac{2}{3\sqrt{3}}Z^{3/2}\left(1-\frac{2}{3}Zr+\frac{2}{27}Z^2r^2\right)e^{-Zr/3}$
	1	1	3p	$\frac{4\sqrt{2}}{27\sqrt{3}}Z^{5/2}r\left(1-\frac{1}{6}Zr\right)e^{-Zr/3}$
	2	0	3d	$\frac{4}{81\sqrt{30}}Z^{7/2}r^2e^{-Zr/3}$

径向概率分布

$$r^2 dr \int d\Omega |\psi_{nlm}(r, \theta, \varphi)|^2 = [R_{nl}(r)]^2 r^2 dr$$

$$= [\chi_{nl}(r)]^2 dr$$

与Bohr早期量子论不同，在量子力学中，电子并无严格的轨道的概念，而只能研究其位置分布概率。然而分布有最大值，比如基态

$$|\chi_{10}|^2 = (R_{10})^2 r^2 = \frac{4}{a^3} r^2 \exp(-2r/a)$$

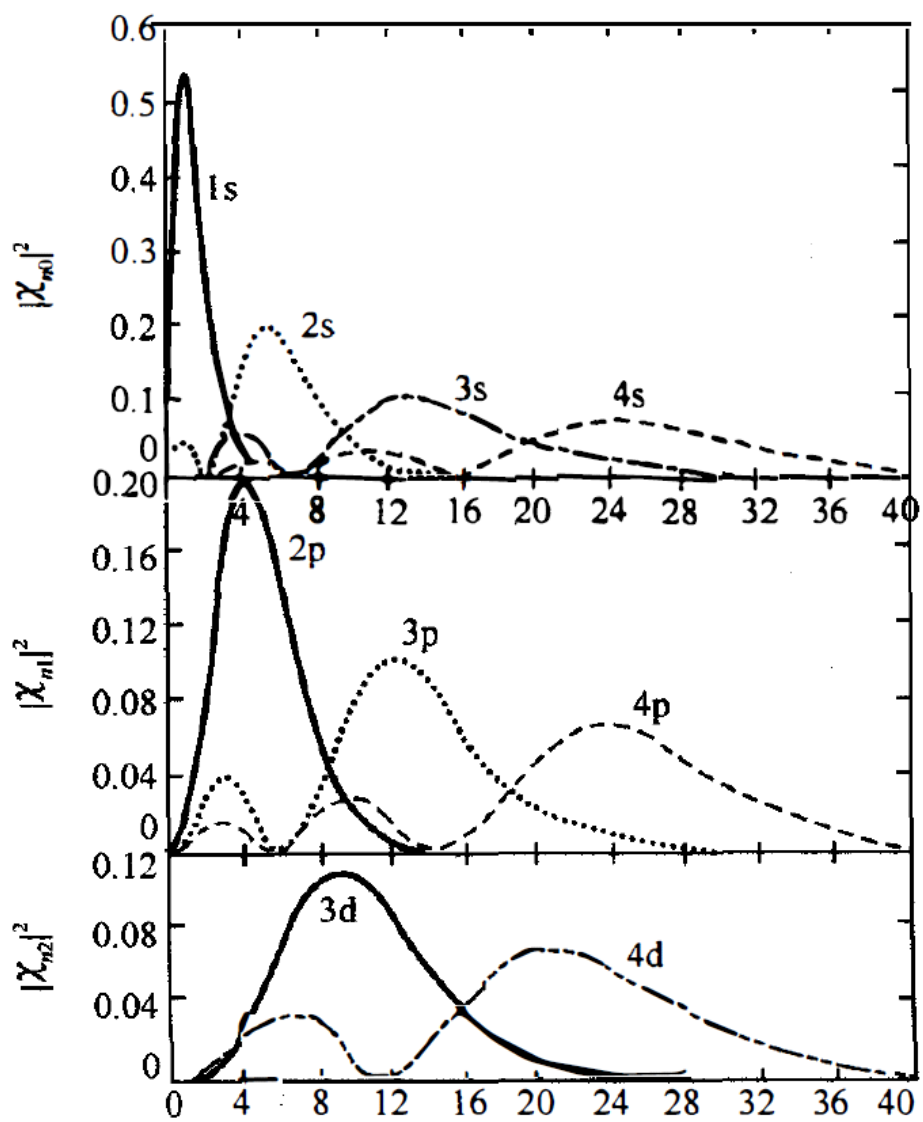
$$\frac{d}{dr} |\chi_{10}|^2 = 0$$

$$r = a \quad (\text{Bohr 半径})$$

最概然半径与Bohr理论相对应。

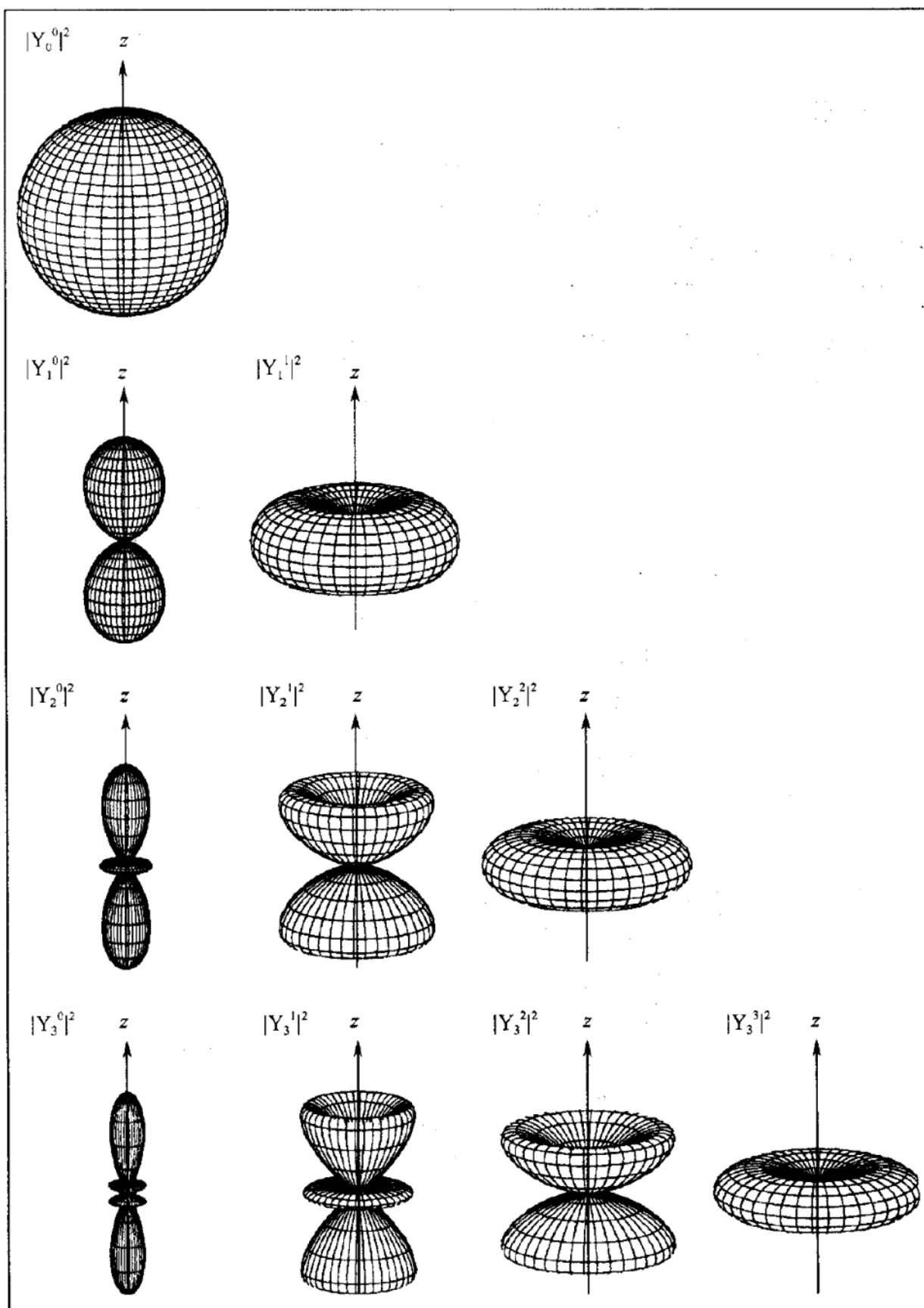
$|\chi_{m-1}|^2$ 的极值点

$$r = n^2 a \quad (n = 1, 2, 3, \dots)$$



角度概率分布

$$|Y_l^m(\theta, \varphi)|^2 d\Omega \propto |P_l^m(\cos\theta)|^2 d\Omega$$

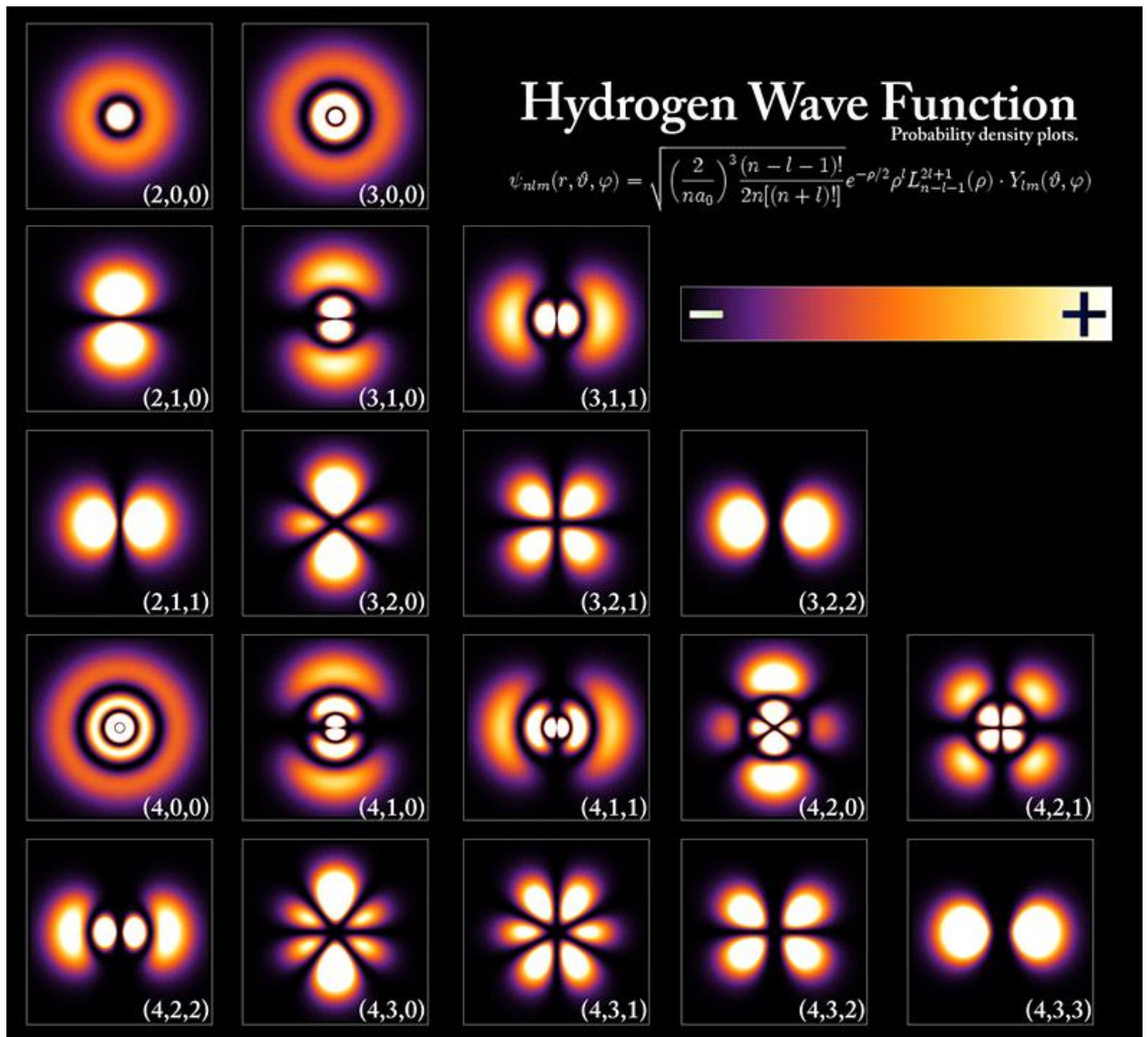


可以看出角度概率分布与 φ 无关

$$\sum_{m=-l}^l Y_l^{*m}(\theta, \varphi) Y_l^m(\theta, \varphi) = \text{常数 (与 } \theta, \varphi \text{ 无关)}$$

由此证明在 (nl) 能级上填满电子的情况下,电荷分布是各向同性的.

电子云 ($|\psi_{nlm}|^2$, 横坐标 x 纵坐标 z 与 φ 无关)



氢原子的电流分布和磁矩

概率守恒方程

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

$$\mathbf{j} = -\frac{i\hbar}{2\mu} (\psi^* \nabla \psi - \psi \nabla \psi^*) = \frac{1}{2\mu} (\psi^* \hat{\mathbf{p}} \psi - \psi \hat{\mathbf{p}} \psi^*)$$

(概率流密度：单位时间内通过S流入Ω的概率)

💡 电流=单位时间通过的电量： $I = \frac{Q}{t}$

概率流密度×电荷=电流密度

$$-e\mathbf{j} = \frac{ie\hbar}{2\mu} (\psi_{nlm}^* \nabla \psi_{nlm} - \psi_{nlm} \nabla \psi_{nlm}^*)$$

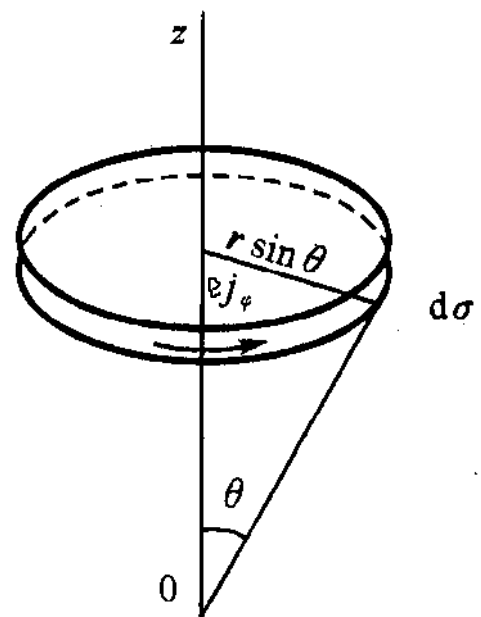
$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi}$$

$$\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \varphi)$$

$$= R_{nl}(r) N_{lm} P_l^m(\cos \theta) e^{im\varphi} = \phi_{nl}(\theta, \varphi) e^{im\varphi}$$

$\phi_{nl}(\theta, \varphi)$ 为实函数，于是

$$\begin{aligned} \psi_{nlm}^* \nabla \psi_{nlm} - \psi_{nlm} \nabla \psi_{nlm}^* \\ = \phi_{nl}(\theta, \varphi) e^{-im\varphi} \nabla [\phi_{nl}(\theta, \varphi) e^{im\varphi}] - \phi_{nl}(\theta, \varphi) e^{im\varphi} \nabla [\phi_{nl}(\theta, \varphi) e^{-im\varphi}] \end{aligned}$$



$$= 2|\phi_{nl}(\theta, \varphi)|^2 \cdot im\nabla\varphi$$

$$= e_\varphi \frac{2im|\phi_{nl}(\theta, \varphi)|^2}{r\sin\theta} = e_\varphi \frac{2im|\psi_{nlm}|^2}{r\sin\theta}$$

于是电流密度为绕 z 轴的环状电流密度

$$-ej_\varphi = -\frac{em\hbar}{\mu r \sin\theta} |\psi_{nlm}|^2$$

考虑一无穷薄截面 $d\sigma$, 环状电流元 $dI = ej_\varphi d\sigma$ 对磁矩的贡献为

$$\mu_z = \int S dI = \int \pi(r\sin\theta)^2 \left(-\frac{em\hbar}{\mu r \sin\theta} |\psi_{nlm}|^2 \right) d\sigma$$

$$= -\frac{em\hbar}{2\mu} \int |\psi_{nlm}|^2 2\pi r \sin\theta d\sigma$$

$$= -\frac{em\hbar}{2\mu} \int |\psi_{nlm}|^2 d\tau = -\frac{em\hbar}{2\mu} = -m\mu_B$$

Bohr 磁子 (magneton)

$$\mu_B = \frac{e\hbar}{2\mu}$$

$$\mu_z = -\frac{e}{2\mu} \hat{L}_z = -\gamma \hat{L}_z \quad \gamma \text{ 旋磁比 (gyromagnetic ration)}$$

FH 定理和Virial 定理在中心力场中的应用

Feynman-Hellmann 定理

若 λ 是 \hat{H} 中的一个参数, 则对其束缚态 ψ_n, E_n 而言, 必有

$$\frac{\partial \hat{H}}{\partial \lambda} = \frac{\partial E_n}{\partial \lambda}$$

能量本征值与角动量量子数

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + V(r) = \frac{\hat{p}_r^2}{2\mu} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)$$

$$\frac{\partial \hat{H}}{\partial l} = \frac{(2l+1)\hbar^2}{2\mu} \frac{1}{r^2} = \frac{\partial E_n}{\partial l} > 0$$

所以给定 n_r , 中心力场基态必为 s 态 ($l=0$)

离心势能 $\frac{\hat{L}^2}{2\mu r^2}$

1. 类氢离子

$$\frac{\partial \hat{H}}{\partial l} = \frac{(2l+1)\hbar^2}{2\mu} \frac{1}{r^2} = \frac{\partial E_n}{\partial l} = -\frac{\partial}{\partial l} \frac{e^2 Z^2}{2an^2} = \frac{e^2 Z^2}{an^3}$$

$$\frac{\hat{L}^2}{2\mu r^2} = \frac{l(l+1)\hbar^2}{2\mu} \frac{1}{r^2} = \frac{l(l+1)}{2l+1} \frac{\mu e^2 Z^2}{an^3} = -\frac{l(l+1)}{\left(l+\frac{1}{2}\right)n} E_n = \frac{l(l+1)}{\left(l+\frac{1}{2}\right)n} T$$

l 越大, 离心势能在动能中比例越大

2. 三维各向同性谐振子

$$\frac{\partial \hat{H}}{\partial l} = \frac{(2l+1)\hbar^2}{2\mu} \frac{1}{r^2} = \frac{\partial E_n}{\partial l} = \hbar\omega$$

$$\frac{\hat{L}^2}{2\mu r^2} = \frac{l(l+1)\hbar^2}{2\mu} \frac{1}{r^2} = \frac{l(l+1)}{2l+1} \hbar\omega = \frac{l(l+1)}{(2l+1)(n+3/2)} E_n = \frac{l(l+1)}{(2l+1)(2n+3)} T$$

$$\frac{\overline{\hat{p}_r^2}}{2\mu} = \bar{T} - \frac{\overline{\hat{L}^2}}{2\mu r^2} = \left[\frac{n}{2} + \frac{3}{4} - \frac{l(l+1)}{2l+1} \right] \hbar\omega$$

$$l \gg 1$$

$$\frac{\overline{\hat{L}^2}}{2\mu r^2} \approx \left(l + \frac{1}{2} \right) \frac{\hbar\omega}{2}$$

$$\frac{\overline{\hat{p}_r^2}}{2\mu} \approx (n - l + 1) \frac{\hbar\omega}{2} = \left(n_r + \frac{1}{2} \right) \hbar\omega$$

位力 (virial) 定理

设粒子处于势场V(r)中，对于n次齐次势的定态有

$$2\bar{T} = n\bar{V}$$

$$\bar{V} = \frac{2}{2+n} \bar{E}$$

A. 类氢离子

$$V = -\frac{Ze^2}{r}, E_n = -\frac{e^2 Z^2}{2an^2} \Rightarrow \bar{V} = 2\bar{E} = -\frac{e^2 Z^2}{an^2} \Rightarrow \frac{1}{r} = \frac{Z}{n^2 a}$$

B. 三维各向同性谐振子

$$V = \frac{1}{2} \mu \omega^2 r^2, E_n = \left(n + \frac{3}{2} \right) \hbar\omega \Rightarrow \bar{V} = \frac{1}{2} \bar{E} = \frac{1}{2} \left(n + \frac{3}{2} \right) \hbar\omega \Rightarrow \overline{r^2} = \left(n + \frac{3}{2} \right) \frac{\hbar}{\mu\omega}$$