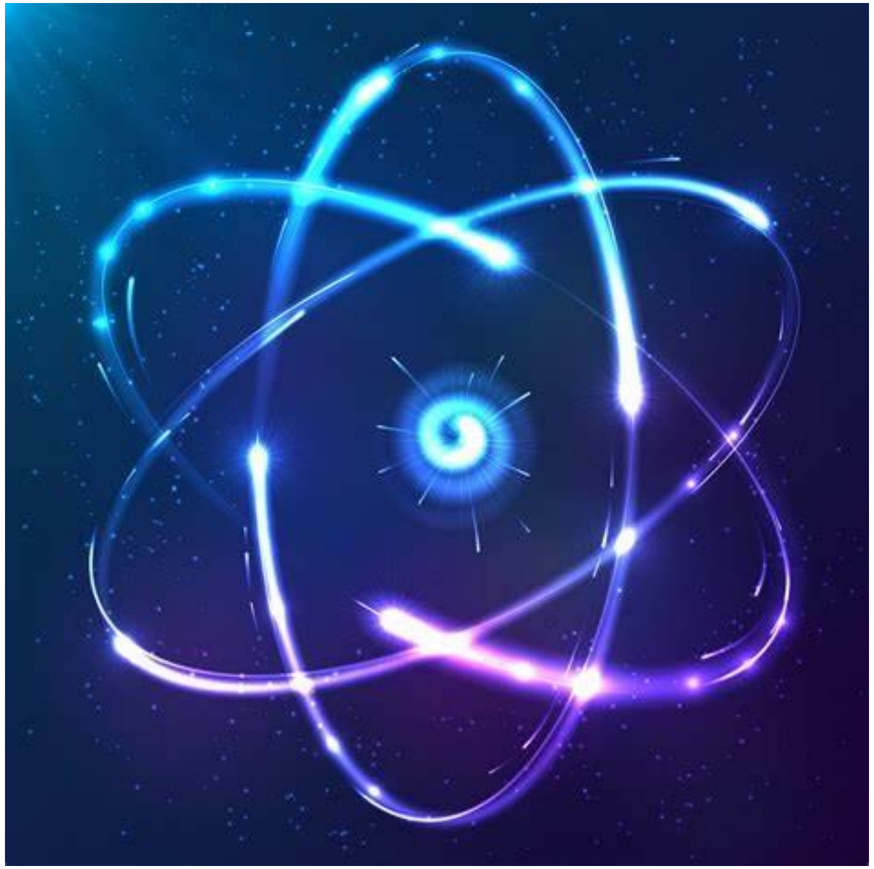

氢原子解

球坐标系的薛定谔方程

径向方程和角向方程

束缚态和散射态

径向波函数和球谐函数

电子云

反射对称形和宇称

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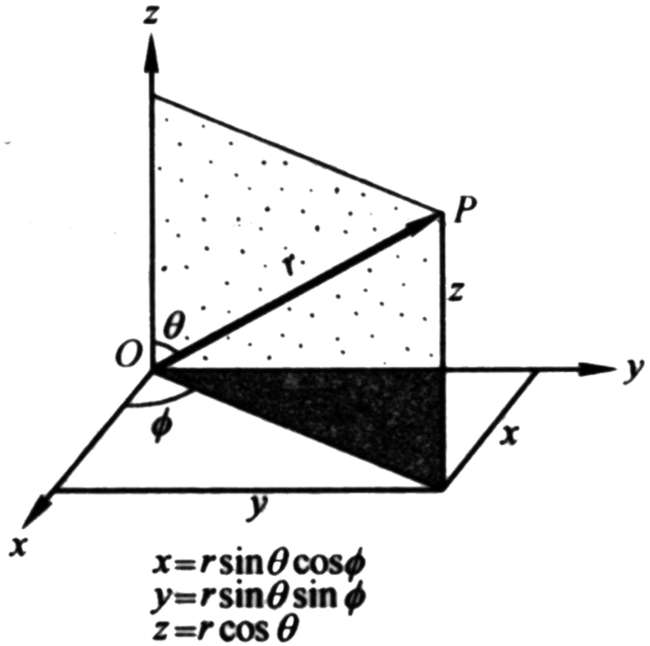
球坐标系中的薛定谔方程

库伦势

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

哈密顿算符

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$



定态薛定谔方程：

$$-\frac{\hbar^2}{2m}\nabla^2 u(r,\theta,\varphi) - \frac{e^2}{4\pi\varepsilon_0 r}u(r,\theta,\varphi) = Eu(r,\theta,\varphi)$$

Hermann Klaus Hugo Weyl
德国数学家、物理学家、哲学家
曾帮助薛定谔求解氢原子波函数

拉普拉斯算符*

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases}$$

雅可比矩阵

$$\frac{\partial(r,\theta,\varphi)}{\partial(x,y,z)} = \begin{pmatrix} \sin\theta\cos\varphi & \sin\theta\sin\varphi & \cos\theta \\ \frac{1}{r}\cos\theta\cos\varphi & \frac{1}{r}\cos\theta\cos\varphi & -\frac{1}{r}\sin\theta \\ -\frac{1}{r}\csc\theta\sin\varphi & \frac{1}{r}\csc\theta\cos\varphi & 0 \end{pmatrix}$$

梯度

$$\frac{\partial}{\partial r_j} = \frac{\partial \xi^\alpha}{\partial r_j}\frac{\partial}{\partial \xi^\alpha} \Rightarrow \begin{cases} \frac{\partial}{\partial x} = \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\csc\theta\sin\varphi\frac{\partial}{\partial\varphi} \\ \frac{\partial}{\partial y} = \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} + \frac{1}{r}\csc\theta\cos\varphi\frac{\partial}{\partial\varphi} \\ \frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta} \end{cases}$$

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

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

拉普拉斯算符-微分几何*

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases}$$

$$\partial_\alpha \stackrel{\text{def}}{=} \frac{\partial}{\partial \xi^\alpha}$$

梯度

$$\frac{\partial}{\partial r_j} = \frac{\partial \xi^\alpha}{\partial r_j}\frac{\partial}{\partial \xi^\alpha}$$

$$\nabla^2 = \frac{\partial}{\partial r_j}\frac{\partial}{\partial r_j} = \frac{\partial \xi^\alpha}{\partial r_j}\partial_\alpha \frac{\partial \xi^\beta}{\partial r_j}\partial_\beta = \cdots = \frac{1}{\sqrt{g}}\partial_\alpha\sqrt{g}g^{\alpha\beta}\partial_\beta$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

雅可比矩阵

$$J = (\partial_\alpha \vec{r}) = \frac{\partial(x,y,z)}{\partial(r,\theta,\varphi)} = \begin{pmatrix} \sin\theta\cos\varphi & r\cos\theta\cos\varphi & -r\sin\theta\sin\varphi \\ \sin\theta\sin\varphi & r\cos\theta\sin\varphi & r\sin\theta\cos\varphi \\ \cos\theta & -r\sin\theta & 0 \end{pmatrix}$$

弧长

$$ds^2 = dx^2 + dy^2 + dz^2 = g_{\alpha\beta}d\xi^\alpha d\xi^\beta$$

度规矩阵

$$(g_{\alpha\beta}) \stackrel{\text{def}}{=} (\partial_\alpha\vec{r})\cdot(\partial_\beta\vec{r}) = J^TJ = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2\sin^2\theta \end{pmatrix}$$

逆矩阵

$$(g^{\alpha\beta}) \stackrel{\text{def}}{=} (g_{\mu\nu})^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/r^2 & 0 \\ 0 & 0 & 1/(r^2\sin^2\theta) \end{pmatrix}$$

行列式

$$g \stackrel{\text{def}}{=} \det(g_{\mu\nu}) = r^4\sin^2\theta$$

$$\sqrt{g} = r^2\sin\theta$$

分离变量

$$-\frac{\hbar^2}{2m}\nabla^2 u(r,\theta,\varphi)-\frac{e^2}{4\pi\varepsilon_0 r}u(r,\theta,\varphi)=Eu(r,\theta,\varphi)$$

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

分离变量：

$$u(r,\theta,\varphi)=R(r)\Theta(\theta)\Phi(\varphi)$$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2mr^2}{\hbar^2}\sin^2\theta\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$\boxed{\frac{\partial^2\Phi}{\partial\varphi^2}+m_l^2\Phi=0}$$

继续分离变量

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$\boxed{\frac{m_l^2}{\sin^2\theta}\Theta-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)=l(l+1)\Theta}$$

把Θ对θ展开为Taylor series，代入方程，
考虑$\theta=0,\pi$处，⇒欲使波函数有限，l必须取非负整数

$$\boxed{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=l(l+1)R}$$

径向方程

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径向运动的有效势

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=l(l+1)R$$

$$\updownarrow$$

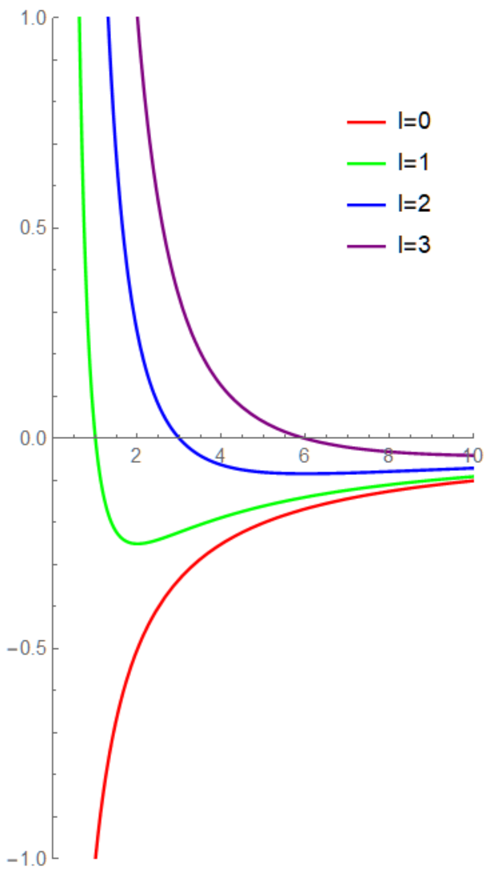
$$\left\{-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right\}R(r)=E\,R(r)$$

惯性离心势 中心位垒

Centrifugal barrier

等效势

$$V_{\text{effective}}(r)\stackrel{\text{def}}{=}\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\varepsilon_0 r}$$



求解1

$$\frac{\partial^2\Phi}{\partial\varphi^2}+m_l^2\Phi=0$$

$$\Phi(\varphi)=Ae^{im_l\varphi}$$

波函数单值

$$\Phi(\varphi)=\Phi(\varphi+2\pi)$$

$$m_l\in\mathbb{Z}$$

$$\boxed{\Phi(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im_l\varphi},\qquad m_l=0,\pm1,\pm2,\cdots}$$

求解2

$$\frac{m_l^2}{\sin^2\theta}\Theta-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)=l(l+1)\Theta$$

$$\boxed{\Theta(\theta)=B\cdot P_l^{m_l}(\theta)}$$

associated Legendre polynomial

$P_n^m(x)=(-1)^m(1-x^2)^{m/2}(d^m/dx^m)P_n(x)$

$$l=|m_l|,|m_l|+1,|m_l|+2,\cdots$$

$$\Updownarrow$$

$$\begin{cases} l=0,1,2,\cdots \\ m_l=0,\pm1,\pm2,\cdots,\pm l \end{cases}$$

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球谐函数
spherical harmonic function

$P_l^m(\theta)\Phi_m(\varphi) \propto Y_{lm}(\theta,\varphi)$ 参看数理方程教材

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

$$l = 0,1,2,\cdots; \quad m = -l, -l+1, \cdots, l-1, l.$$

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{l'm'}(\theta,\phi) Y_{lm}(\theta,\phi)\, d\Omega = \delta_{ll'}\delta_{mm'}$$

球面上平方可积函数的完备基

多极展开，分波展开

角向波函数

l	m_l	Θ_{lm_l}	Φ_{m_l}	l	m_l	Θ_{lm_l}	Φ_{m_l}
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	3	0	$\frac{\sqrt{14}}{4}(-3\cos\theta + 5\cos^3\theta)$	$\frac{1}{\sqrt{2\pi}}$
1	0	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	3	±1	$\mp\frac{\sqrt{42}}{8}(-1+5\cos^2\theta)\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\varphi}$
1	±1	$\mp\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\varphi}$	3	±2	$\frac{\sqrt{105}}{4}\cos\theta\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\varphi}$
2	0	$\frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	3	±3	$\mp\frac{\sqrt{70}}{8}\sin^3\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm 3i\varphi}$
2	±1	$\mp\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\varphi}$				
2	±2	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\varphi}$			$Y_{lm}(\theta,\varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi)$	

求解3

$$\left\{-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right\}R(r)=E\,R(r)$$

$$\chi(\rho)\stackrel{\text{def}}{=}rR(r),n\stackrel{\text{def}}{=}\frac{1}{\hbar}\sqrt{\frac{m}{2|E|}}\frac{e^2}{4\pi\varepsilon_0}$$

$$\rho\stackrel{\text{def}}{=}\frac{2}{\hbar}\sqrt{2m|E|}r=\frac{2r}{na_0},a_0\stackrel{\text{def}}{=}\frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

$$\frac{d^2\chi}{d\rho^2}+\left\{\frac{n}{\rho}\pm\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right\}\chi=0$$

其中$E>0$时取“＋”，$E<0$时取“－”

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散射态解($E > 0$)

$$\frac{d^2\chi}{d\rho^2} + \left\{\frac{n}{\rho} + \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right\}\chi = 0$$

n可以取连续的正数，E可以取任何正值

相当于单电子原子电离的情形，

电子可以运动到距离原子核无穷远处

解略

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束缚态解（$E < 0$）

$$\frac{d^2\chi}{d\rho^2} + \left\{\frac{n}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right\}\chi = 0 \quad \Longrightarrow \quad R_{nl} = C_{nl} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho)$$

缔合拉盖尔多项式
associated Laguerre polynomials

波函数的归一化条件

$$dxdydz = r^2 \sin\theta\, dr d\theta d\varphi$$
$$= r^2 dr d\Omega$$
$$\int_0^\infty |R|^2 r^2 dr = 1$$

并且n为$\geq l+1$的整数时，
才能使径向波函数在无穷远有限

合流超几何函数
confluent hypergeometric function

$$\boxed{\begin{gathered} R_{n,l}(r) = N_{n,l} e^{-\rho/2} \rho^l F(-n+l+1, 2l+2, \rho) \\ N_{n,l} \equiv \frac{2}{a_0^{3/2} n^2 (2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}}, \qquad \rho \overset{\text{def}}{=} \frac{2r}{n a_0}, \qquad a_0 \overset{\text{def}}{=} \frac{4\pi\varepsilon_0\hbar^2}{me^2} \end{gathered}}$$

径向波函数正交归一：$\int_0^\infty R_{n',l'}^*(r) R_{n,l}(r) r^2 dr = \delta_{n'n}\delta_{l'l}$

正交：哈密顿算符是厄密的，厄密算符的本征态相互正交
归一：做了归一化

定态径向波函数

n	l	R_{nl}	n	l	R_{nl}
1	0	$\frac{2}{a_0^{3/2}}\exp\left(-\frac{r}{a_0}\right)$	4	0	$\frac{1}{768a_0^{3/2}}\left(192-144\frac{r}{a_0}+24\frac{r^2}{a_0^2}-\frac{r^3}{a_0^3}\right)\exp\left(-\frac{r}{4a_0}\right)$
2	0	$\frac{1}{(2a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$	4	1	$\frac{1}{256\sqrt{15}a_0^{3/2}}\left(80\frac{r}{a_0}-20\frac{r^2}{a_0^2}+\frac{r^3}{a_0^3}\right)\exp\left(-\frac{r}{4a_0}\right)$
2	1	$\frac{1}{2\sqrt{6}a_0^{3/2}}\frac{r}{a_0}\exp\left(-\frac{r}{2a_0}\right)$	4	2	$\frac{1}{768\sqrt{5}a_0^{3/2}}\left(12\frac{r^2}{a_0^2}-\frac{r^3}{a_0^3}\right)\exp\left(-\frac{r}{4a_0}\right)$
3	0	$\frac{2}{81\sqrt{3}a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)\exp\left(-\frac{r}{3a_0}\right)$	4	3	$\frac{1}{768\sqrt{35}a_0^{3/2}}\frac{r^3}{a_0^3}\exp\left(-\frac{r}{4a_0}\right)$
3	1	$\frac{4}{81\sqrt{6}a_0^{3/2}}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)\exp\left(-\frac{r}{3a_0}\right)$			
3	2	$\frac{4}{81\sqrt{30}a_0^{3/2}}\frac{r^2}{a_0^2}\exp\left(-\frac{r}{3a_0}\right)$			

指数因子上，分母的系数为n

多项式因子中r的最低幂次为l

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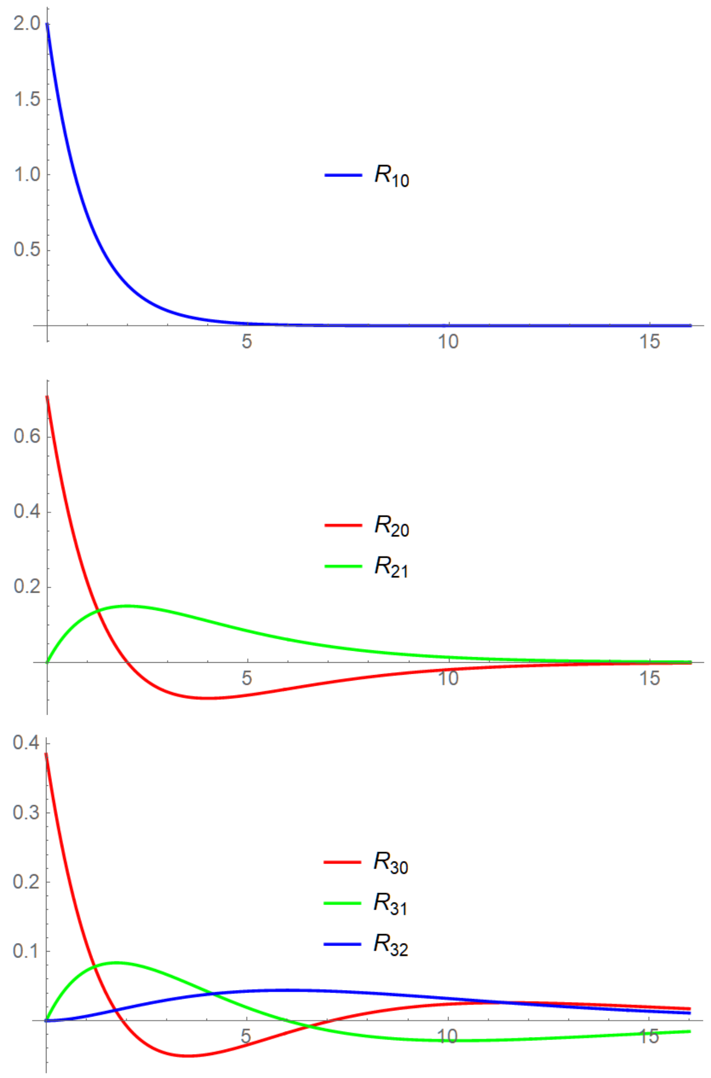
定态径向波函数图

零点的数目随n递增

节点数$n_r = n - l - 1$

R_{32}的零点是重根



$n = 1$, 0个

$n = 2$, 1个

$n = 3$, 2个

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总波函数

定态空间波函数

$$u_{nlm_l}(r,\theta,\varphi)=R_{nl}(r)\mathrm{Y}_{lm_l}(\theta,\varphi)$$

$n=1,2,3,\cdots$
$l=0,1,2,\cdots,n-1$
$m_l=-l,-l+1,\cdots,l-1,l$

定态波函数

$$\psi_{nlm_l}(\vec{r},t)=u_{nlm_l}(r,\theta,\varphi)\mathrm{e}^{-\frac{iE_n}{\hbar}t}$$

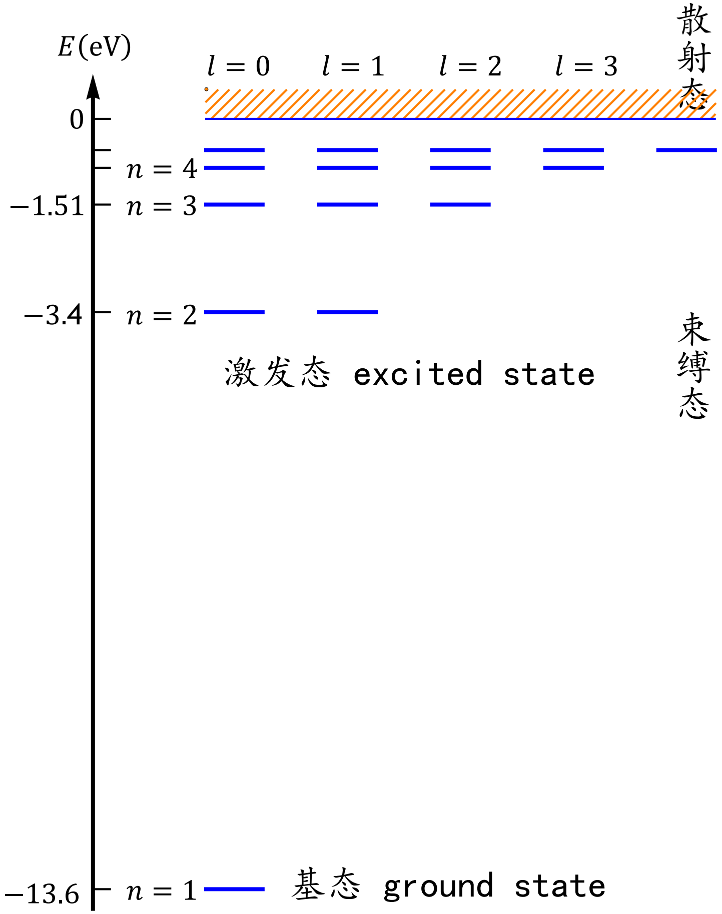
含时波函数的一般解

$$\psi(\vec{r},t)\equiv\sum_{n,l,m_l}c_{nlm_l}\psi_{nlm_l}(\vec{r},t)$$

展开系数c_{nlm_l}由初值决定

量子数的物理解释-主量子数

能量只依赖于主量子数



$$\hat{H}u_{nlm_l}(r,\theta,\phi) = Eu_{nlm_l}(r,\theta,\phi)$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R_{nl}}{\partial r}\right) + \frac{2m_e r^2}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)R_{nl} = l(l+1)R_{nl}$$

$$E_n = -\alpha^2\frac{mc^2Z^2}{2n^2} = -\frac{\hbar^2}{2ma_0^2n^2}$$

$$= -13.6\text{eV}\cdot\frac{Z^2}{n^2}$$

$$\alpha \stackrel{\text{def}}{=} \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$$

n^2重简并（不同状态具有相同能量；考虑自旋后$2n^2$），

$$m_l = 0, \pm 1, \dots, \pm l$$

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

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量子数的物理解释-
轨道角动量量子数和磁量子数

l, m_l和轨道角动量的本征值有关，

l：角动量量子数

m_l：磁量子数（原子磁矩与它成正比）

$$n = 1,2,3\cdots$$
$$l = 0,1,2,\cdots,n-1$$
$$m_l = 0,\pm 1,\pm 2,\pm l$$

l可以取0，与玻尔模型不同

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特征

指数因子上，分母的系数为n
指数因子前r最高幂次项为$n-1$次

相因子上$i\varphi$的倍数为m

solid spherical harmonic function

$$r^l Y_{lm}(\theta,\varphi)$$

是关于x,y,z的l次齐次多项式

多项式因子中r的最低幂次为l

从定态波函数读出量子数
或用算符作用，求出量子数

表 3.1.3 类氢离子的波函数

n	l	m_l	$u_{n,l,m_l}(r,\theta,\varphi)$
1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Zr}{a_0}\right)$
2	0	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)$
2	1	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}\cos\theta\exp\left(-\frac{Zr}{2a_0}\right)$
2	1	±1	$\frac{1}{8\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}\sin\theta\exp\left(-\frac{Zr}{2a_0}\right)e^{\pm i\varphi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+\frac{Z^2r^2}{a_0^2}\right)\exp\left(-\frac{Zr}{3a_0}\right)$
3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}\cos\theta\exp\left(-\frac{Zr}{3a_0}\right)$
3	1	±1	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}\sin\theta\exp\left(-\frac{Zr}{3a_0}\right)e^{\pm i\varphi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2(3\cos^2-1)\exp\left(-\frac{Zr}{3a_0}\right)$
3	2	±1	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2\sin\theta\cos\theta\exp\left(-\frac{Zr}{3a_0}\right)e^{\pm i\varphi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2\sin^2\theta\exp\left(-\frac{Zr}{3a_0}\right)e^{\pm 2i\varphi}$

角向概率分布

定态波函数

$$\boldsymbol{u_{nlm}(r,\theta,\varphi) = R_{n,l}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)}$$

$$R_{n,l}(r) = N_{n,l}e^{-\xi/2}\xi^l F(-n+l+1, 2l+1, \xi)$$

$$\Theta_{lm}(\theta) = P_l^m(\theta)$$

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

定态的几率密度

$$\boldsymbol{\rho dxdydz = |u_{nlm}|^2 r^2 dr \sin\theta\, d\theta d\varphi}$$

$$P_\theta d\theta = |\Theta_{lm}|^2 \sin\theta\, d\theta \iint |R_{nl}(r)|^2 |\Phi_m|^2 r^2 dr d\varphi = |\Theta_{lm}|^2 \sin\theta\, d\theta$$

$$P_\varphi d\varphi = |\Phi_m|^2 d\varphi \iint |R_{nl}(r)|^2 |\Theta_{lm}|^2 r^2 dr \sin\theta\, d\theta = \frac{1}{2\pi} d\varphi$$

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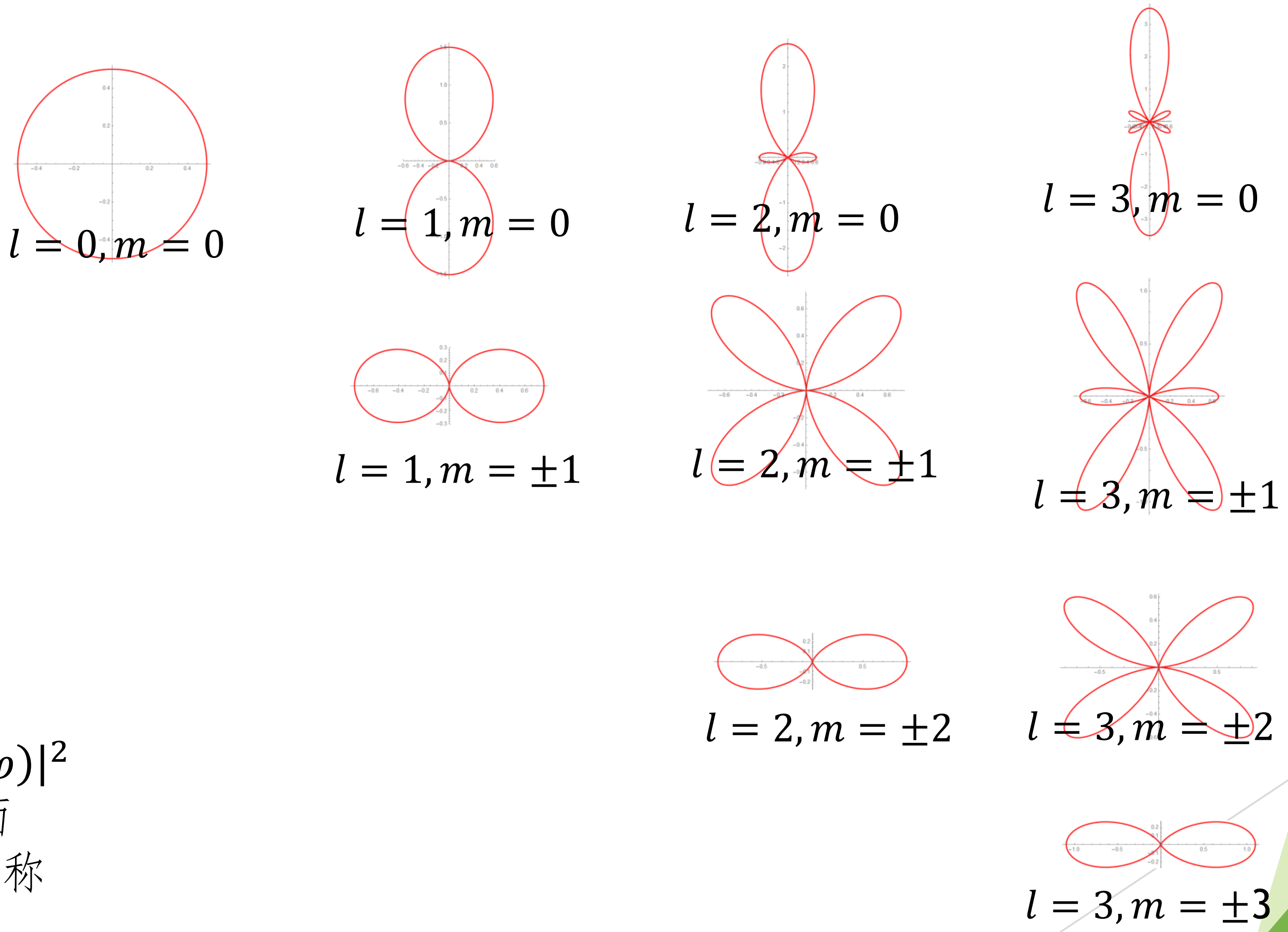
角向概率分布图



$$\rho_\Omega \stackrel{\text{def}}{=} |Y_{lm}(\theta,\varphi)|^2$$

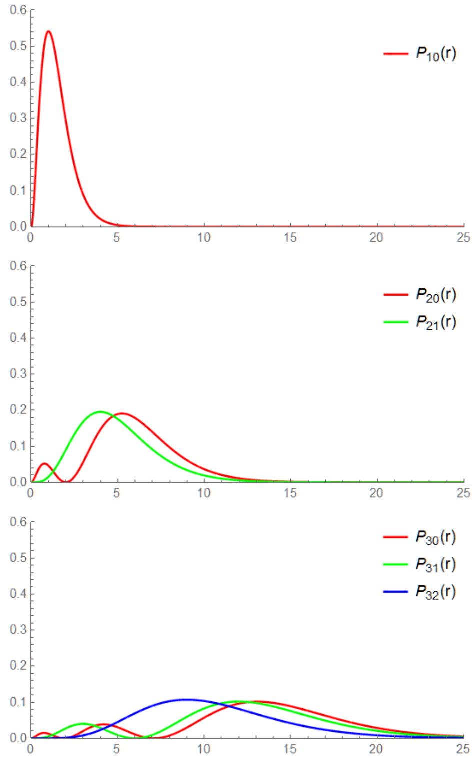
xz平面剖面

绕z轴旋转对称

- 22:45:38

径向概率密度

$$P_r dr = |R_{nl}(r)|^2 r^2 dr \iint |Y_{lm}(\theta,\varphi)|^2 \sin\theta \, d\theta d\varphi$$
$$= |R_{nl}(r)|^2 r^2 dr$$



公式：

$$\langle r^k \rangle = \iiint u_{nlm}^* r^k u_{nlm} r^2 dr d\Omega = \int_0^\infty R_{nl}^* r^k R_{nl} r^2 dr = \left(\frac{n}{2}\right)^k \frac{J_{n+l,2l+1}^{(k+1)}}{J_{n+l,2l+1}^{(1)}}$$

$$J_{\lambda,\mu}^{(\sigma)} \stackrel{\text{def}}{\equiv} \begin{cases} (-1)^\sigma \dfrac{\lambda!\,\sigma!}{(\lambda-\mu)!} \displaystyle\sum_{\beta=0}^{\sigma} (-1)^\beta \binom{\sigma}{\beta}\binom{\lambda+\beta}{\sigma}\binom{\lambda+\beta-\mu}{\sigma}, & \sigma \geq 0; \\ \dfrac{\lambda!}{(\lambda-\mu)!\,(s+1)!} \displaystyle\sum_{\gamma=0}^{s} (-1)^{s-\gamma} \frac{\binom{s}{\gamma}\binom{\lambda-\mu+\gamma}{s}}{\binom{\mu+s-\gamma}{s+1}}, & \sigma - -(s+1) \leq -1. \end{cases}$$

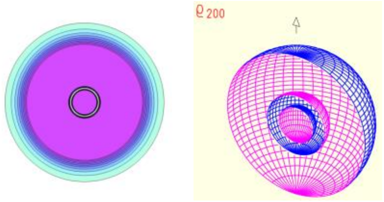
H. A. Bethe and E. E. Salpeter. Quantum Mechanics of One- and Two-Electron Atoms. Academic Press, New York, 1957.

$$\bar{r} = \frac{1}{2}\{3n^2 - l(l+1)\}\frac{a_0}{Z}$$
$$\overline{r^2} = \frac{1}{2}\{5n^2 + 1 - 3l(l+1)\}n^2\left(\frac{a_0}{Z}\right)^2$$
$$\overline{r^{-1}} = \frac{1}{n^2}\left(\frac{a_0}{Z}\right)^{-1}$$

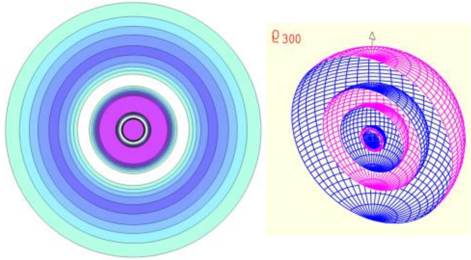
$$\overline{r^{-2}} = \frac{1}{n^3\left(l+\frac{1}{2}\right)}\left(\frac{a_0}{Z}\right)^{-2}$$
$$\overline{r^{-3}} = \frac{1}{n^3(l+1)\left(l+\frac{1}{2}\right)l}\left(\frac{a_0}{Z}\right)^{-3}, \qquad l > 0.$$

电子云图

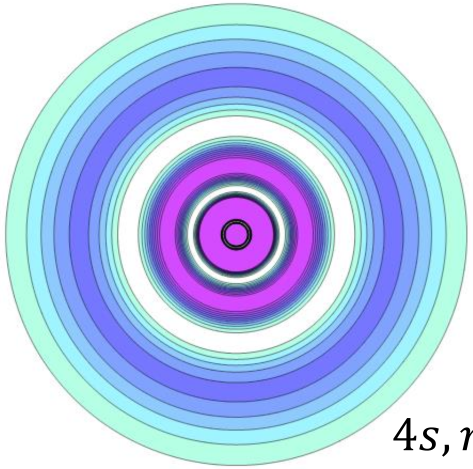
$1s, m = 0$



$2s, m = 0$



$3s, m = 0$

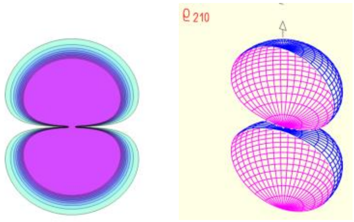


$4s, m = 0$

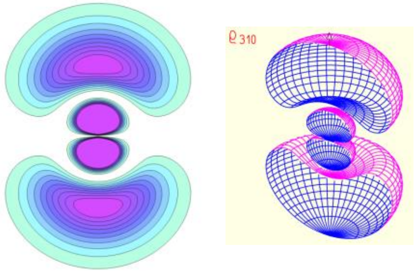
等密度面，截断，xz平面剖面

$\rho(r,\theta) = |u_{nlm}(r,\theta,\varphi)|^2$

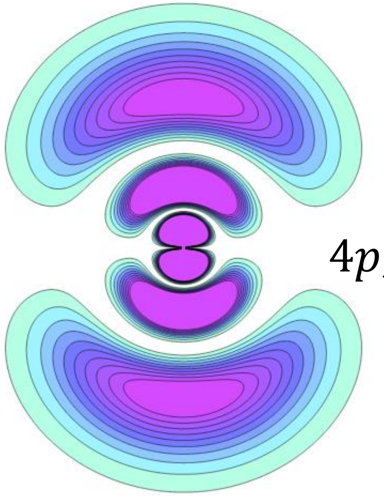
本征态绕z−轴旋转对称



$2p, m = 0$



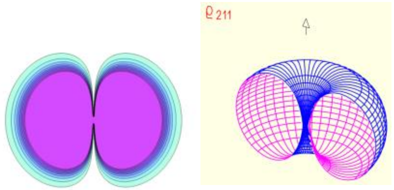
$3p, m = 0$



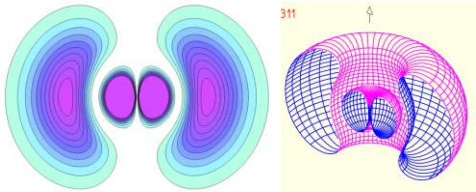
$4p, m = 0$

光谱学记号s, p, d, f

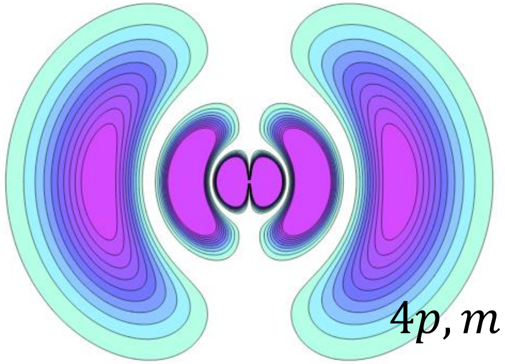
$l = 0, 1, 2, 3$



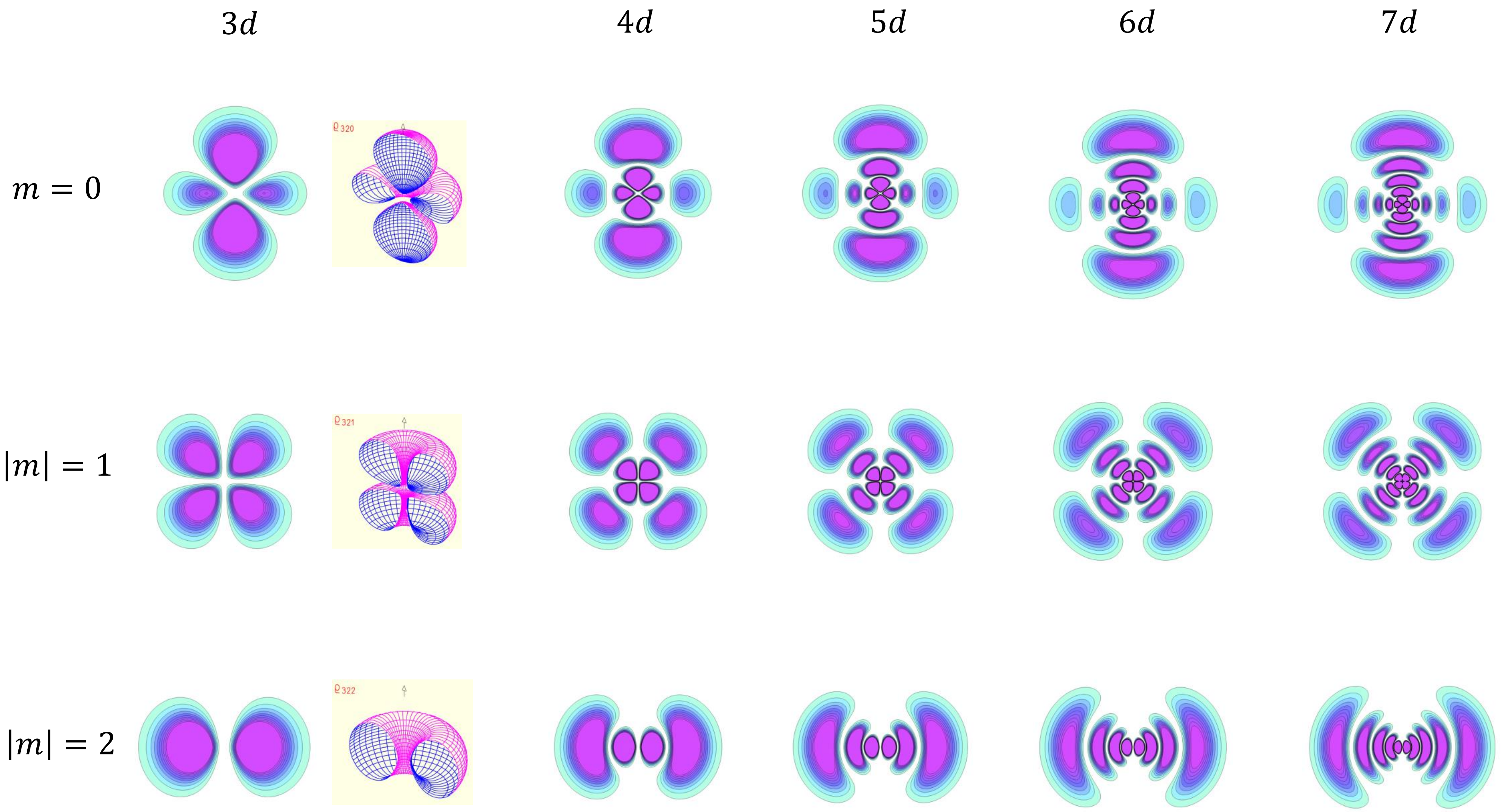
$2p, m = \pm 1$



$3p, m = \pm 1$



$4p, m = \pm 1$



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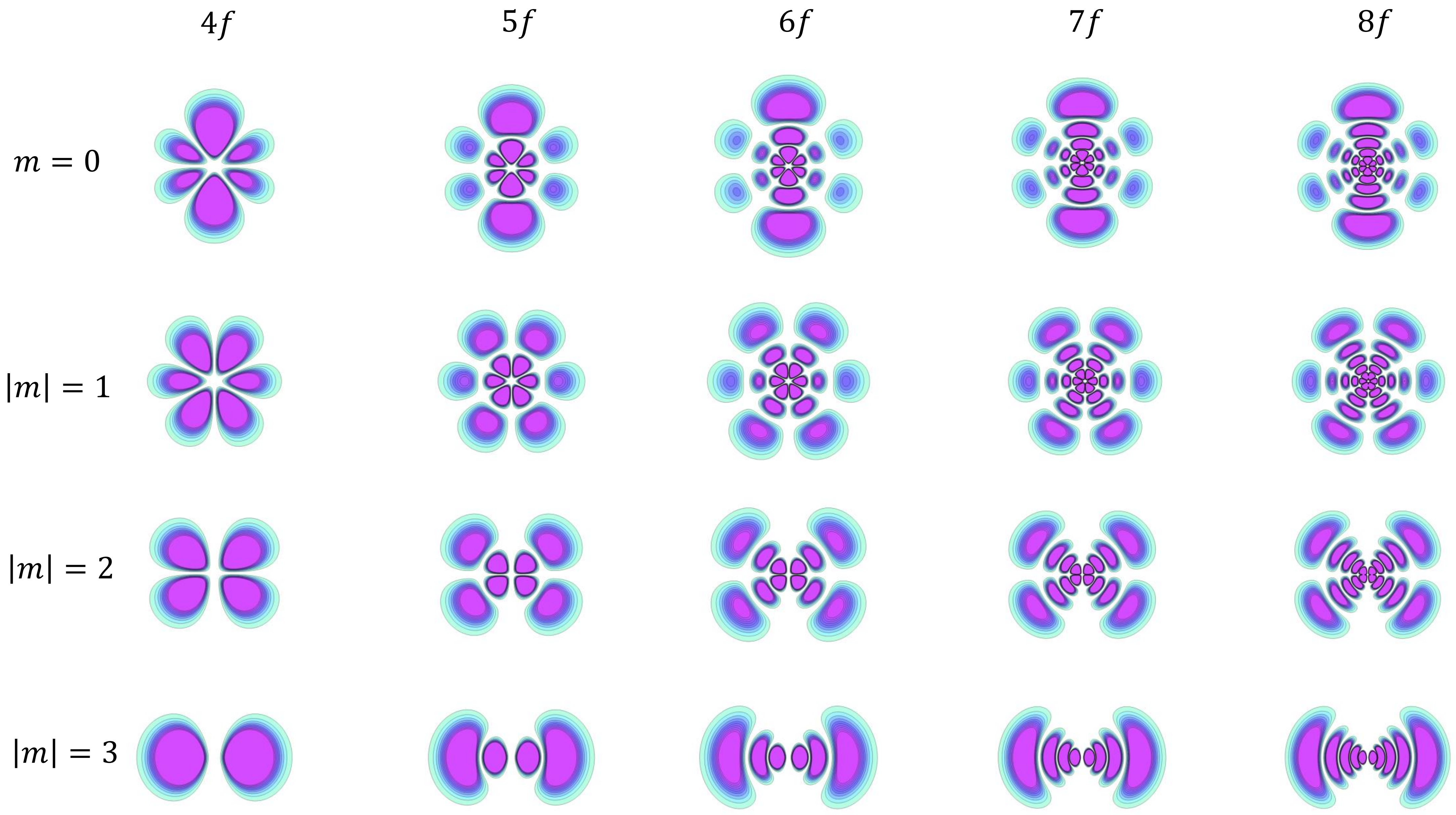

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空间反射和宇称 Space Reflection Parity

空间反射

$$\vec{r} = P\vec{r}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \to \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

在球坐标系，

$$(r, \theta, \varphi) \to (r, \pi - \theta, \varphi + \pi)$$

两次反射为恒等操作：$P^2 = \mathbf{1}_{3\times 3}$

量子力学中空间反射为算符$\hat{P}$

$\hat{P}^2 = 1 \Rightarrow$特征值为

$$\eta = \pm 1$$

用之于氢原子的定态波函数

$$u_{nlm}(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m}(\theta, \varphi)$$

$$\hat{P} u_{nlm}(r, \theta, \varphi) = R_{n,l}(r) \hat{P} Y_{l,m}(\theta, \varphi)$$

$r^l Y_{lm}$是x, y, z的l次多项式，所以

$$\hat{P} Y_{l,m}(\theta, \varphi) = Y_{l,m}(\pi - \theta, \varphi + \pi)$$
$$= (-1)^l Y_{l,m}(\theta, \varphi)$$

$u_{nlm}(r, \theta, \varphi)$的宇称为$(-1)^l$

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
$rY_{1,0} = \sqrt{\frac{3}{8\pi}} z$
$rY_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} (x + iy)$
$r^2 Y_{2,0} = \sqrt{\frac{5}{16\pi}} (2z^2 - x^2 - y^2)$
$r^2 Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} (x \pm iy) z$
$r^2 Y_{2,\pm 2} = \mp \sqrt{\frac{15}{32\pi}} (x \pm iy)^2$
$r^3 Y_{3,0} = \sqrt{\frac{7}{16\pi}} [2z^3 - 3(x^2 + y^2) z]$
$r^3 Y_{3,\pm 1} = \mp \sqrt{\frac{21}{64\pi}} (x \pm iy)(4z^2 - x^2 - y^2)$
$r^3 Y_{3,\pm 2} = \sqrt{\frac{105}{32\pi}} (x \pm iy)^2 z$
$r^3 Y_{3,\pm 3} = \mp \sqrt{\frac{35}{64\pi}} (x \pm iy)^3$

反射对称和宇称守恒*

态矢的空间反射

$$|\psi\rangle \rightarrow \hat{P}|\psi\rangle$$

算符的空间反射

$$\hat{A} \rightarrow \hat{P}\hat{A}\hat{P}^{-1}$$

电磁相互作用反射对称

$$\hat{P}\hat{H}\hat{P}^{-1} = \hat{H}$$

$$[\hat{P}, \hat{H}] = 0$$

$$\frac{d}{dt}A_{fi} = \left\langle \psi_f \middle| \frac{\partial \hat{A}}{\partial t} + \frac{1}{i\hbar}[\hat{A}, \hat{H}] \middle| \psi_i \right\rangle$$

$$\frac{d\bar{P}}{dt} = \left\langle \frac{\partial \hat{P}}{\partial t} + \frac{1}{i\hbar}[\hat{P}, \hat{H}] \right\rangle = 0$$

反射对称⟺宇称守恒

跃迁选择定则

对称性主导理论物理学：

爱因斯坦（广义相对论）杨振宁（规范场）

WS模型、QCD、超对称……

分析力学中的诺特定理：

作用量的可微对称性与守恒量一一对应

Emmy Noether

人们对自然界的各种对称性，连续的和分立的，一直深信不疑

李政道和杨振宁

1956年 弱相互作用宇称不守恒

1957年 诺贝尔物理学奖

先有对称性，后有物理学