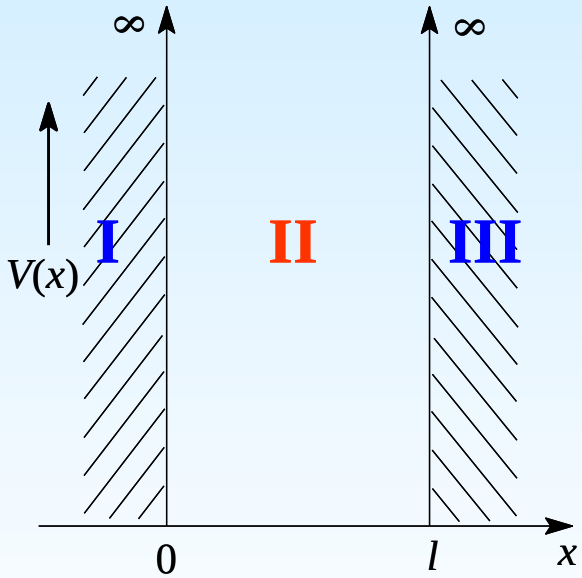
第二章 量子力学简单体系

Quantum Mechanics of Some Simple Systems

§2.1 势箱中的粒子 The particle in a box

2.1.1 一维势箱中的粒子 The Partical in a One-Dimensional Box



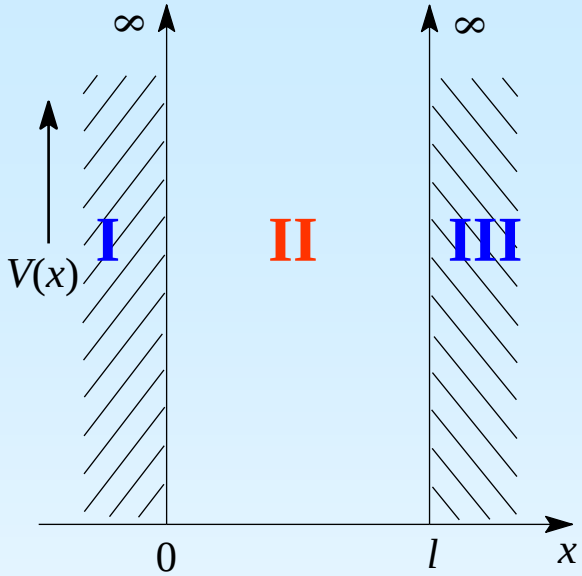
区域I和III V=∞ ($x \le 0, x \ge l$)

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \infty\psi(x) = E\psi(x)$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = (\infty - E)\psi(x) = \infty\psi(x)$$

$$\psi(x) = \frac{1}{\infty}\frac{d^2\psi(x)}{dx^2}$$

$\psi_{\mathrm{I}}(x) = 0$ $\psi_{\mathrm{III}}(x) = 0$



区域II V=0 (0< x < l)

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x)$$

$$\psi_{\mathrm{II}}(x)=A\cos kx+B\sin kx \qquad k=\sqrt{2mE}/\hbar$$

$$\lim_{x\to 0}\psi_{\mathrm{I}}=\lim_{x\to 0}\psi_{\mathrm{II}} \Longrightarrow A=0$$

$$\lim_{x\to l}\psi_{\mathrm{III}}=\lim_{x\to l}\psi_{\mathrm{II}} \Longrightarrow B\sin kl=0 \xrightarrow{B\neq 0} kl=\pm n\pi,\quad n=0,1,2\ldots$$

$\Downarrow$ $n\neq 0$

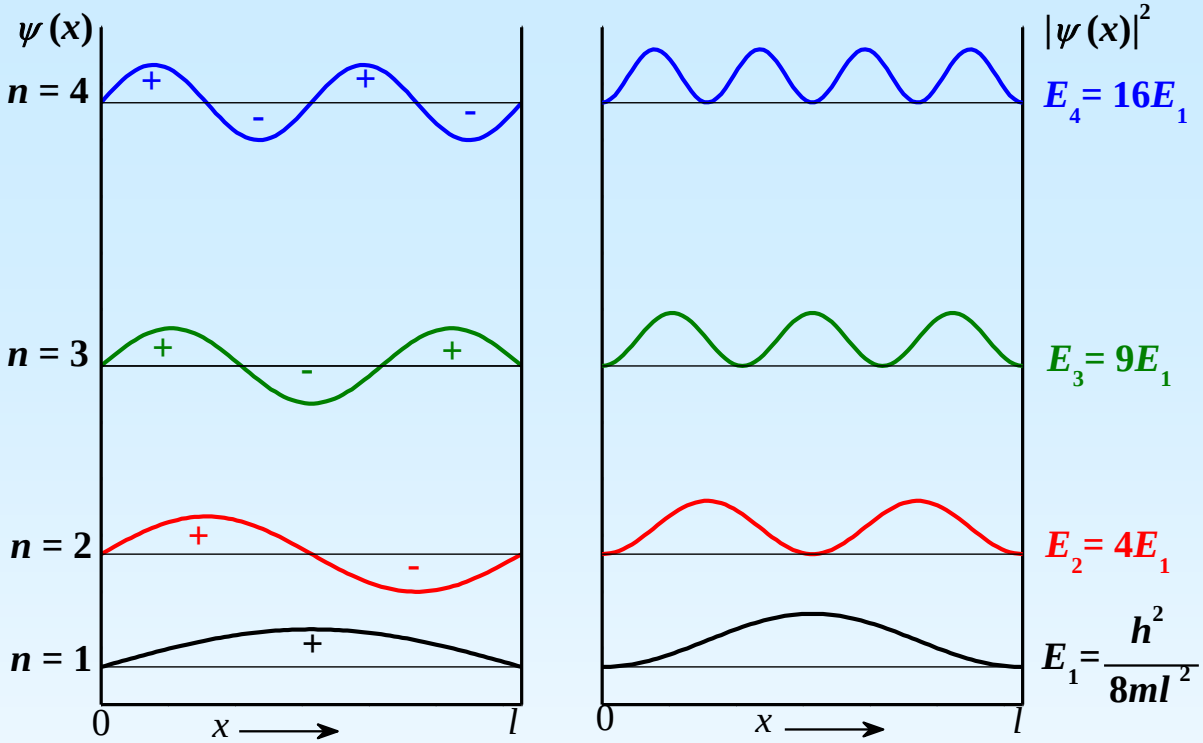
$$\boxed{E=\frac{n^2h^2}{8ml^2}\quad n=1,2,3\cdots}$$

$$\psi_{\mathrm{II}}(x)=B\sin\frac{n\pi x}{l}$$

$$\int_{-\infty}^{\infty}|\psi|^2dx=\int_{-\infty}^{0}|\psi_{\mathrm{I}}|^2dx+\int_0^l|\psi_{\mathrm{II}}|^2dx+\int_l^{\infty}|\psi_{\mathrm{III}}|^2dx=|B|^2\int_0^l\sin^2(n\pi x/l)dx=|B|^2\frac{l}{2}=1$$

$$|B|=\sqrt{2/l} \qquad B=\sqrt{2/l}e^{i\alpha} \xrightarrow[\text{取}\alpha=0]{} B=\sqrt{2/l}$$

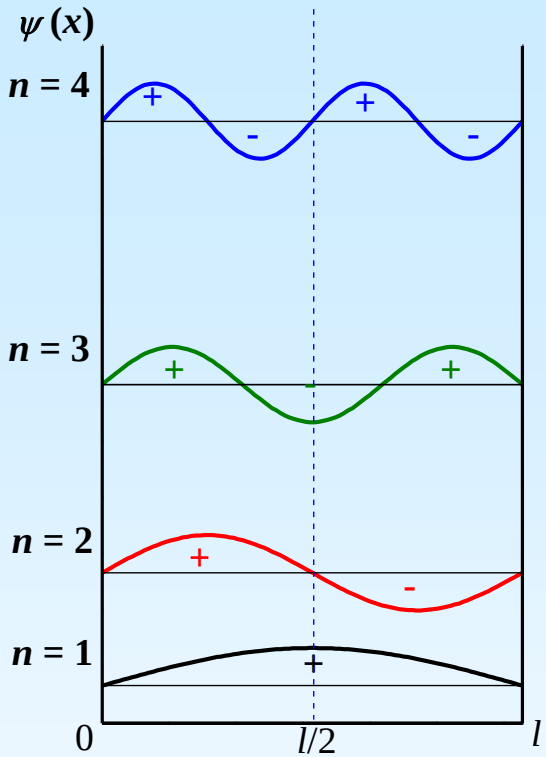
$$\boxed{\psi_{\mathrm{II}}=\sqrt{\frac{2}{l}}\sin\frac{n\pi}{l}x}$$



$$\psi_{\mathrm{II}} = \sqrt{\frac{2}{l}} \sin \frac{n\pi}{l} x$$

$$E = \frac{n^2 h^2}{8ml^2} \qquad n = 1, 2, 3 \cdots$$

- 单一量子数n决定波函数和能级
- $n \to \infty$时，粒子在箱中各个位置出现的概率密度趋于相同
- 箱中粒子位置不确定度是有限的,因此动量的不确定度不能为零→零点能(zero-point energy)
- $\Delta E = E_{n+1} - E_n = (2n+1)h^2/8ml^2$，当$l \to \infty$时，$\Delta E \to 0$，粒子变为自由粒子



波函数的对称性

定义一个反映算符 $\hat{R}$　$\psi(x)$已归一化

$$\hat{R}\psi(x)=\psi(-x+l)$$

通过$x=l/2$镜面反映

$$\hat{R}\hat{T}=\hat{R}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)=-\frac{\hbar^2}{2m}\frac{d^2}{d(-x+l)^2}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}=\hat{T}$$

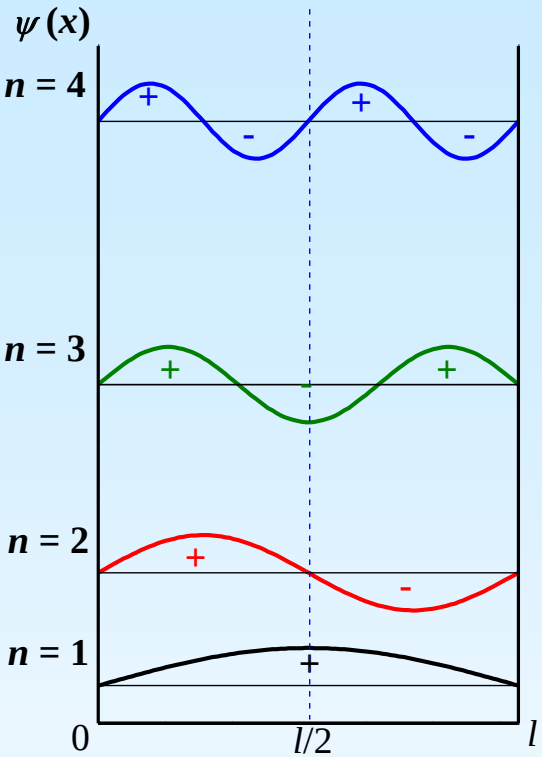
$$\hat{R}\hat{V}=\hat{V}$$

$$\hat{R}\hat{H}=\hat{R}(\hat{T}+\hat{V})=\hat{R}\hat{T}+\hat{R}\hat{V}=\hat{T}+\hat{V}=\hat{H}$$

$$\hat{H}\psi(x)=E\psi(x)\Longrightarrow(\hat{R}\hat{H})[\hat{R}\psi(x)]=(\hat{R}E)[\hat{R}\psi(x)]$$

$$\Longrightarrow\hat{H}[\hat{R}\psi(x)]=E[\hat{R}\psi(x)]$$

$$\hat{R}\psi(x)=c\psi(x)\qquad\int_0^l\left[\hat{R}\psi(x)\right]^2dx=1=c^2\qquad c=\pm1$$



$\hat{R}\psi = +\psi$ 对称(*symmetric*), 偶(*even*)

$\hat{R}\psi = -\psi$ 反对称(*antisymmetric*), 奇(*odd*)

ψ_1和ψ_3为偶函数， ψ_2和ψ_4为奇函数

如果ψ是非简并波函数，那么对于$\hat{H}$不变的变换， ψ一定是对称的或反对称的。

波函数的正交性

$$\int_0^l \psi_m(x)\psi_n(x)dx = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

2.1.2 二维势箱中的粒子 Partical in a two-dimensional well

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\psi(x,y)=E\psi(x,y)$$

变数分离法求解

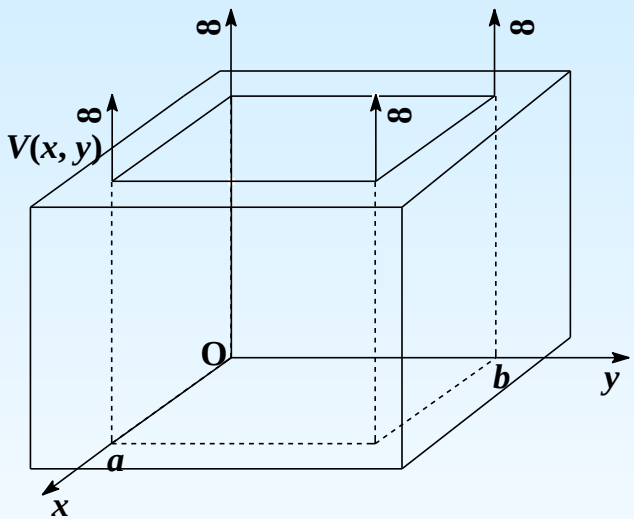
$$\psi(x,y)=X(x)Y(y)$$

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=-\frac{2mE}{\hbar^2}$$

$$\frac{1}{X(x)}\frac{d^2 X(x)}{dx^2}=-\frac{2mE_x}{\hbar^2}$$

$$\frac{1}{Y(y)}\frac{d^2 Y(y)}{dy^2}=-\frac{2mE_y}{\hbar^2}$$

$$E=E_x+E_y$$

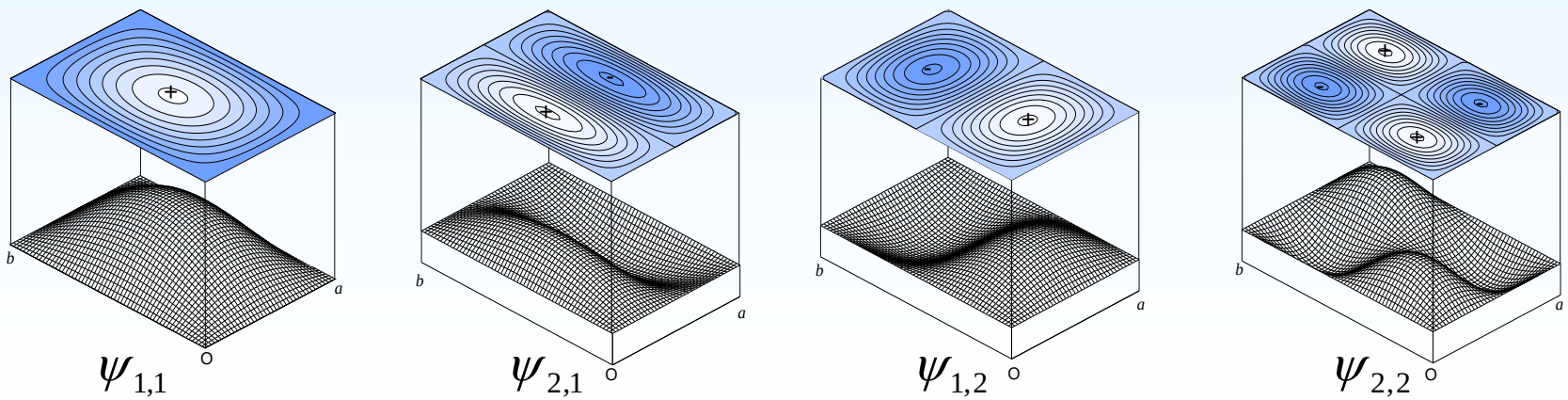


$$\begin{cases} X(x)=\sqrt{\dfrac{2}{a}}\sin\dfrac{n_x\pi}{a}x \\ Y(y)=\sqrt{\dfrac{2}{b}}\sin\dfrac{n_y\pi}{b}y \end{cases} \qquad E_x=\frac{n_x^2h^2}{8ma^2} \qquad n_x=1,\ 2,\ 3\ldots$$

$$E_y=\frac{n_y^2h^2}{8mb^2} \qquad n_y=1,\ 2,\ 3\ldots$$

$$\psi(x,y)=\frac{2}{\sqrt{ab}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)$$

$$E=E_x+E_y=\frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right) \qquad n_x=1,\ 2,\ 3\ldots \quad n_y=1,\ 2,\ 3\ldots$$



2.1.3 三维势箱中的粒子 Partical in a three-dimensional box

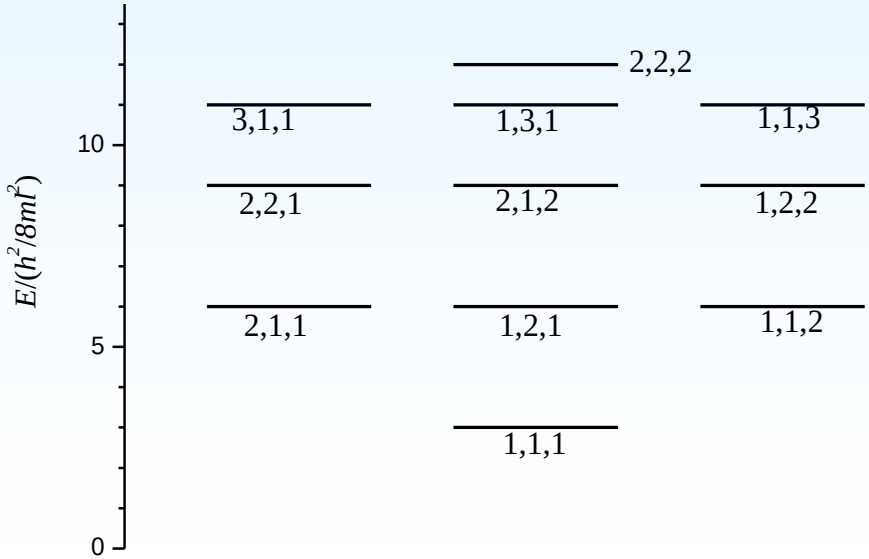
$$\psi(x,y,z)=\frac{2\sqrt{2}}{\sqrt{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right)$$

$$E_{n_x,n_y,n_z}=\frac{n_x^2h^2}{8ma^2}+\frac{n_y^2h^2}{8mb^2}+\frac{n_z^2h^2}{8mc^2}$$

n_x=1, 2, 3…; n_y=1, 2, 3…; n_z=1, 2, 3…

三维方箱

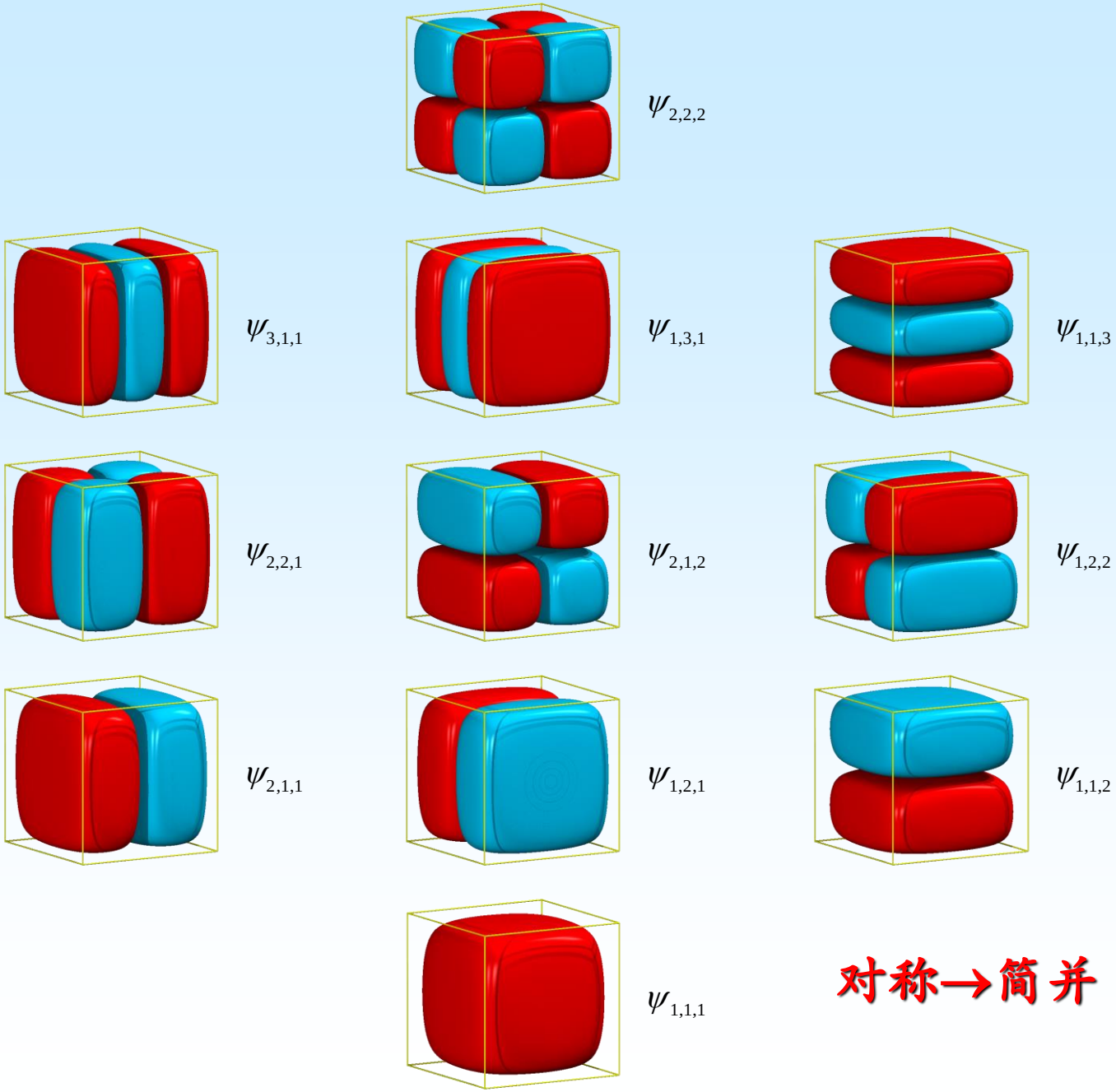
$a=b=c=l$



简并

degeneracy

三维势箱能波函数轮廓图



对称→简并

2.1.4 一维自由粒子 The free partical in one dimension

一维自由粒子，势能保持一定，令$V(x)=0$，Schrödinger方程：

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2}+\frac{2mE}{\hbar^2}\psi(x)=0 \xrightarrow{k=\frac{\sqrt{2mE}}{\hbar}} \text{特征方程 } r^2+k^2=0$$

$$\Downarrow$$

$$r=\pm ik$$

$$\psi(x)=c_1e^{ikx}+c_2e^{-ikx}$$

$$\psi(x)=A\cos kx+B\sin kx$$

若$E<0$，则 $ik=i\cdot i\sqrt{2m|E|}/\hbar=-\sqrt{2m|E|}/\hbar<0$

$x\to+\infty$ 时，$e^{-ikx}\to+\infty$

$x\to-\infty$ 时，$e^{ikx}\to+\infty$ $\Rightarrow$ **$E\geq0$**

自由粒子的能谱是连续的

$\psi(x)$不能归一化

$$\psi_1(x)=c_1e^{ikx} \qquad \psi_2(x)=c_2e^{-ikx}$$

$$\hat{p}_x\psi_1=-i\hbar\frac{d\psi_1}{dx}=\sqrt{2mE}c_1e^{ikx}=|p_x|\psi_1 \qquad \hat{p}_x\psi_2=-|p_x|\psi_2$$

ψ_1，ψ_2是$\hat{H}$和 $\hat{p}_x$的本征函数

$$\Psi_1=\psi_1e^{-iE_xt/\hbar}=c_1\,exp\left[\frac{i}{\hbar}\left(|p_x|x-E_xt\right)\right] \qquad \Psi_2=c_2\,exp\left[\frac{-i}{\hbar}\left(|p_x|x+E_xt\right)\right]$$

Ψ_1表示沿+x方向运动，具有确定动量+$|p_x|$的平面波，Ψ_2表示沿–x方向运动，具有确定动量–$|p_x|$的平面波

Ψ_1发现粒子在x与$x+dx$间的概率

$$dW=\Psi_1^*\Psi_1dx=\psi_1^*\psi_1dx=c_1^*c_1dx$$

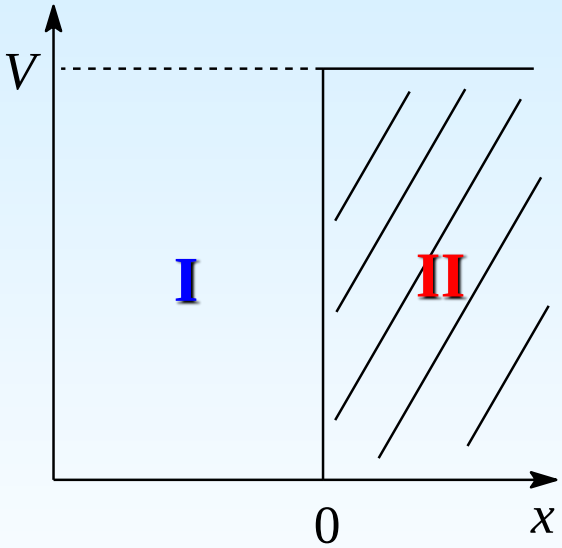
概率密度=$c_1^*c_1$=常数

粒子x轴上任何点出现的概率密度都相等，即p_x完全确定时，x位置完全不确定

$\psi(x)=c_1e^{ikx}+c_2e^{-ikx}$ **不是 $\hat{p}_x$ 的本征函数**

§2.2 势垒贯穿 Penetration into and through barriers

2.2.1 An infinitely thick potential wall



区域I (x<0)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\psi_{\mathrm{I}} = Ae^{ikx} + Be^{-ikx}$$

$$k = \sqrt{2mE}/\hbar$$

区域II (x≥0)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

$$\psi_{\mathrm{II}} = A'e^{ik'x} + B'e^{-ik'x}$$

$$k' = \sqrt{2m(E-V)}/\hbar$$

经典力学：*E*<*V*时，粒子不可能出现在*x*>0的区域

区域II $\psi_{\mathrm{II}} = A'e^{ik'x} + B'e^{-ik'x}$ $k' = \sqrt{2m(E-V)}/\hbar$

$E<V$，k'为虚数，设$k'=i\kappa$

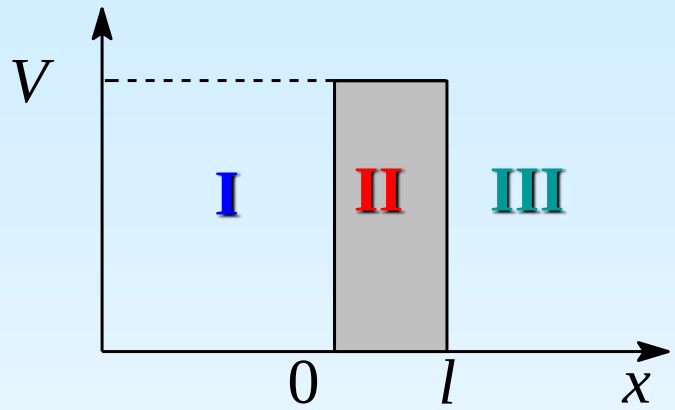
$$\psi_{\mathrm{II}} = A'e^{-\kappa x} + B'e^{\kappa x} \qquad \kappa = \sqrt{2m(V-E)}/\hbar$$

$x\to\infty$，$e^{\kappa x}\to\infty$，

$$\psi_{\mathrm{II}} = A'\,e^{-\kappa x}$$

- **区域II中，粒子的波函数不为零**
- **波函数衰减到零的速度取决于κ，$1/\kappa$为penetration depth**

2.2.2 方形势垒 A barrier of finite width



Zone I ($x<0$): $V(x)=0$
Zone II ($0\le x\le l$): $V(x)=V$
Zone III ($x>l$): $V(x)=0$
粒子自左向右射入势垒

A. $E>V$ 时

$$\psi_{\mathrm{I}} = Ae^{ikx} + Be^{-ikx} \qquad k=\sqrt{2mE}/\hbar$$

$$\psi_{\mathrm{II}} = A'e^{ik'x} + B'e^{-ik'x} \qquad k'=\sqrt{2m(E-V)}/\hbar$$

$$\psi_{\mathrm{III}} = A''e^{ikx} + B''e^{-ikx} \qquad k=\sqrt{2mE}/\hbar$$

- I 区：Ae^{ikx}为入射波，Be^{-ikx}为反射波
- II区：$A'e^{ik'x}$为右行波，$B'e^{-ik'x}$为左行波
- III区：$A''e^{ikx}$为透射波，$B''=0$

$$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0) \Longrightarrow A+B=A'+B'$$

$$\left(\frac{d\psi_{\mathrm{I}}}{dx}\right)_{x=0} = \left(\frac{d\psi_{\mathrm{II}}}{dx}\right)_{x=0} \Longrightarrow kA-kB=k'A'-k'B'$$

$$\psi_{\mathrm{II}}(l)=\psi_{\mathrm{III}}(l) \Longrightarrow A'e^{ik'l}+B'e^{-ik'l}=A''e^{ikl}$$

$$\left(\frac{d\psi_{\mathrm{II}}}{dx}\right)_{x=l}=\left(\frac{d\psi_{\mathrm{III}}}{dx}\right)_{x=l} \Longrightarrow k'A'e^{ik'l}-k'B'e^{-ik'l}=kA''e^{ikl}$$

$$A''=\frac{4kk'e^{-ikl}}{(k+k')^2e^{-ik'l}-(k-k')^2e^{ik'l}}A \qquad B=\frac{2i(k^2-k'^2)\sin k'l}{(k-k')^2e^{ik'l}-(k+k')^2e^{-ik'l}}A$$

概率流密度

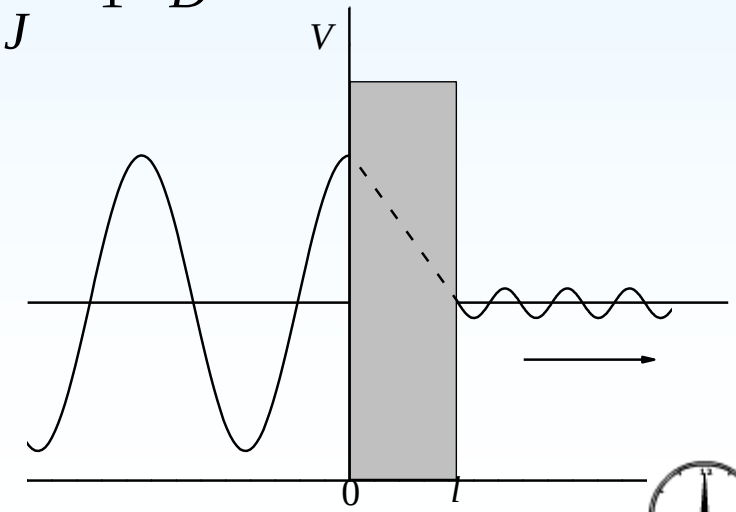
入射波 $J=\frac{\hbar k}{m}|A|^2$

透射波 $J_D=\frac{\hbar k}{m}|A''|^2$

反射波 $J_R=\frac{\hbar k}{m}|B|^2$

贯穿系数 $D=\frac{J_D}{J}=\frac{4k^2k'^2}{(k^2-k'^2)\sin^2(k'l)+4k^2k'^2}$

反射系数 $R=\frac{J_R}{J}=1-D$

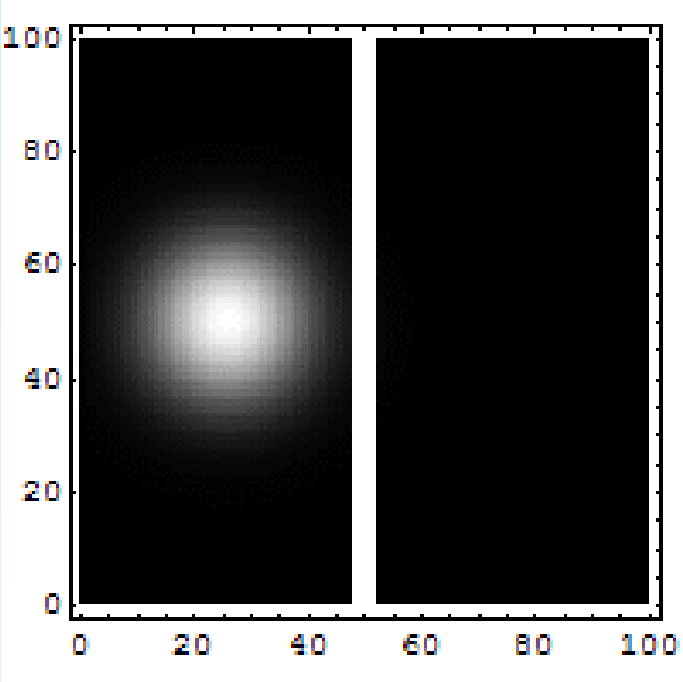


B. $E < V$ 时

k'为虚数，设$k'=i\kappa$

$$A'' = \frac{2ik\kappa e^{-ikl}}{(k^2-\kappa^2)^2\,\mathrm{sh}(l\kappa)+2ik\kappa\,\mathrm{ch}(l\kappa)}A$$

$$D = \frac{4k^2\kappa^2}{(k^2+\kappa^2)\mathrm{sh}^2(\kappa l)+4k^2\kappa^2}$$



如 $l\kappa \gg 1 \quad \mathrm{sh}^2(l\kappa) = (e^{\kappa l} - e^{-\kappa l})/2 \approx e^{2\kappa l}/4$

$$D \propto e^{-2\kappa l} = e^{-\frac{2l}{\hbar}\sqrt{2m(V-E)}}$$

贯穿系数随势垒的加宽(l增大)和增高(V增大)而减小，随粒子质量m增加而减小，宏观粒子没有隧道效应

§ 2.3 谐振子 The harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{mkx^2}{\hbar^2}\right)\psi = 0$$

令 $\alpha = 2mE/\hbar^2$ $\quad \beta = \sqrt{mk}/\hbar$

$$\frac{d^2\psi}{dx^2} + \left(\alpha - \beta^2 x^2\right)\psi = 0$$

$$z = \sqrt{\beta}x$$

$$\frac{d^2\psi}{dz^2} + \left(\frac{\alpha}{\beta} - z^2\right)\psi = 0$$

$z \to \infty$ $\quad z^2 >> \alpha/\beta$ 该区间 ψ 近似满足 $d^2\psi/dz^2 = z^2\psi$

该方程的近似解为 $\psi = e^{\pm z^2/2}$ $\qquad \frac{d^2}{dz^2}e^{\pm z^2/2} = e^{\pm z^2/2}(z^2+1) \cong z^2 e^{\pm z^2/2}$

由于 $z \to \infty$ 时，$e^{z^2/2} \to \infty$

猜想 $\frac{d^2\psi}{dz^2} + \left(\frac{\alpha}{\beta} - z^2\right)\psi = 0$ 的解为 $\qquad \psi(z) = e^{-z^2/2}U(z)$

$$\frac{dU^2}{dz^2}-2z\frac{dU}{dz}+\left(\frac{\alpha}{\beta}-1\right)U=0$$

用幂级数法求解

$$\begin{cases} U=\sum_{k=0}^{\infty}a_k z^k \\ \frac{dU}{dz}=\sum_{k=0}^{\infty}a_k k z^{k-1} \\ \frac{d^2U}{dz^2}=\sum_{k=0}^{\infty}a_{k+2}(k+1)(k+2)z^k \end{cases}$$

$$\sum_{k=0}^{\infty}a_{k+2}(k+1)(k+2)z^k-\sum_{k=0}^{\infty}2a_k k z^k+\sum_{k=0}^{\infty}\left(\frac{\alpha}{\beta}-1\right)a_k z^k=0$$

对任意z, 该式恒等, z^k的系数必须为0

必有： $a_{k+2}(k+1)(k+2)+(\alpha/\beta-1-2k)\,a_k=0$

$$a_{k+2}=\frac{2k+1-\alpha/\beta}{(k+1)(k+2)}a_k \qquad k=0,1,2,\ldots,\infty$$

若α/β不是整数，则k可递推到∞，U为无穷级数，不能满足ψ为有限值的要求。为避免U为无穷级数，令$\alpha/\beta=2n+1$ $(n=0,1,2,\ldots)$ 这时，$a_{n+2}=a_{n+4}=\ldots=0$ U为多项式而不是无穷级数。

$$\frac{\alpha}{\beta}=\frac{2}{\hbar}\sqrt{\frac{m}{k}}E=2n+1$$

$$\boxed{E=\frac{\hbar}{2}\sqrt{\frac{k}{m}}(2n+1)=(n+\frac{1}{2})h\nu}\qquad (n=0,1,2,\ldots)$$

$$\frac{dU^2}{dz^2}-2z\frac{dU}{dz}+2nU=0$$

Hermite微分方程

$$U(z)=H_n(z)=\sum_{k=0}^{n}a_k z^k \qquad a_{k+2}=\frac{-2(n-k)}{(k+1)(k+2)}a_k$$

$$\psi_n(x)=N_n e^{-z^2/2}H_n(z) \qquad z=\sqrt{\beta}x$$

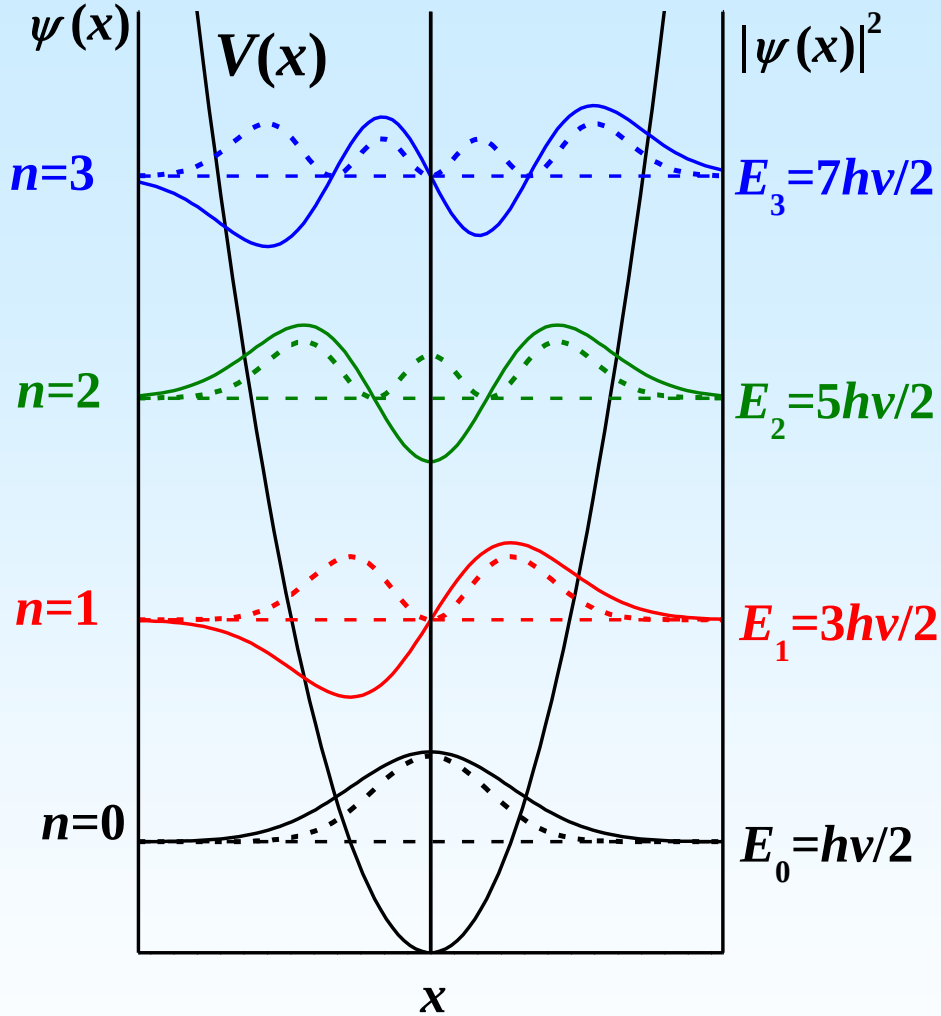
$$\psi_n(x)=\left(\frac{1}{2^n n!}\sqrt{\frac{\beta}{\pi}}\right)^{\frac{1}{2}}H_n(\beta^{\frac{1}{2}}x)e^{-\frac{1}{2}\beta x^2}$$

$$\boxed{\boldsymbol{zH_n = ½H_{n+1} + nH_{n-1}}}$$

$H_0(z)=1$ $\qquad$ $H_1(z)=2z$

$H_2(z)=4z^2-2$ $\qquad$ $H_3(z)=8z^3-12z$

$H_4(z)=16z^4-48z^2+12$ $\qquad$ $H_5(z)=32z^5-160z^3+120z$



$$E = (n + \frac{1}{2})h\nu$$

$$\langle T \rangle = \langle V \rangle$$

- 能级差为常数
- 波函数对x=0的反映或是对称的，或是反对称的
- 零点能
- 隧道效应

$$\psi_n(x) = \left(\frac{1}{2^n n!} \sqrt{\frac{\beta}{\pi}} \right)^{\frac{1}{2}} H_n(\beta^{\frac{1}{2}} x) e^{-\frac{1}{2}\beta x^2}$$

§ 2.4 环上粒子 Partical on a ring

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

质量为m的粒子在xy平面上半径为r的圆上运动，势能为0

$x = r\cos\phi$
$y = r\sin\phi$

极坐标

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

r为常数

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

波函数只与ϕ有关，设波函数为 Φ

$$\frac{d^2\Phi}{d\phi^2} = -\frac{2IE}{\hbar^2}\Phi$$

通解 $\Phi = Ae^{im_l\phi} + Be^{-im_l\phi}$ $\quad m_l = \sqrt{2IE}/\hbar$

周期性边界条件 $\Phi(\phi) = \Phi(\phi + 2\pi)$

$$e^{im_l 2\pi} = \cos(m_l 2\pi) + i\sin(m_l 2\pi) = 1$$

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I}$$

$m_l = 0, \pm1, \pm2, \ldots$

$$\hat{M}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial \phi}$$

当B=0时 $\Phi_{m_l} = Ae^{im_l\phi}$

$$\boxed{\hat{M}_z\Phi_{m_l} = m_l\hbar\Phi_{m_l}}$$

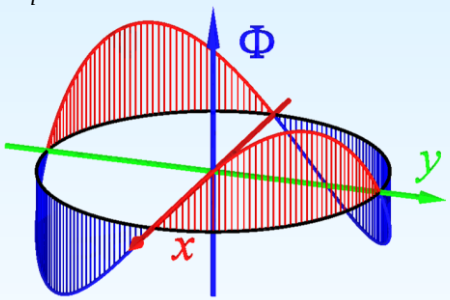
$$\int_0^{2\pi}\Phi^*\Phi d\phi = 2\pi|A|^2 = 1$$

$$\Phi_{m_l} = (2\pi)^{-1/2}e^{im_l\phi} = (2\pi)^{-1/2}(\cos m_l\phi + i\sin m_l\phi)$$

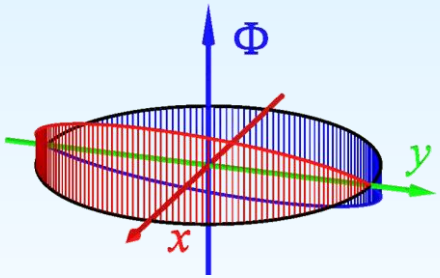
实函数解

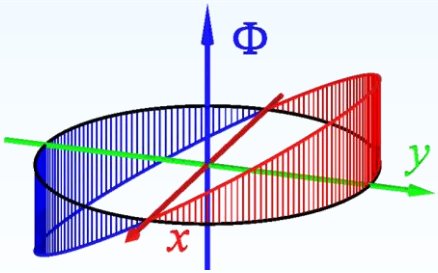
$$\Phi_{\pm m_l}^{\cos}(\phi) = \sqrt{1/\pi}\cos|m_l|\phi$$

$$\Phi_{\pm m_l}^{\sin}(\phi) = \sqrt{1/\pi}\sin|m_l|\phi$$

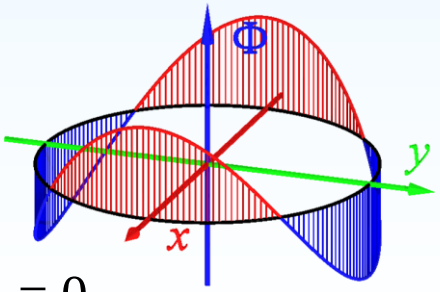


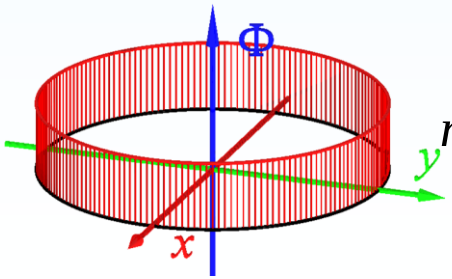
$m_l = \pm 2$





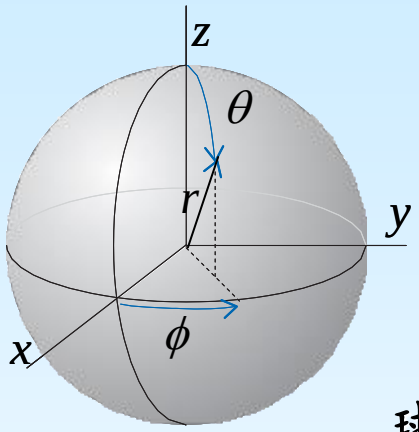
$m_l = \pm 1$





$m_l = 0$

§ 2.5 球面上粒子 Partical on a sphere



球极坐标

$x=r\sin\theta\cos\phi$

$y=r\sin\theta\sin\phi$

$z=r\cos\theta$

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2$$

$$\Lambda^2=\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

球面上运动的粒子r为常数 $\hat{H}=-\frac{\hbar^2}{2mr^2}\Lambda^2=-\frac{\hbar^2}{2I}\Lambda^2$

$$-\frac{\hbar^2}{2I}\Lambda^2\psi=E\psi \qquad \Lambda^2\psi=-\frac{2IE}{\hbar^2}\psi=-k\psi$$

将球面看成是由许多圆环组成，粒子可在圆环间运动

$$\psi(\theta,\phi)=\Theta(\theta)\Phi(\phi) \qquad \Phi_{m_l}(\phi)=(2\pi)^{-1/2}e^{im_l\phi} \qquad m_l=0,\pm1,\pm2,\ldots$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}-\frac{m_l^2\Theta}{\sin^2\theta}+k\Theta=0$$

设$z=r\cos\theta$ $P(z)=\Theta(\theta)$

$$\frac{d\Theta}{d\theta}=\frac{dP}{dz}\frac{dz}{d\theta}=-\frac{dP}{dz}\sin\theta$$

$$\frac{d}{dz}\left[(1-z^2)\frac{dP}{dz}\right]+\left[k-\frac{m_l^2}{1-z^2}\right]P=0$$

$$P(z)=(1-z^2)^{|m_l|/2}G(z)$$

$$(1-z^2)G''-2(|m_l|+1)zG'+\left[k-|m_l|(|m_l|+1)\right]G=0$$

$$G=\sum_n a_n z^n$$

$$(n+1)(n+2)a_{n+2}+\left\{\left[k-|m_l|(|m_l|+1)\right]-2n(|m_l|+1)-n(n-1)\right\}a_n=0$$

$$a_{n+2}=\frac{\left[k-|m_l|(|m_l|+1)\right]-2n(|m_l|+1)-n(n-1)}{(n+1)(n+2)}a_n$$

$$=\frac{k-(n+|m_l|)(n+|m_l|+1)}{(n+1)(n+2)}a_n$$

$k=(n+|m_l|)(n+|m_l|+1)$ 时，G为多项式，否则G为无穷级数，在$z=\pm1$时发散，不满足合格波函数条件

引入新量子数$l=n+|m_l|$，　$l=|m_l|, |m_l|+1, \ldots$

$$\boxed{\begin{aligned} &l = 0,1,2,\ldots \\ &m_l = l, l-1, \ldots, -l \end{aligned}}$$

$$k = l(l+1)$$

$$\Lambda^2\psi = l(l+1)\psi$$

$$\Theta(\theta) = (-1)^{\frac{m+|m|}{2}} \left\{ \left(\frac{2l+1}{2} \right) \frac{(l-|m_l|)!}{(l+|m_l|)!} \right\}^{1/2} P_l^{|m_l|}(\cos\theta)$$

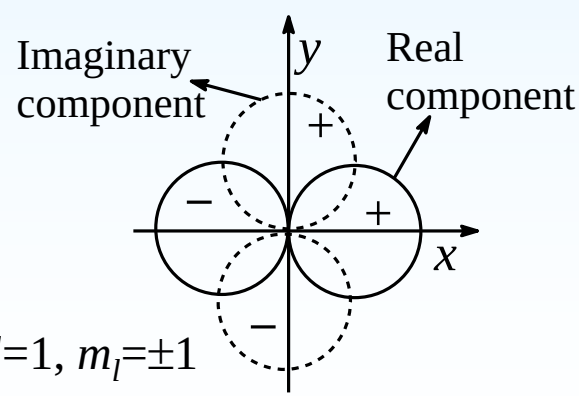
Condon–Shortley phase
与升降算符匹配

Associated Legendre functions

$$Y_{lm_l}(\theta,\phi) = \Theta_{l,m_l}(\theta)\phi_{m_l}(\phi)$$

Spherical harmonics

$$\boxed{E_{lm_l} = l(l+1)\frac{\hbar^2}{2I}}$$ 简并度 $2l+1$



$l=1, m_l=\pm1$

l	m_l	$Y_{lm_l}(\theta,\phi)$
0	0	$\pi^{1/2}/2$
1	0	$\frac{1}{2}(3/\pi)^{1/2}\cos\theta$
	±1	$\mp(3/2\pi)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}(5/\pi)^{1/2}(3\cos^2\theta - 1)$
	±1	$\mp\frac{1}{2}(15/2\pi)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}(15/2\pi)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}(7/\pi)^{1/2}(2-5\sin^2\theta)\cos\theta$
	±1	$\mp\frac{1}{8}(21/2\pi)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}(105/2\pi)^{1/2}\cos\theta\sin^2\theta\, e^{\pm 2i\phi}$
	±3	$\mp\frac{1}{8}(35/\pi)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

经典物理：$E = \frac{1}{2} I\omega^2$

角动量大小：$l = I\omega$

$E = l^2/2I$

I:转动惯量, ω:角速度

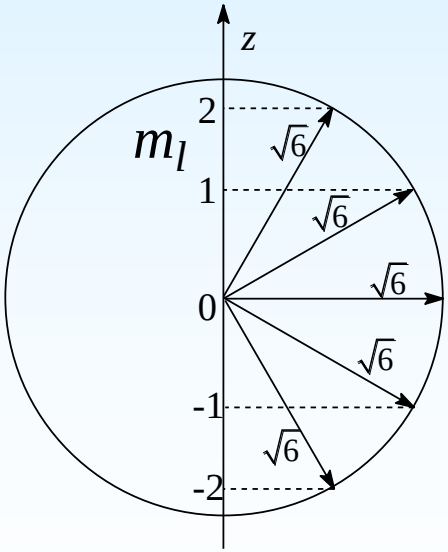
球面上运动的粒子

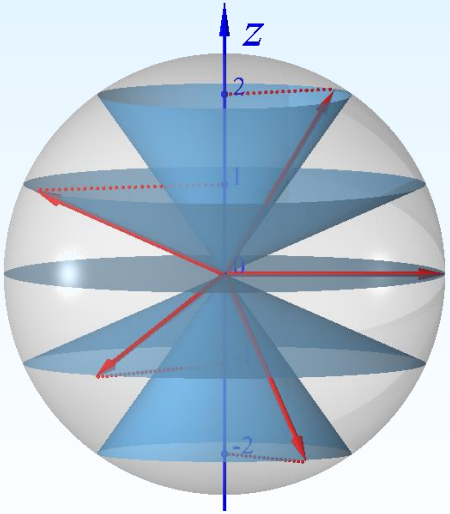
角动量大小 $= \sqrt{l(l+1)}\hbar$

角动量大小是量子化的

l为角量子数

angular momentum quantum number





球谐函数是角动量z分量算符的本征函数

$$\hat{M}_z Y_{lm_l} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\left(\Theta_{lm_l}\frac{e^{im_l\phi}}{\sqrt{2\pi}}\right) = m_l\hbar$$

$$Y_{lm}(\theta,\phi)=(-1)^{\frac{m+|m|}{2}}\left\{\left(\frac{2l+1}{2}\right)\frac{(l-|m_l|)!}{(l+|m_l|)!}\right\}^{1/2}P_l^{|m_l|}(\cos\theta)\frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

$$=NP_l^{|m_l|}(\cos\theta)\exp(im\phi)$$

$$N=(-1)^{\frac{m+|m|}{2}}\sqrt{\frac{(2l+1)(l-|m_l|)!}{4\pi(l+|m_l|)!}}$$

量子化学中原子轨道波函数的角度部分(球谐函数)常采用实函数形式

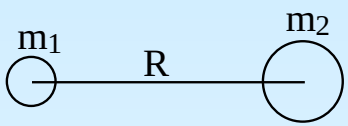
$$p_+=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \qquad p_x=\frac{1}{\sqrt{2}}(p_- - p_+)=\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$\Longrightarrow$$

$$p_-=\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \qquad p_y=\frac{i}{\sqrt{2}}(p_- + p_+)=\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$$

注：《结构化学》书中球谐函数未加Condon–Shortley相因子，公式有所不同

§ 2.6 刚性转子 The rigid rotor



$$\hat{H} = -\frac{\hbar^2}{2m_1} - \frac{\hbar^2}{2m_2} = -\frac{\hbar^2}{2}\left(\frac{1}{m}\nabla_{cm}^2 + \frac{1}{\mu}\nabla^2\right)$$

$$m = m_1 + m_2$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$-\frac{\hbar^2}{2m}\nabla_{cm}^2\Psi - \frac{\hbar^2}{2\mu}\nabla^2\Psi = E_{total}\Psi$$

$$\Psi = \psi_{cm}\psi \Longrightarrow \begin{cases} -\dfrac{\hbar^2}{2m}\nabla_{cm}^2\psi_{cm} = E_{cm}\psi_{cm} & \text{平动} \\ -\dfrac{\hbar^2}{2\mu}\nabla^2\psi = E\psi \end{cases}$$

$$\Downarrow$$

$$-\frac{\hbar^2}{2\mu R^2}\Lambda^2\psi = E\psi$$

$$I = \mu R^2$$

$$\Longleftarrow$$

$$\boxed{E_{JM_J} = J(J+1)\frac{\hbar^2}{2I}}$$

§ 2.7 氢原子 Hydrogenic atoms

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{\hbar^2}{2m}\nabla_{cm}^2 - \frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\Lambda^2\psi + \frac{Ze^2\mu}{2\pi\varepsilon_0\hbar^2 r}\psi = -\frac{2\mu E}{\hbar^2}\psi$$

$$\Downarrow \quad \psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$\frac{1}{r}\frac{d^2(rR)}{dr^2} + \left\{\frac{Ze^2\mu}{2\pi\varepsilon_0\hbar^2 r} - \frac{l(l+1)}{r^2}\right\}R = -\frac{2\mu E}{\hbar^2}R$$

$$\Downarrow \quad u = rR$$

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left\{\frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right\}u = -\frac{2\mu E}{\hbar^2}u$$

$$\frac{d^2u}{dr^2}+\frac{2\mu}{\hbar^2}\left\{\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)\hbar^2}{2\mu r^2}\right\}u=-\frac{2\mu E}{\hbar^2}u$$

$$\lambda^2=\frac{2\mu|E|}{\hbar^2} \qquad E<0 \qquad a=\frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0} \qquad b=l(l+1)$$

$$u''+\left(\frac{a}{r}-\frac{b}{r^2}\right)u=\lambda^2 u \xrightarrow{r\to\infty} u''\simeq\lambda^2 u \Longrightarrow u\simeq e^{\pm\lambda r}$$

合格波函数条件

$$u\simeq e^{-\lambda r} \longrightarrow u=L(r)e^{-\lambda r}$$

$$L''-2\lambda L+\left(\frac{a}{r}-\frac{b}{r^2}\right)L=0$$

$$L(r)=\sum_n c_n r^n$$

$$\sum_n c_n\left\{\left[n(n+1)-b\right]r^{n-2}-(2n\lambda-a)r^{n-1}\right\}=0$$

$$c_{n+1}=\frac{(2n\lambda-a)}{n(n+1)-b}c_n \Longrightarrow 2n\lambda=a \Longrightarrow \boxed{E=-\frac{\mu e^4}{8\varepsilon_0^2 h^2}\cdot\frac{Z^2}{n^2}}$$

$$R_{nl}(r) = Ce^{-\frac{\rho}{2}}\rho^{l}L_{n+1}^{2l+1}(\rho)$$ *associated Laguerre functions*

$$L_{n+1}^{2l+1}(\rho) = \frac{d^{2l+1}}{d\rho^{2l+1}}\left[e^{\rho}\cdot\frac{d^{n+1}}{d\rho^{n+1}}(e^{-\rho}\cdot\rho^{n+1})\right]$$

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

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

Bohr radius

$$R_{1,0}(r) = 2\left(Z/a_0\right)^{3/2}e^{-\rho/2}$$

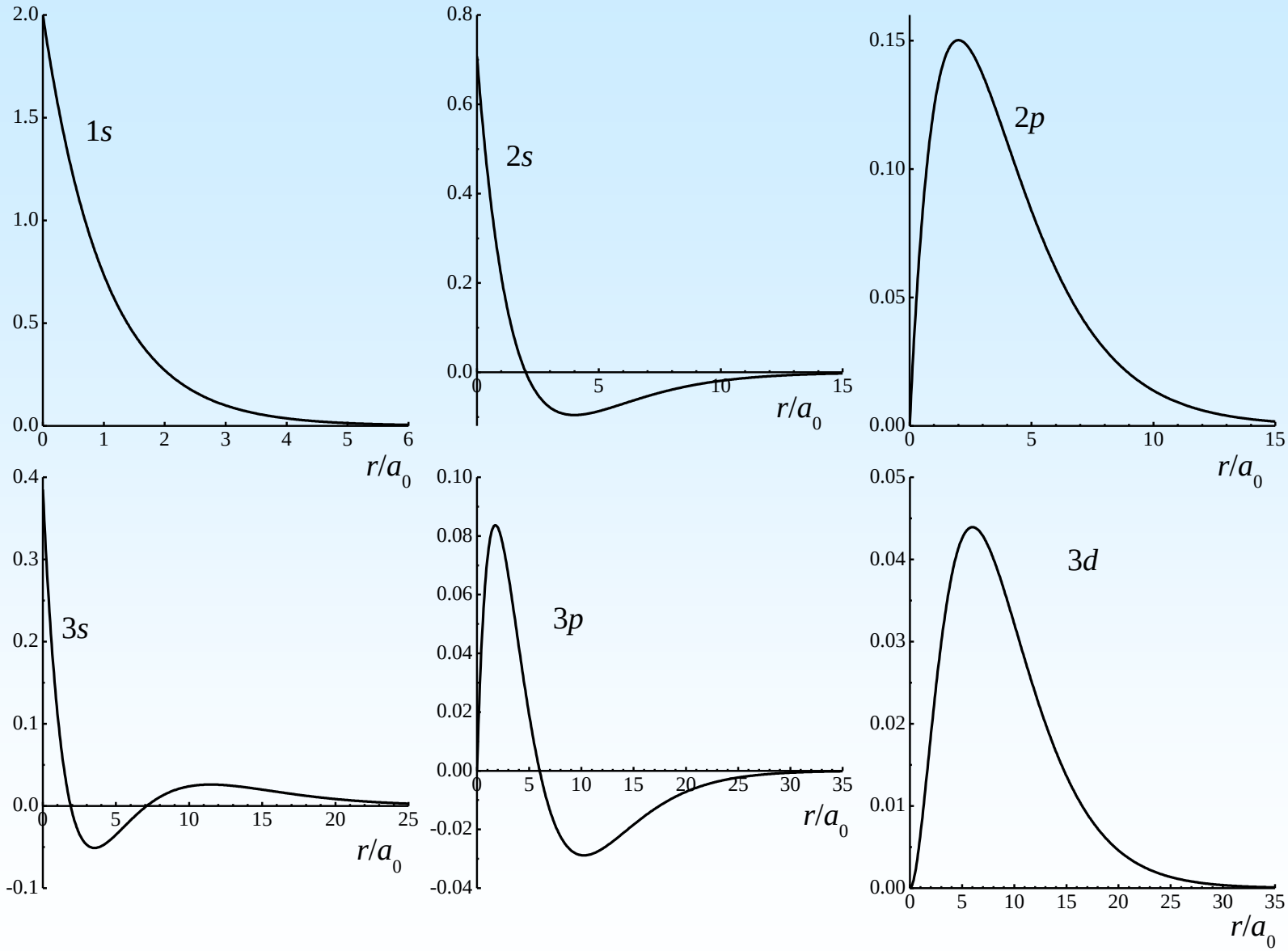
$$R_{2,0}(r) = \frac{1}{2\sqrt{2}}\left(Z/a_0\right)^{3/2}\left(2-\rho\right)e^{-\rho/2}$$

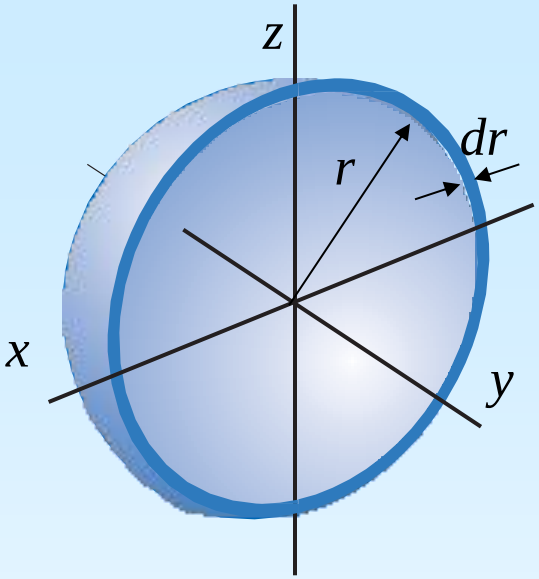
$$R_{2,1}(r) = \frac{1}{2\sqrt{6}}\left(Z/a_0\right)^{3/2}\rho e^{-\rho/2}$$

$$R_{3,0}(r) = \frac{1}{9\sqrt{3}}\left(Z/a_0\right)^{3/2}\left(6-6\rho+\rho^2\right)e^{-\rho/2}$$

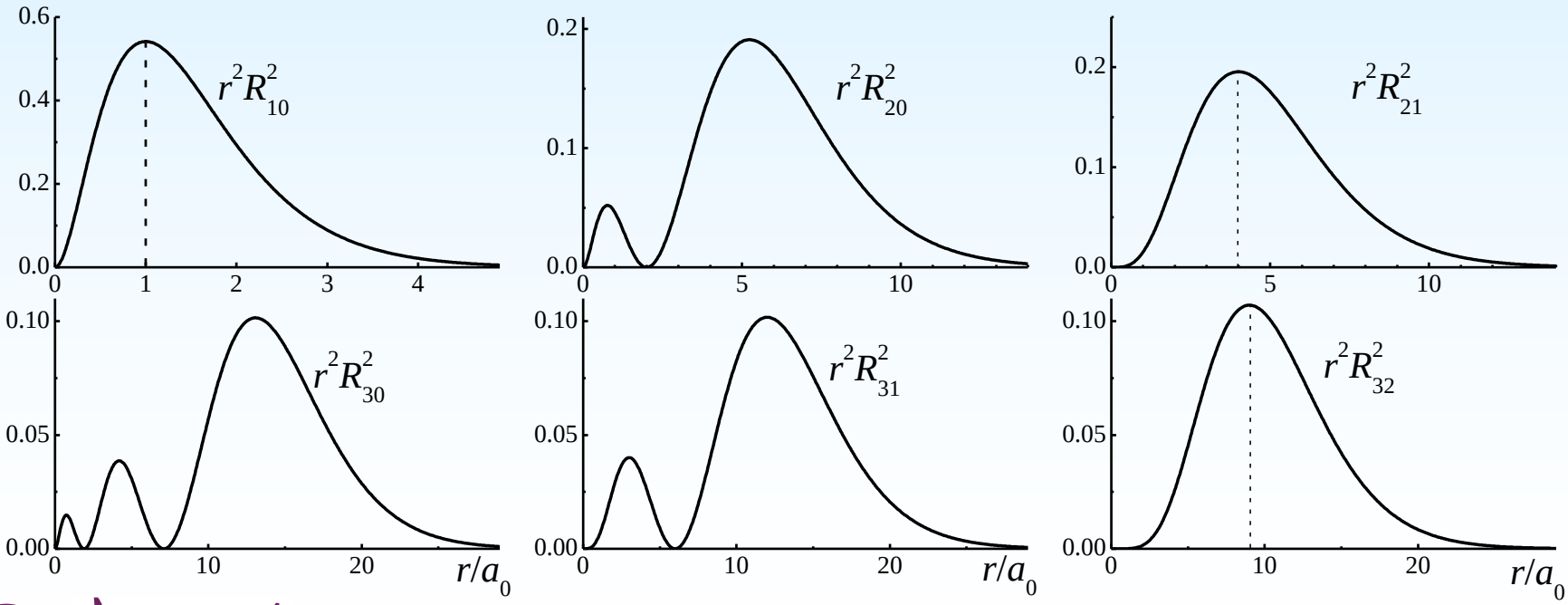
$$R_{3,1}(r) = \frac{1}{9\sqrt{6}}\left(Z/a_0\right)^{3/2}\left(4\rho-\rho^2\right)e^{-\rho/2}$$

$$R_{3,2}(r) = \frac{1}{9\sqrt{30}}\left(Z/a_0\right)^{3/2}\rho^2 e^{-\rho/2}$$

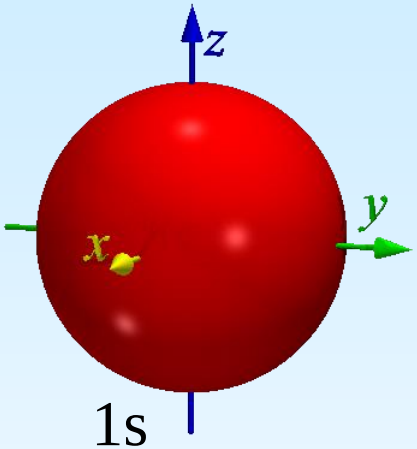

1s
2s
2p
3s
3p
3d
r/a0



$$D(r)dr = \int_0^{\pi}\int_0^{2\pi} R_{nl}^2 \left|Y_{lm_l}\right|^2 r^2 \sin\theta dr d\theta d\phi$$
$$= R^2 r^2$$



原子轨道轮廓图



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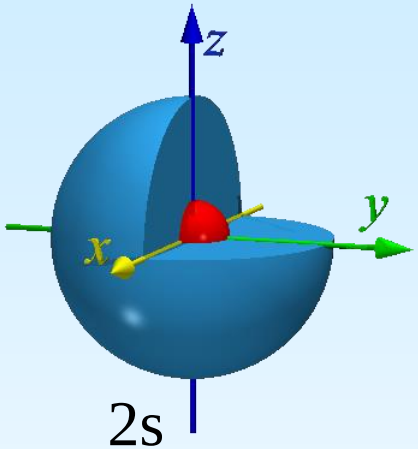
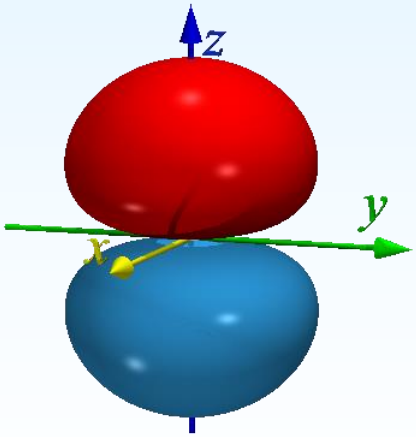
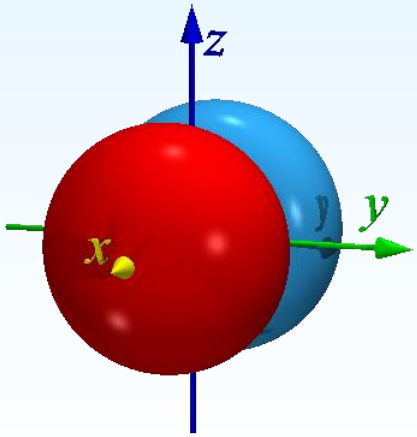


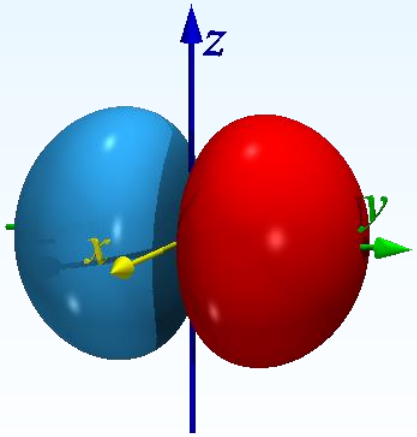
2s



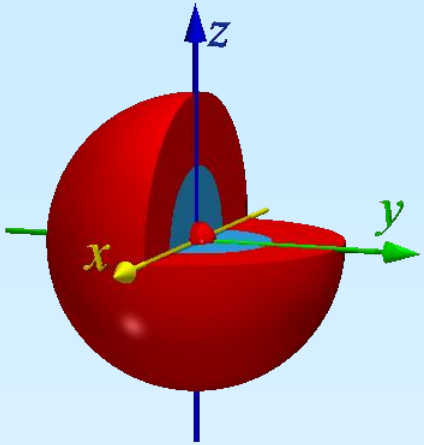
$2p_z$



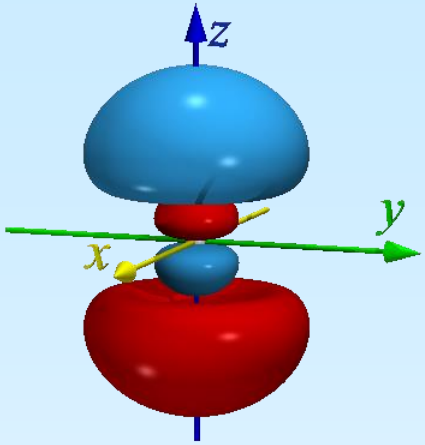
$2p_x$



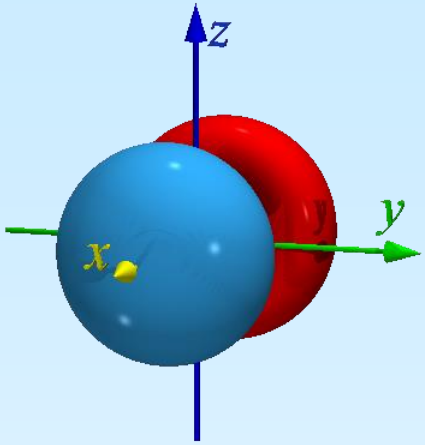
$2p_y$



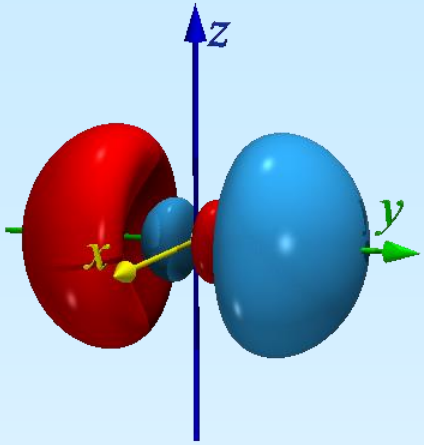
3s



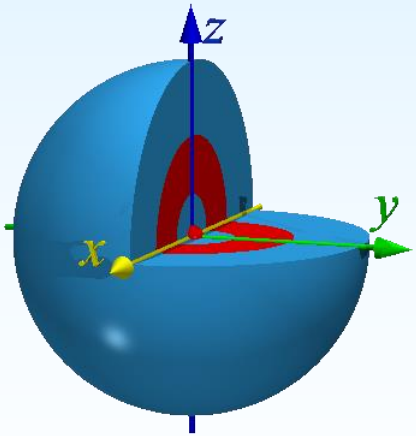
$3p_z$



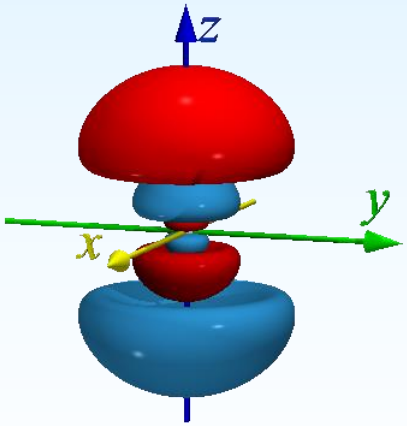
$3p_x$



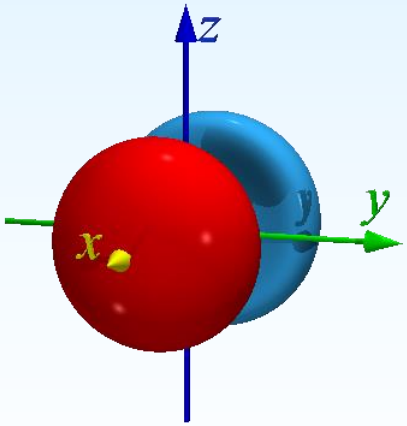
$3p_y$



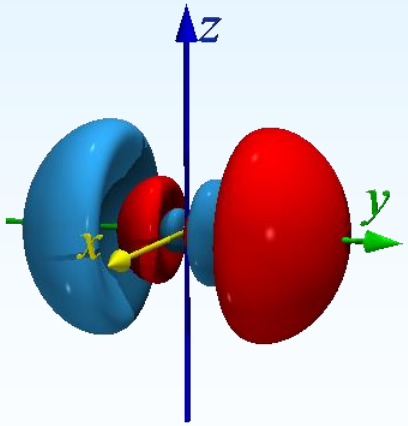
4s



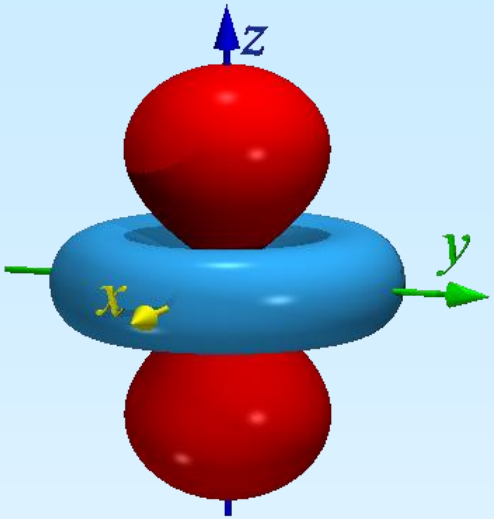
$4p_z$



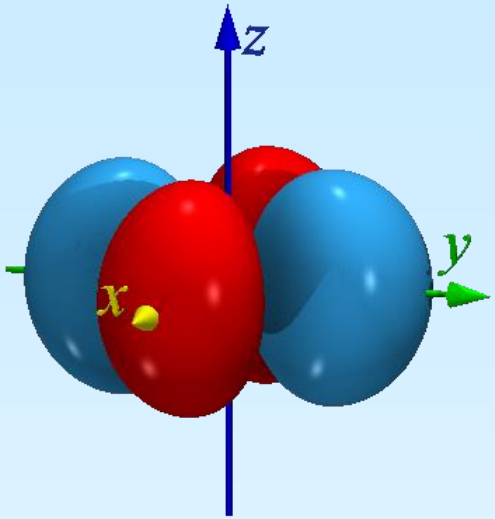
$4p_x$



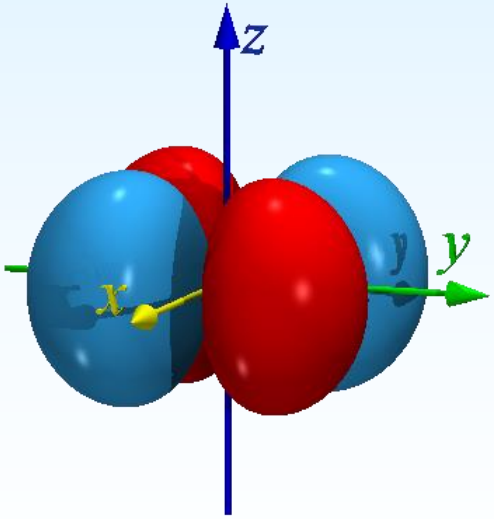
$4p_y$



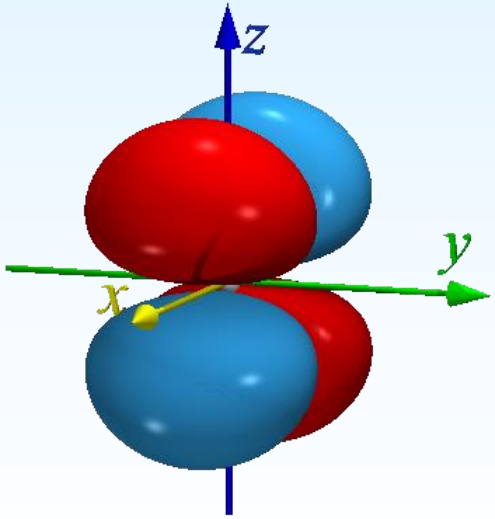
$3d_{z^2}$



$3d_{x^2-y^2}$



$3d_{xy}$



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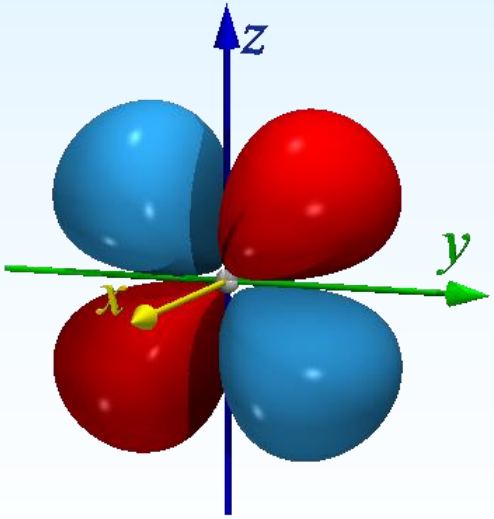
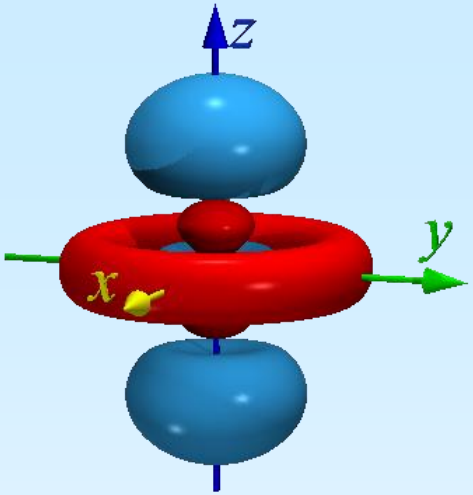
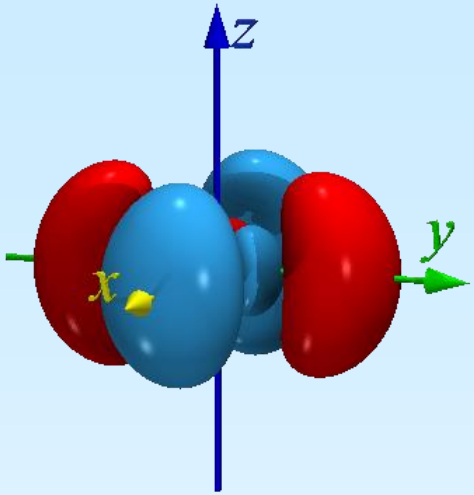


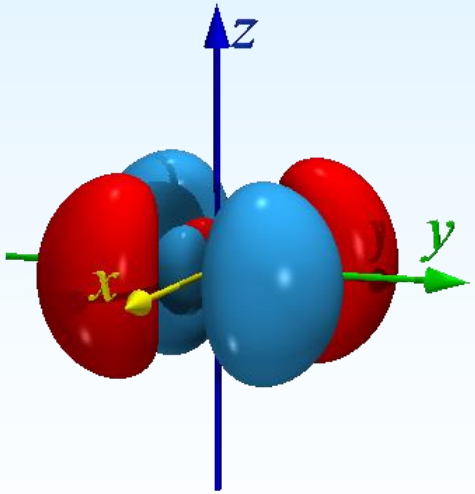
$3d_{yz}$



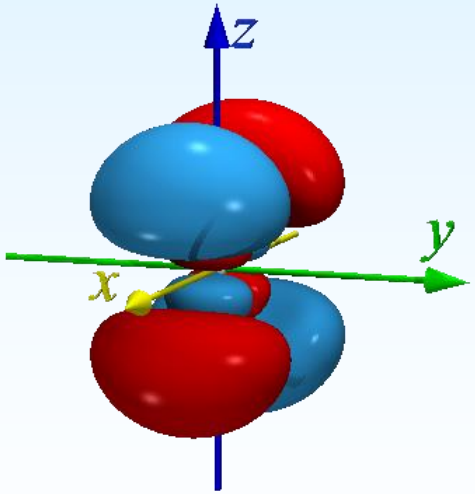
$4d_{z^2}$



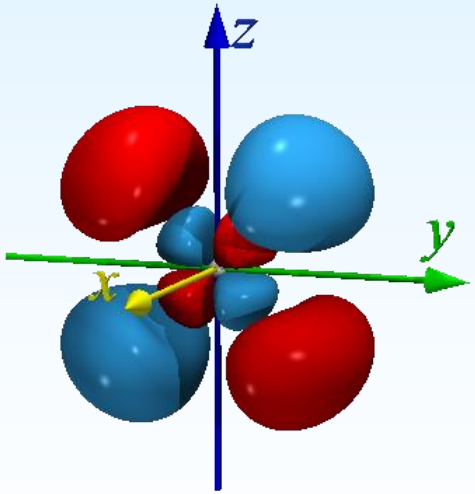
$4d_{x^2-y^2}$



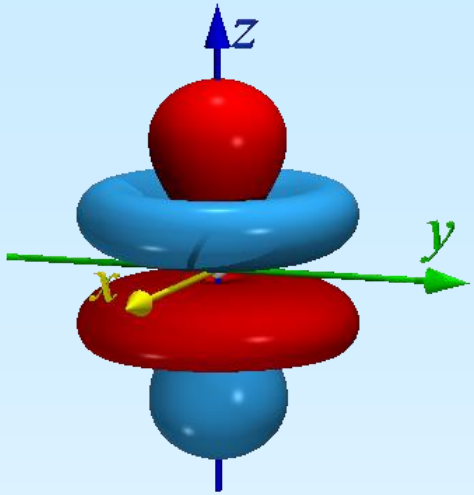
$4d_{xy}$



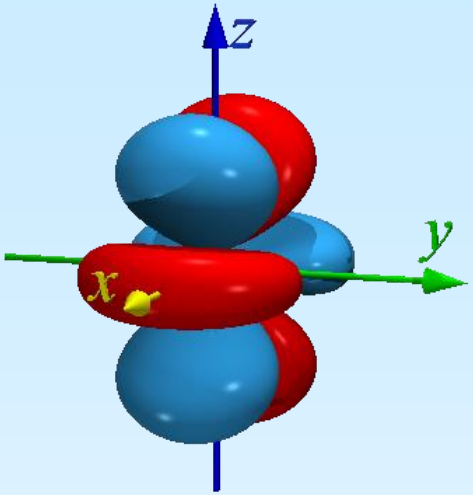
$4d_{xz}$



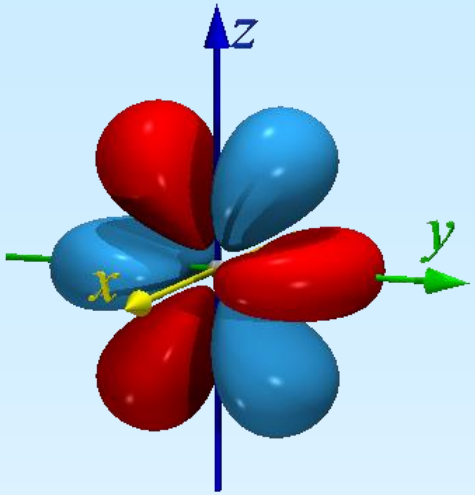
$4d_{yz}$



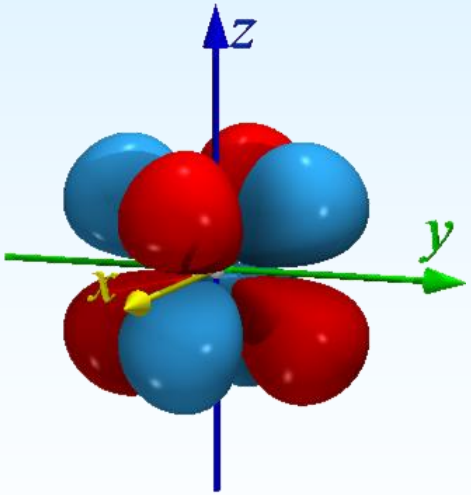
$4f_{z^3}$



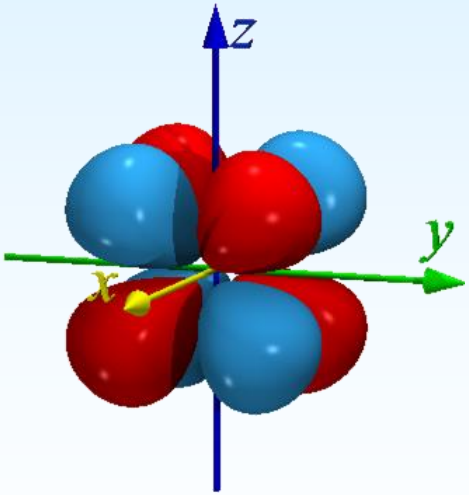
$4f_{xz^2}$



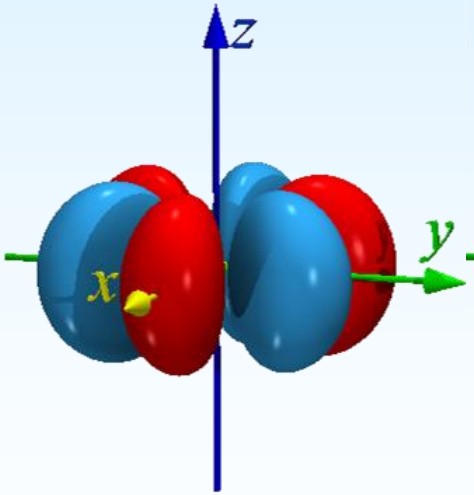
$4f_{yz^2}$



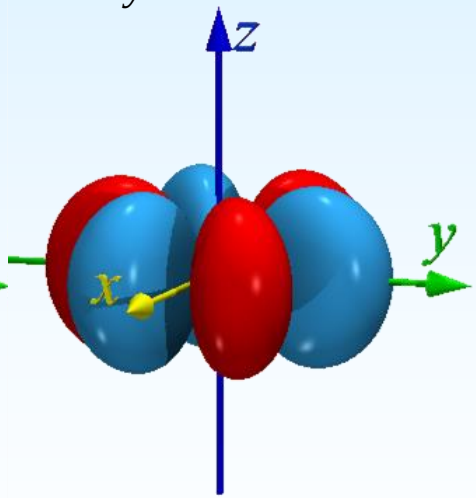
$4f_{z(x^2-y^2)}$



$4f_{zxy}$



$4f_{x(x^2-3y^2)}$



$4f_{y(3x^2-y^2)}$