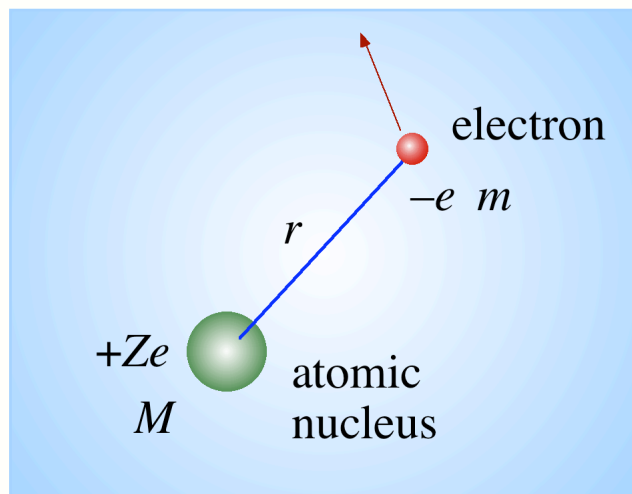


水素原子

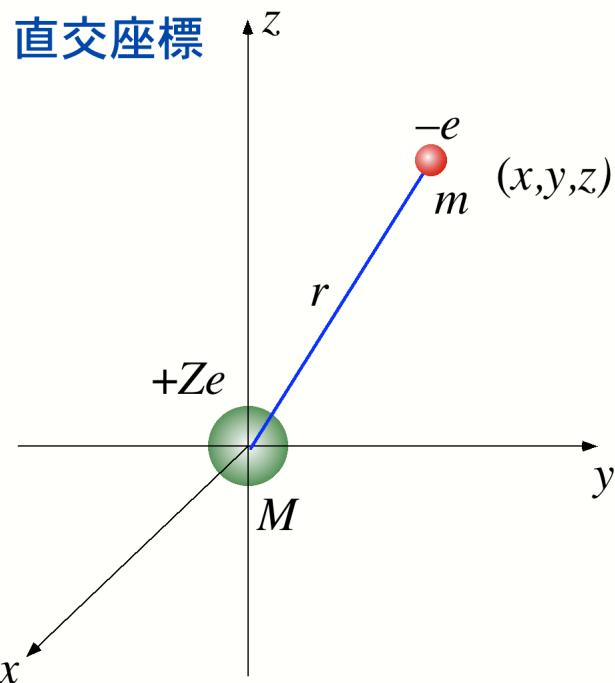
シュレーディンガー方程式の解
が軌道の概念となる

水素原子モデル (シュレーディンガー方程式をたてる)



$$\hat{H}\Psi(x,y,z) = E\Psi(x,y,z)$$

$$\left[-\frac{\hbar^2}{2m}\Delta + U(r)\right]\Psi(x,y,z) = E\Psi(x,y,z)$$



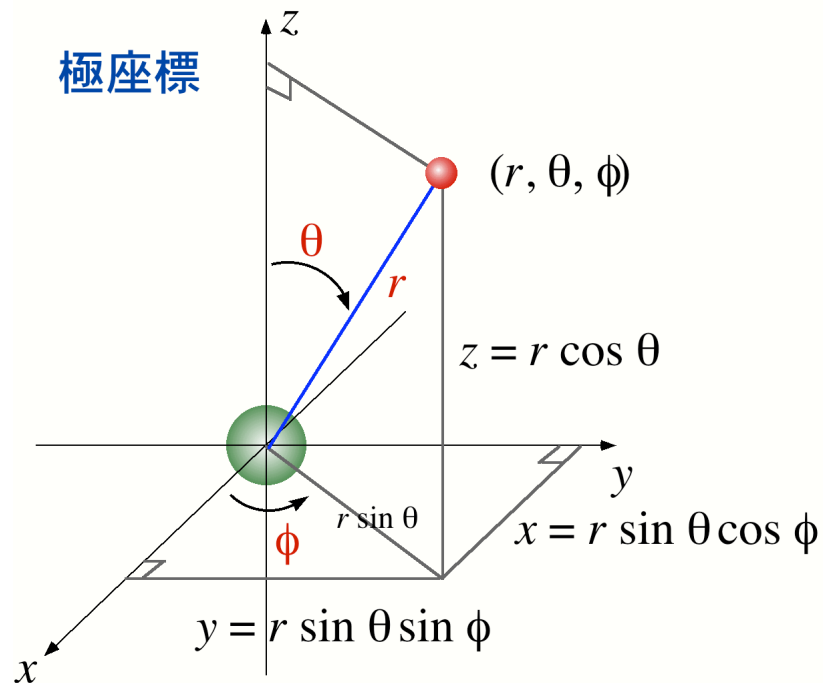
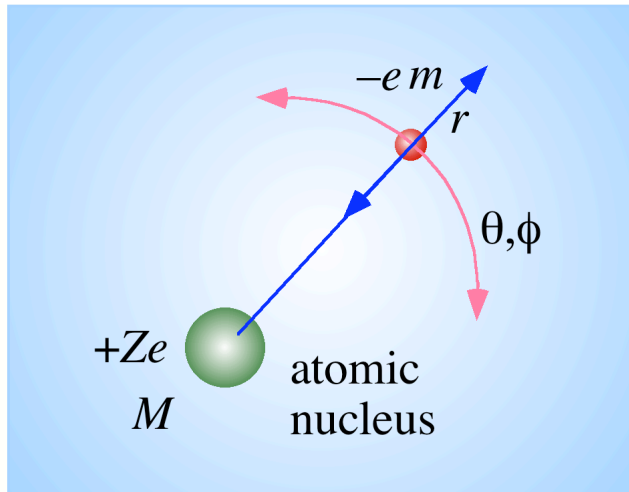
$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\Psi(x,y,z) = E\Psi(x,y,z)$$

直交座標系ハミルトニアン

$$\hat{H}_{x,y,z}$$

このままでは微分方程式を解くことができない!

水素原子モデル (極座標系に変換する)



$$\hat{H}_c \Psi(x,y,z) = E \Psi(x,y,z) \quad (1)$$

極座標に変換

$$\hat{H}_p \Psi(r,\theta,\phi) = E \Psi(r,\theta,\phi) \quad (2)$$

変数分離

$$\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

とおくと(2)は以下の三つの互いに関連した波動方程式 (固有値問題) に分解することができる

$$\hat{E}_r R(r) = E R(r) \quad (3)$$

$$\hat{L}^2 \Theta(\theta) = \lambda \Theta(\theta) \quad (4)$$

$$\hat{L}_z \Phi(\phi) = \mu \Phi(\phi) \quad (5)$$

(3)(4)(5)は厳密に解くことができる

水素原子モデル（シュレーディンガー方程式の解）

極座標系方程式 $\hat{H}_p \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$

波動関数（固有関数） $\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$

変数分離型方程式	固有値	量子数	固有関数
$\hat{E}_r R(r) = E R(r)$	$E = -\frac{me^4 Z^2}{8e_0^2 h^2} \frac{1}{n^2}$ エネルギー	n 主量子数 $n = 1, 2, 3, \dots$	$R_{n,l}(r)$
$\hat{L}^2 \Theta(\theta) = \lambda \Theta(\theta)$	$\lambda = l(l+1)\hbar^2$ 角運動量の二乗 $ L ^2$	l 方位量子数 $l = 0, 1, 2, \dots, n-1$ 一つの n に対して n 個の l	$\Theta_{l,m}(\theta)$
$\hat{L}_z \Phi(\phi) = \mu \Phi(\phi)$	$\mu = m\hbar$ 角運動量の z 成分 L_z	m 磁気量子数 $m = -l, \dots, 0, \dots, l$ 一つの l に対して $2l+1$ 個の m	$\Phi_m(\phi)$

$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi) = R_{n,l}(r) \times Y_{l,m}(\theta, \phi)$$

(1 電子)波動関数 動径波動関数 (動径部分) 角波動関数 (角部分)

水素原子モデル (軌道の概念)

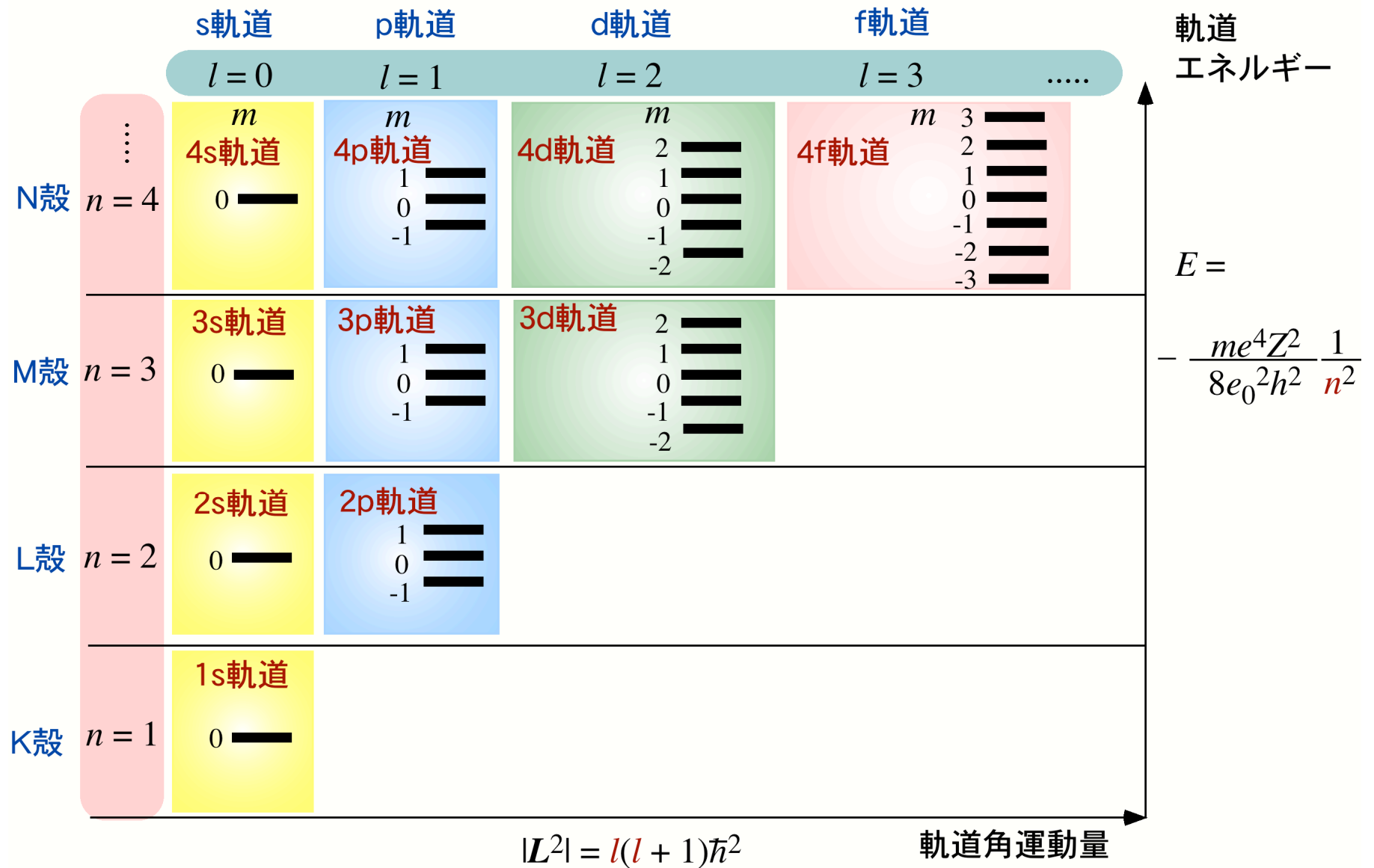
(1 電子)波動関数 $\Psi_{n,l,m} = R_{n,l}(r) \times Y_{l,m}(\theta,\phi)$
 (動径部分) (角部分)

が電子のふるまいのすべてを表現している。個々の波動関数を電子の軌道という。

energy	主量子数	方位量子数	磁気量子数	波動関数 (軌道)	軌道名
$-E_0/16$	$n = 4$	$l = 0$	$m = 0$	Ψ_{400}	Ψ_{4s} x1
		$l = 1$	$m = -1, 0, 1$	Ψ_{410} Ψ_{41-1} Ψ_{411}	Ψ_{4p} x3
				Ψ_{420} Ψ_{42-1} Ψ_{421} Ψ_{42-2} Ψ_{422}	Ψ_{4d} x5
		$l = 3$	$m = -3, -2, -1, 0, 1, 2, 3$	Ψ_{43m}	Ψ_{4f} x7
$-E_0/9$	$n = 3$	$l = 0$	$m = 0$	Ψ_{300}	Ψ_{3s} x1
		$l = 1$	$m = -1, 0, 1$	Ψ_{310} Ψ_{31-1} Ψ_{311}	Ψ_{3p} x3
				Ψ_{320} Ψ_{32-1} Ψ_{321} Ψ_{32-2} Ψ_{322}	Ψ_{3d} x5
$-E_0/4$	$n = 2$	$l = 0$	$m = 0$	Ψ_{200}	Ψ_{2s} x1
		$l = 1$	$m = -1, 0, 1$	Ψ_{210} Ψ_{21-1} Ψ_{211}	Ψ_{2p} x3
$-E_0$	$n = 1$	$l = 0$	$m = 0$	Ψ_{100}	Ψ_{1s} x1

$$E_0 = \frac{me^4Z^2}{8e_0^2h^2}$$

水素原子の軌道の概略



軌道（波動関数）の形を調べる（動径部分）

$$\Psi_{n,l,m} = R_{n,l}(r) Y_{l,m}(\theta, \phi)$$

$$R_{n,l}(r) = A_{n,l} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{2Zr}{na_0}\right)^l [\text{Laguerre}_{n,l}\left(\frac{2Zr}{na_0}\right)] \times \exp\left(-\frac{Zr}{na_0}\right)$$

参考（一般式）

動径波動関数

具体的には

$n = 1$	$l = 0$	$R_{10} = R_{1s} = 2 \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_0}$
$n = 2$	$l = 0$	$R_{20} = R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \rho_0) e^{-\rho_0/2}$
	$l = 1$	$R_{21} = R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0) e^{-\rho_0/2}$
$n = 3$	$l = 0$	$R_{30} = R_{3s} = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\rho_0 + 2\rho_0^2) e^{-\rho_0/3}$
	$l = 1$	$R_{31} = R_{3p} = \frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} (6\rho_0 - \rho_0^2) e^{-\rho_0/3}$
	$l = 2$	$R_{32} = R_{3d} = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3}$
\vdots	\vdots	\vdots

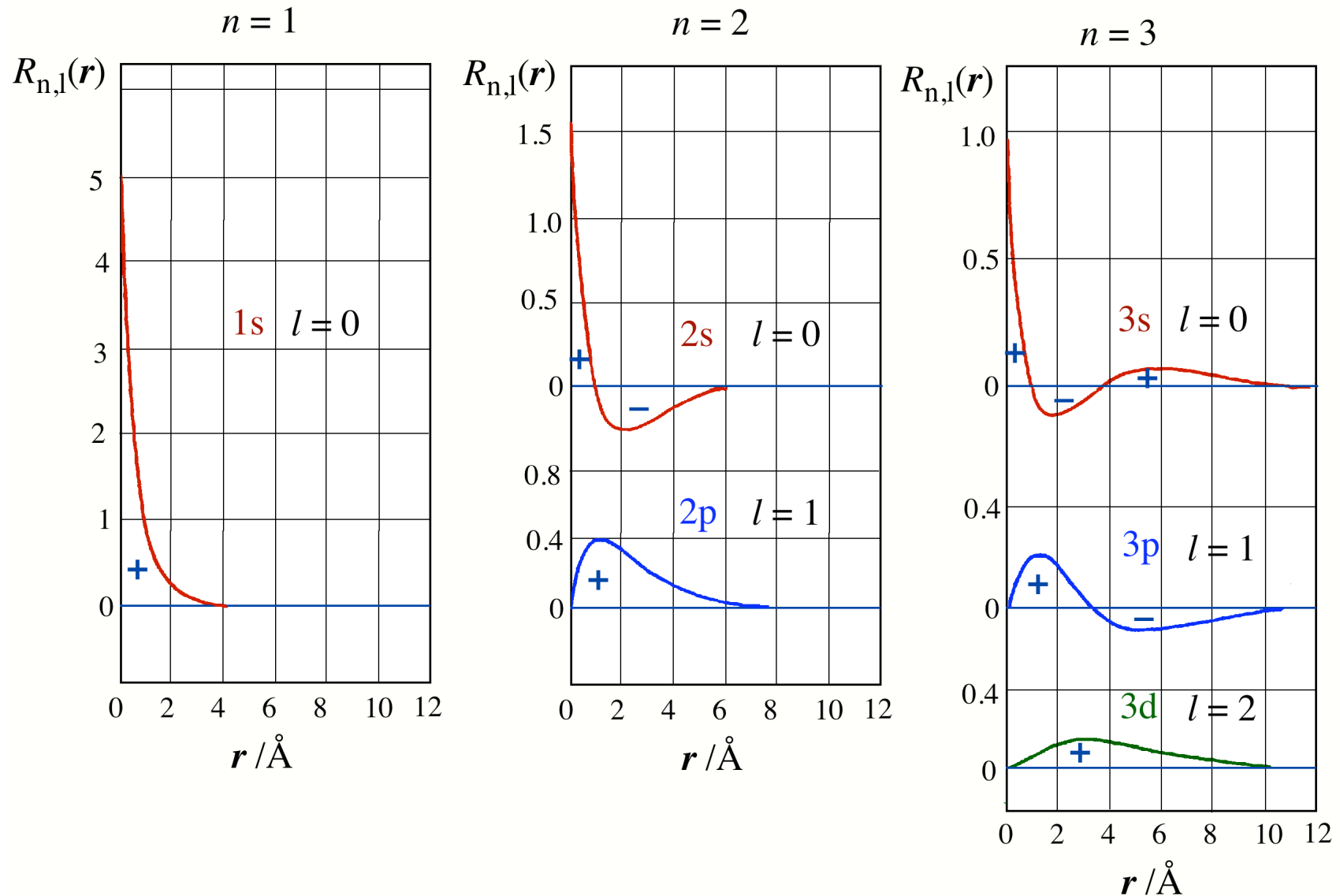
$$\rho_0 = \frac{Zr}{a_0}$$

$$a_0 = 0.53 \text{ \AA}$$

(ボーア半径)

軌道（波動関数）の形を調べる（動径部分）

$R_{n,l}(r)$ は動径 (r) のみを変数とする、三次元的には球対称関数

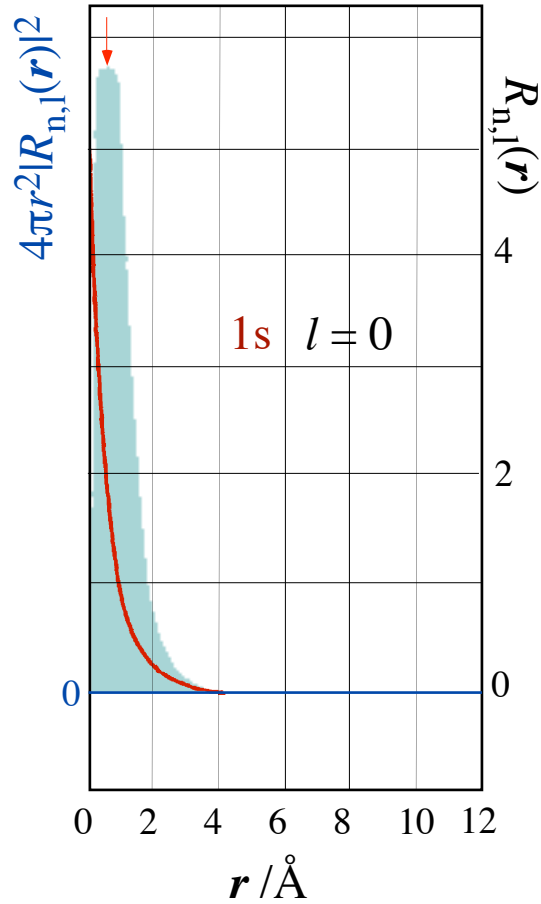


軌道（波動関数）の形を調べる（動径部分）

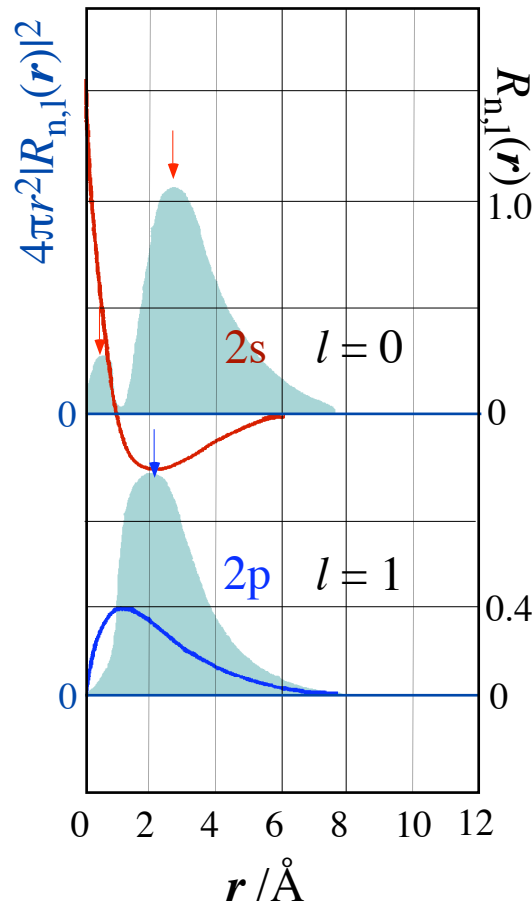
$|R_{n,l}(r)|^2$ 確率密度関数 $4\pi r^2 |R_{n,l}(r)|^2$ 動径分布関数

$$\int |R_{n,l}(r)|^2 dv = \int 4\pi r^2 |R_{n,l}(r)|^2 dr = 1 \quad (\text{規格化})$$

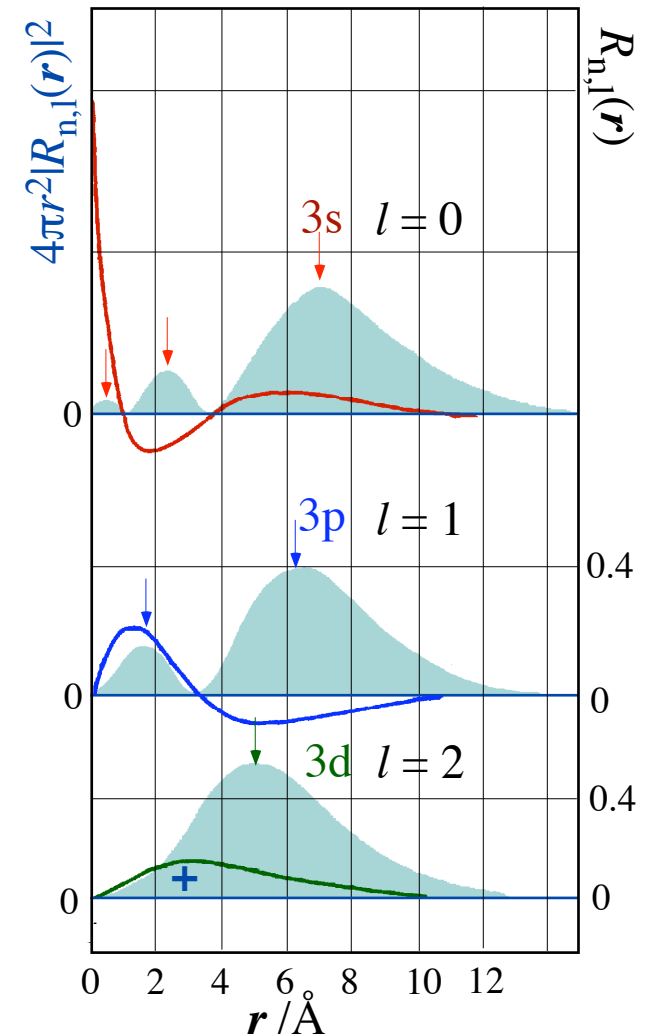
$n = 1$



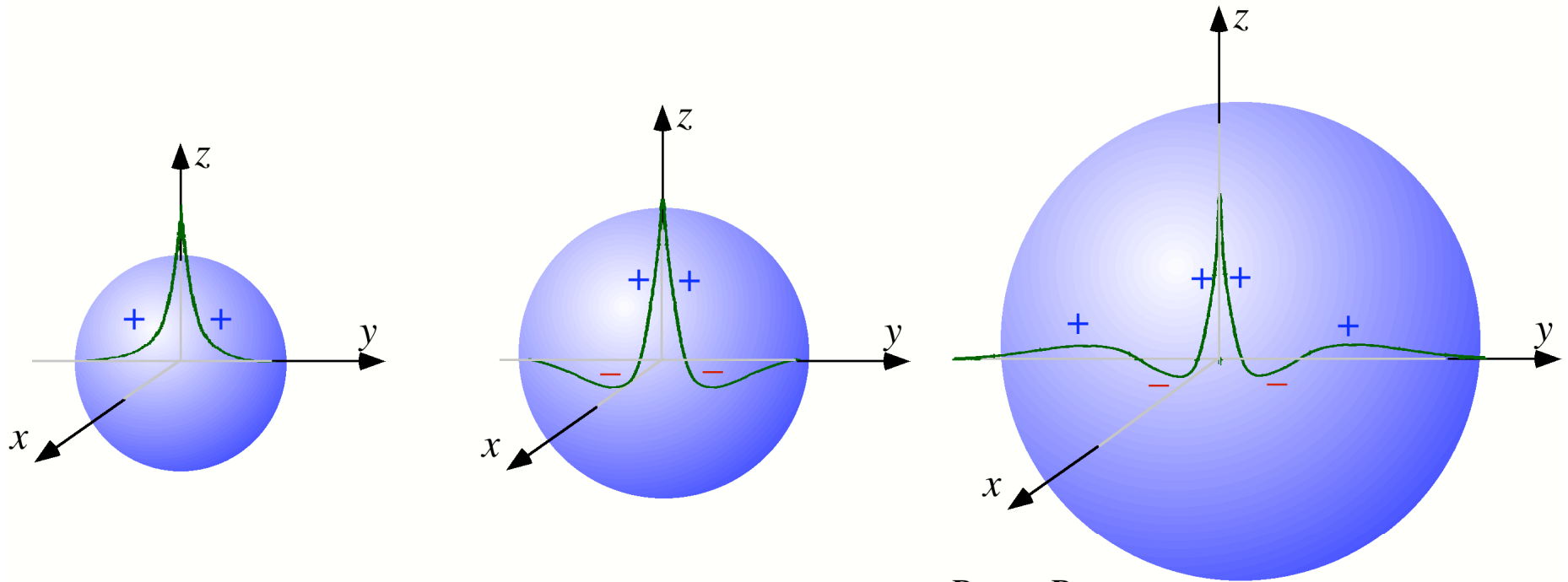
$n = 2$



$n = 3$



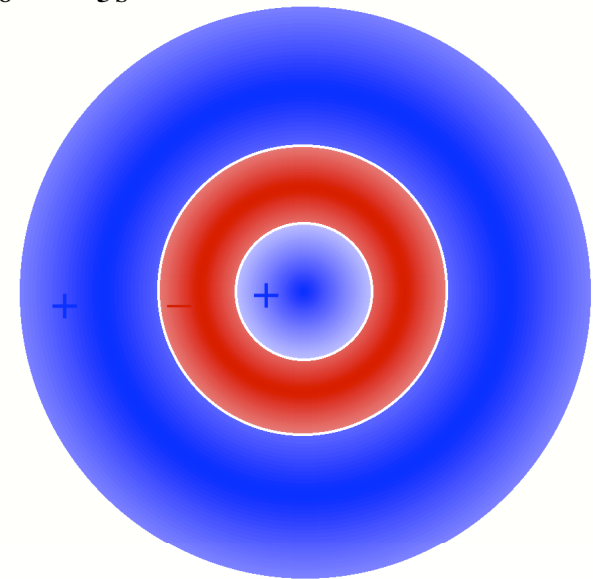
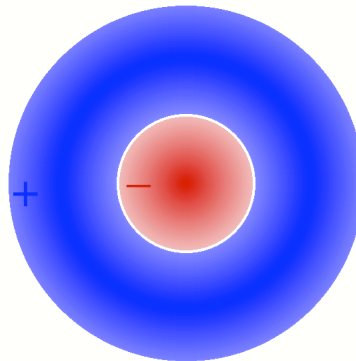
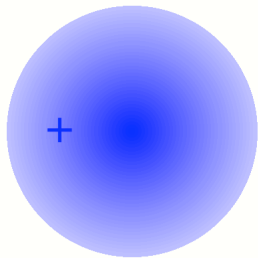
軌道（波動関数）の形を調べる（動径部分）



$$R_{10} = R_{1s}$$

$$R_{20} = R_{2s}$$

$$R_{30} = R_{3s}$$

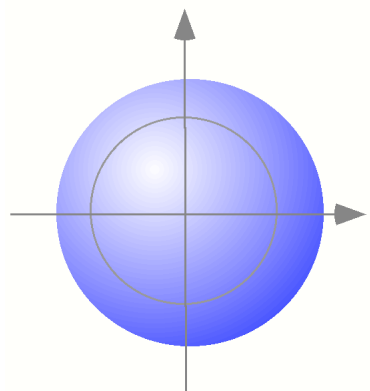


式を使わずに軌道（波動関数）の形を調べる（角部分）

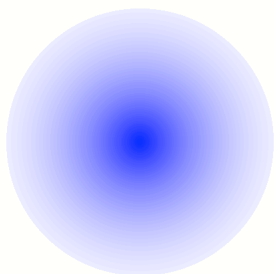
角波動関数の形

$$\Psi_{n,l,m} = R_{n,l}(r) Y_{l,m}(\theta,\phi)$$

$l=0$
s軌道



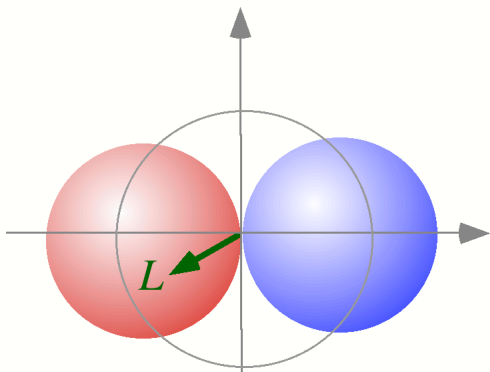
$$L^2 = 0$$



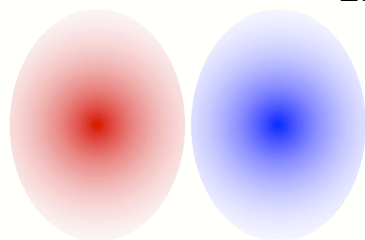
$$m = 0$$

1重縮退

$l=1$
p軌道



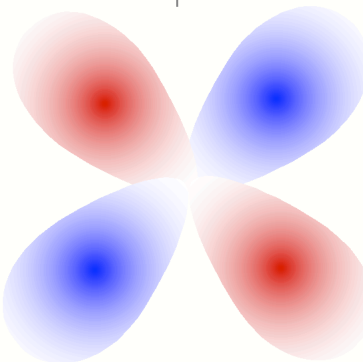
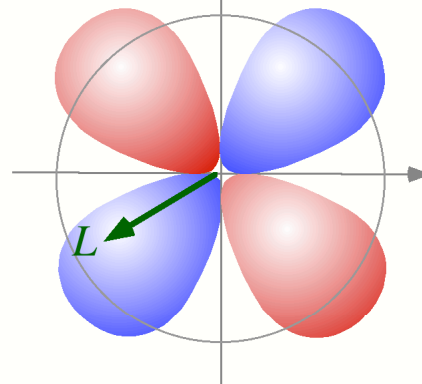
$$L^2 = 2 \frac{h}{2\pi}$$



$$m = 0, \pm 1$$

3重縮退
節面1

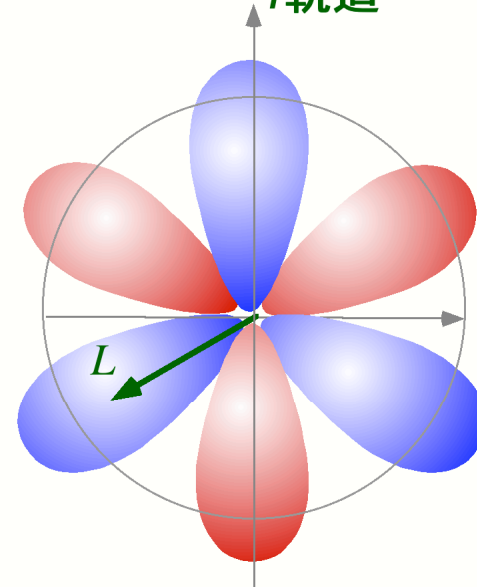
$l=2$
d軌道



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

5重縮退
節面2

$l=3$
f軌道



$$L^2 = 6 \frac{h}{2\pi} \quad L^2 = 12 \frac{h}{2\pi}$$

$$m = 0, \pm 1, \pm 2, \pm 3$$

7重縮退
節面3

軌道（波動関数）の形を調べる（角部分）

$$\Psi_{n,l,m} = R_{n,l}(r) Y_{l,m}(\theta, \phi)$$

$$Y_{l,m}(\theta, \phi) = B_{l,m} [\text{Legendre}_{l,m}(\theta)] e^{im\phi}$$

参考（一般式）

角波動関数 具体的には

<i>s</i>	$l = 0$	$m = 0$	$Y_{00} = Y_{s0} = \sqrt{\frac{1}{4\pi}}$	
<i>p</i>	$l = 1$	$m = 0$	$Y_{10} = Y_{p0} = \sqrt{\frac{3}{4\pi}} \cos \theta$	
		$m = \pm 1$	$Y_{11} = Y_{p1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$	$Y_{1-1} = Y_{p-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$
<i>d</i>	$l = 2$	$m = 0$	$Y_{20} = Y_{d0} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$	
		$m = \pm 1$	$Y_{21} = Y_{d1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{i\phi}$	$Y_{2-1} = Y_{d-1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{-i\phi}$
		$m = \pm 2$	$Y_{22} = Y_{d2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi}$	$Y_{2-2} = Y_{d-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{-2i\phi}$
	⋮	⋮		

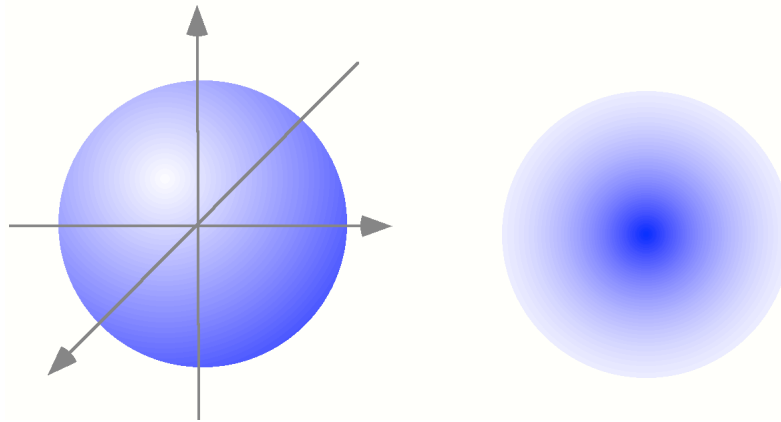
角波動関数の形を調べる

s軌道 $l = 0$ $m = 0$ 1重縮退

$$Y_{00} = Y_{s0} = \sqrt{\frac{1}{4\pi}}$$

θ, ϕ に全く関係しない球対称関数

$L^2 = 0$ 角運動量は0



p軌道 $l = 1$ $m = 0, \pm 1$ 3重縮退

1次独立な3つの複素関数

$$Y_{10} = Y_{p0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{11} = Y_{p1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$$

$$Y_{1-1} = Y_{p-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$$

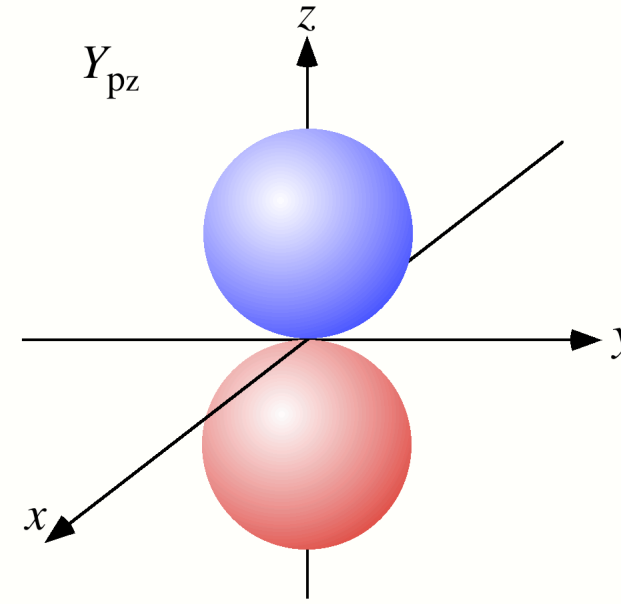
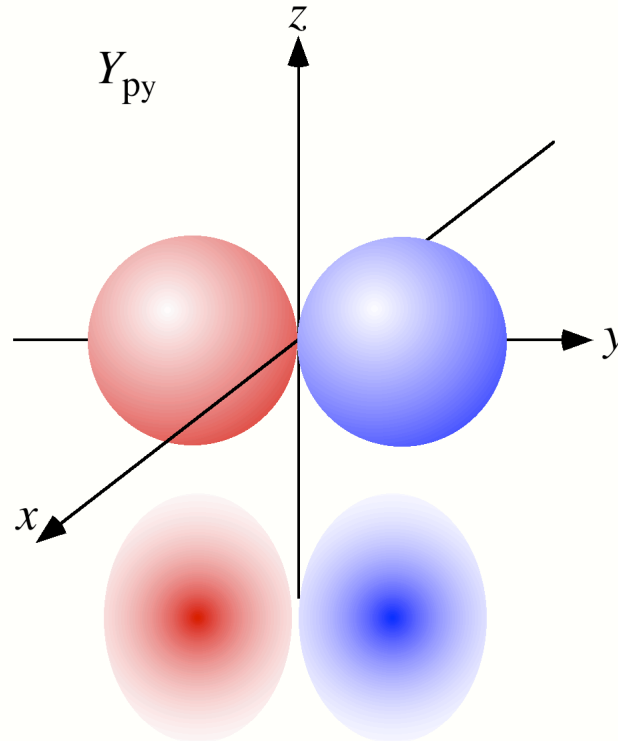
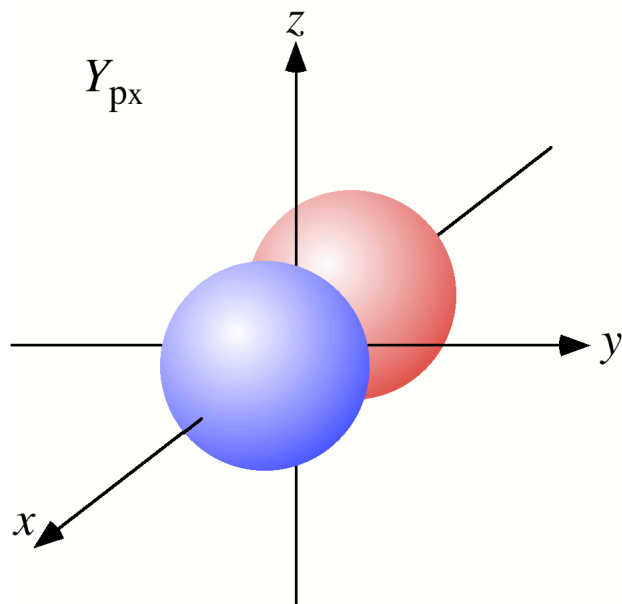
変換

1次独立な3つの実関数

$$Y_{10} = Y_{pz} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$\frac{1}{\sqrt{2}} (Y_{11} + Y_{1-1}) = Y_{px} = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi$$

$$\frac{-i}{\sqrt{2}} (Y_{11} - Y_{1-1}) = Y_{py} = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$$



角波動関数の形を調べる

d 軌道 $l = 2$ $m = 0, \pm 1, \pm 2$ 5重縮退

1 次独立な 5 つの複素関数

$$Y_{20} = Y_{d0} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$$

$$Y_{21} = Y_{d1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{i\phi}$$

$$Y_{2-1} = Y_{d-1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{-i\phi}$$

$$Y_{22} = Y_{d2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi}$$

$$Y_{2-2} = Y_{d-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{-2i\phi}$$

変換

1 次独立な 5 つの実関数

$$Y_{20} = Y_{dz^2} = \sqrt{\frac{5}{16\pi}} (3\frac{z^2}{r^2} - 1) \frac{z}{r} \frac{x}{r}$$

$$\frac{1}{\sqrt{2}} (Y_{21} + Y_{2-1}) = Y_{dxz} = \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \cos\phi \frac{z}{r} \frac{y}{r}$$

$$\frac{-i}{\sqrt{2}} (Y_{21} - Y_{2-1}) = Y_{dyz} = \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \sin\phi$$

$$\frac{-i}{\sqrt{2}} (Y_{22} - Y_{2-2}) = Y_{dxy} = \sqrt{\frac{15}{16\pi}} \sin^2\theta \sin 2\phi \frac{x}{r} \frac{y}{r}$$

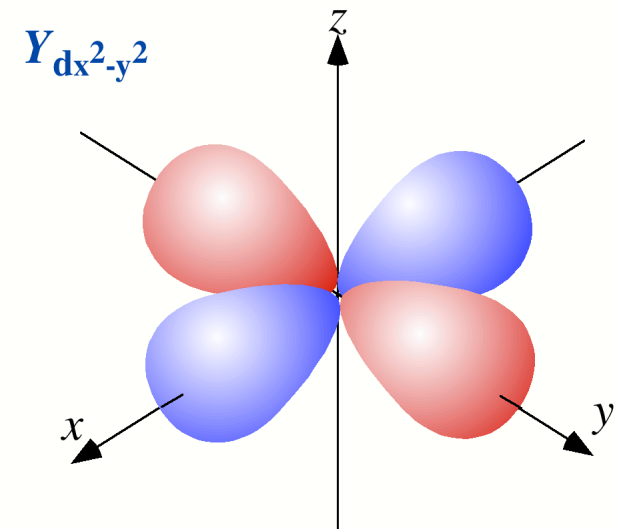
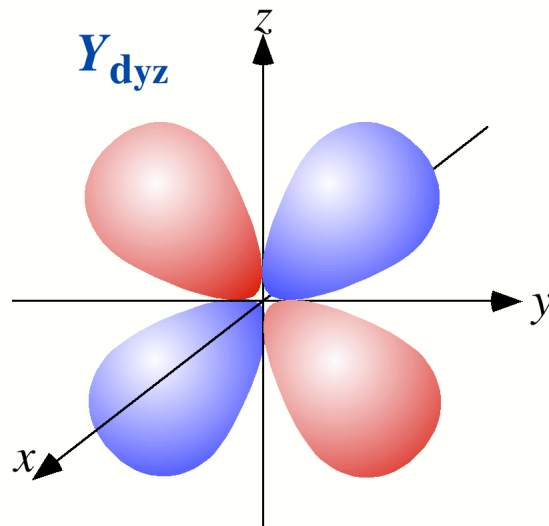
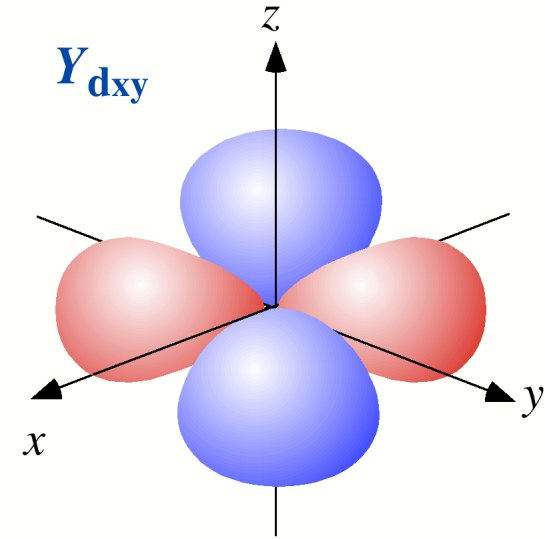
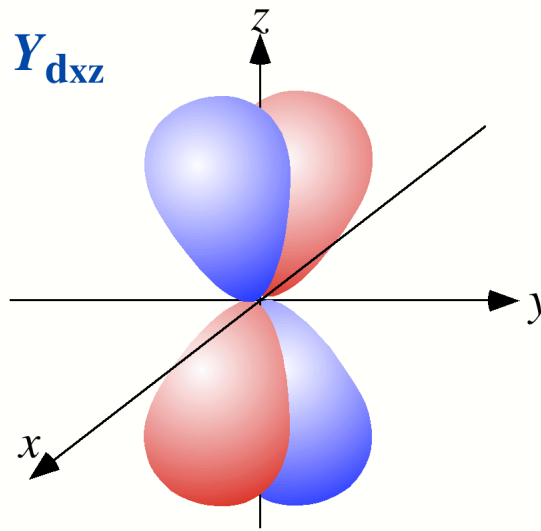
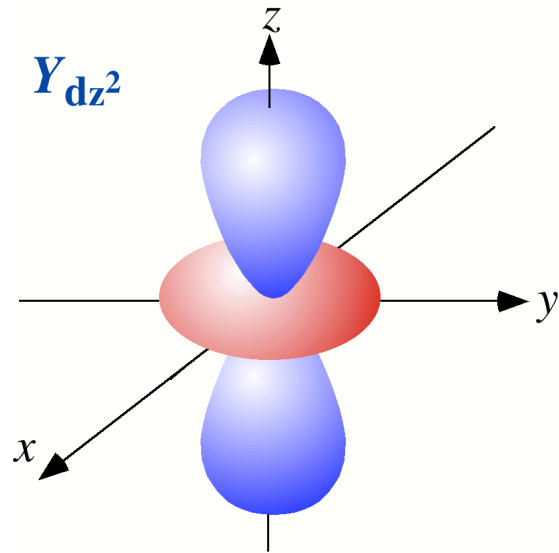
$$= \sqrt{\frac{15}{16\pi}} \sin^2\theta (2\cos\phi \sin\phi)$$

$$\frac{1}{\sqrt{2}} (Y_{22} + Y_{2-2}) = Y_{dx^2-y^2} = \sqrt{\frac{15}{16\pi}} \sin^2\theta \cos 2\phi \frac{x^2}{r^2} - \frac{y^2}{r^2}$$

$$= \sqrt{\frac{15}{16\pi}} \sin^2\theta (\cos^2\phi - \sin^2\phi)$$

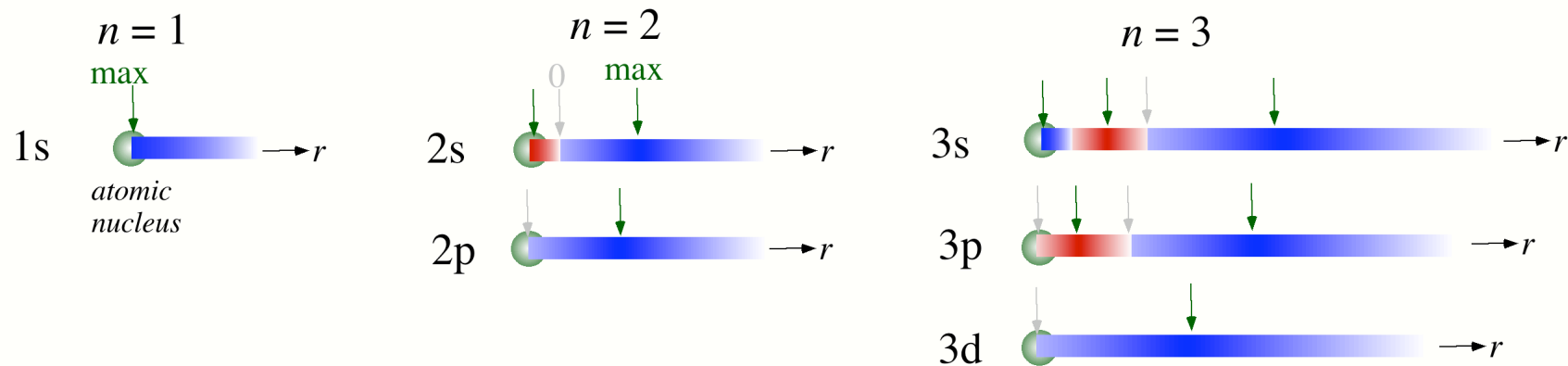
角波動関数の形を調べる

d軌道 $l=2$ $m=0, \pm 1, \pm 2$ 5重縮退

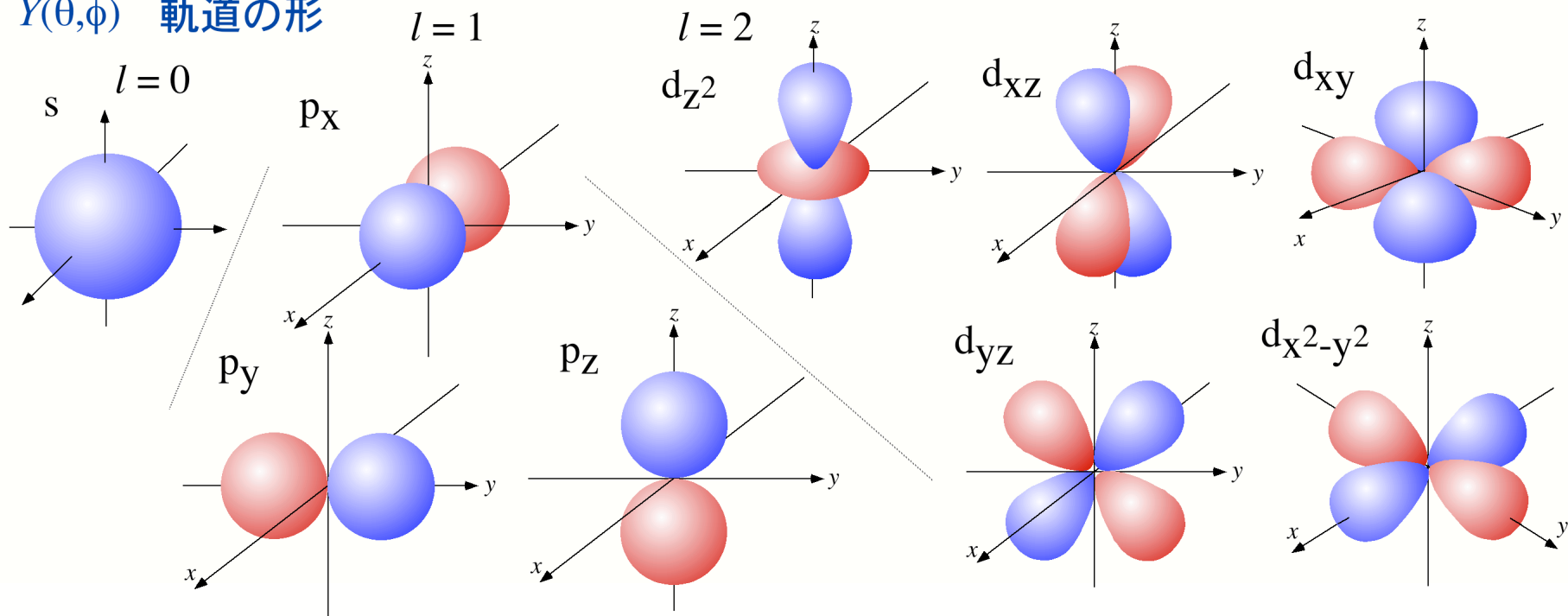


軌道全体の形は 動径部分と角部分の掛け算で決まる

$R(r)$ or $R^2(r)$ 動径方向の広がり



$Y(\theta, \phi)$ 軌道の形

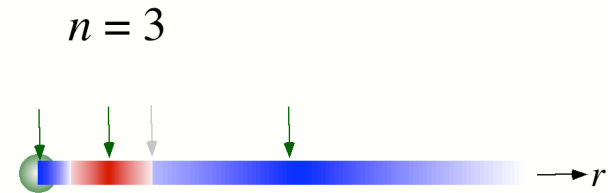
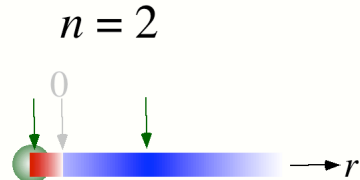
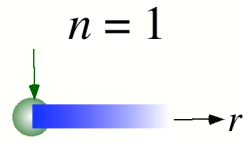


s軌道の形を考えよう

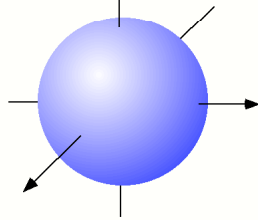
動径方向の広がり

軌道の形

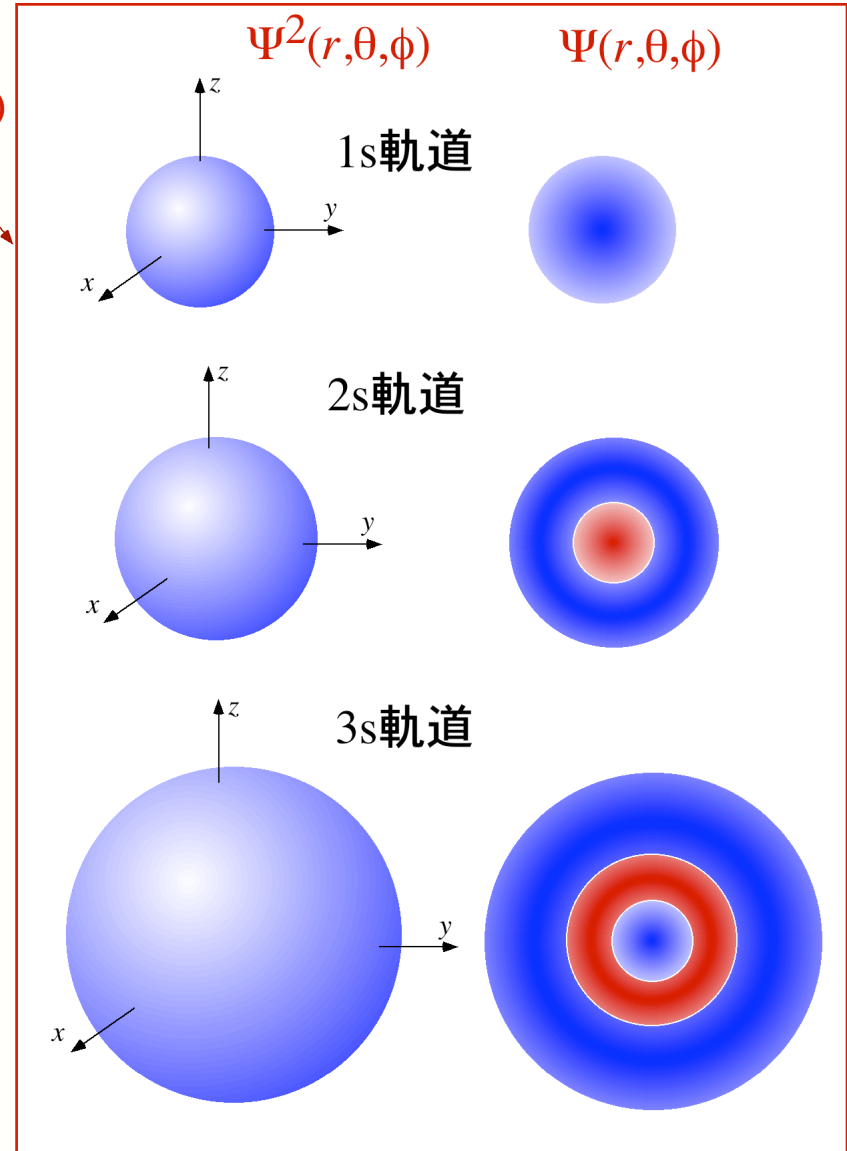
$$R(r) \times Y(\theta, \phi) = \Psi(r, \theta, \phi)$$



$l = 0$



s軌道の形



p軌道の形を考えよう

動径方向の広がり

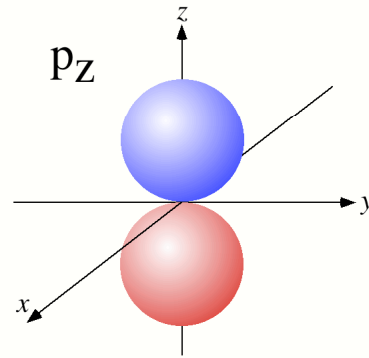
軌道の形

$$R(r) \times Y(\theta, \phi) = \Psi(r, \theta, \phi)$$

$n = 2$



$l = 1$



$n = 3$

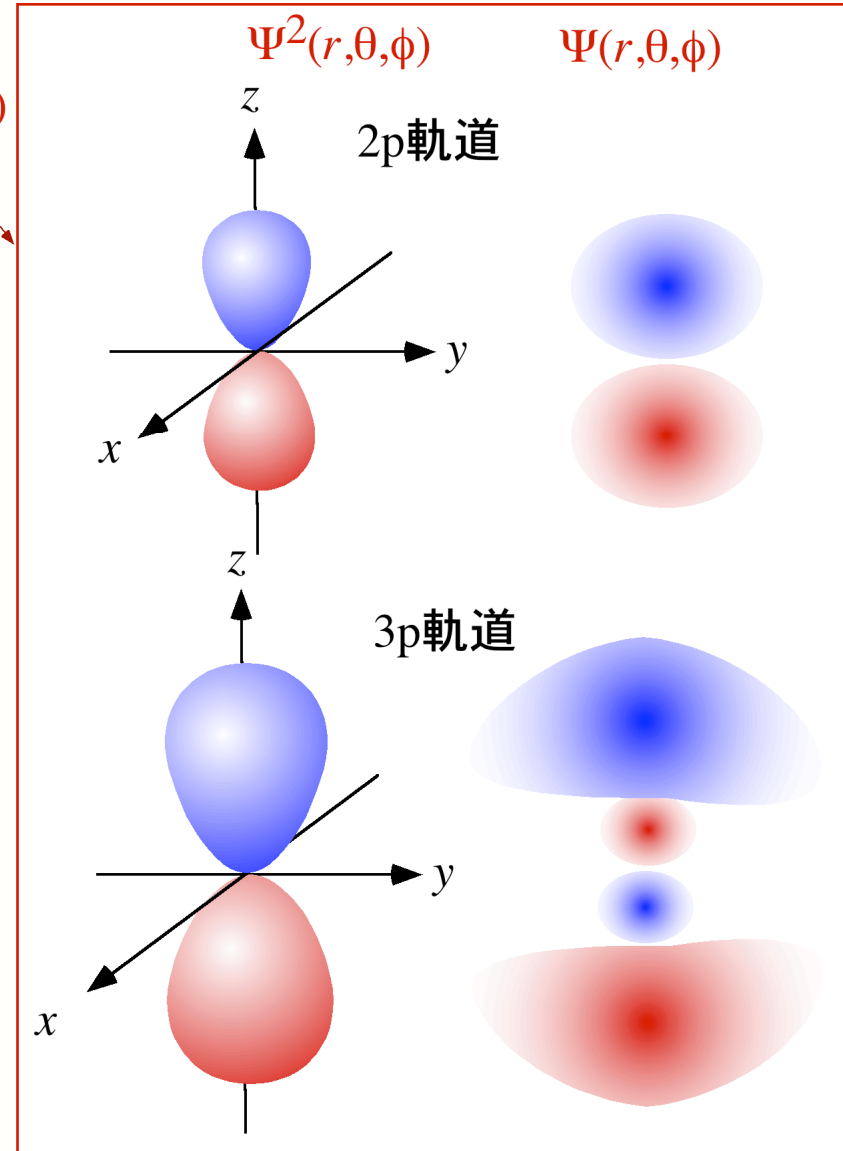


p_x, p_y, p_z

3重に縮退

($m = 0, \pm 1$)

p軌道の形



d軌道の形を考えよう

動径方向の広がり $R(r)$ × 軌道の形 $Y(\theta, \phi) = \Psi(r, \theta, \phi)$

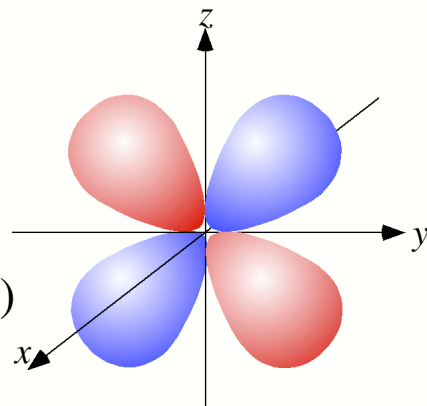
$n = 3$



$l = 2$

5重に縮退

$(m = 0, \pm 1, \pm 2)$



$n = 4$

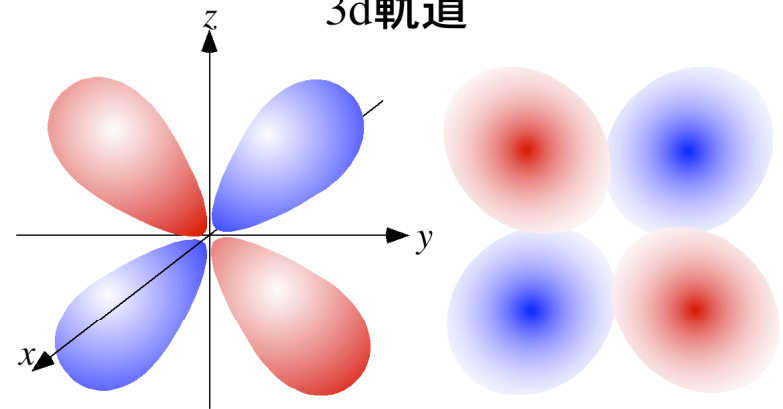


d軌道の形

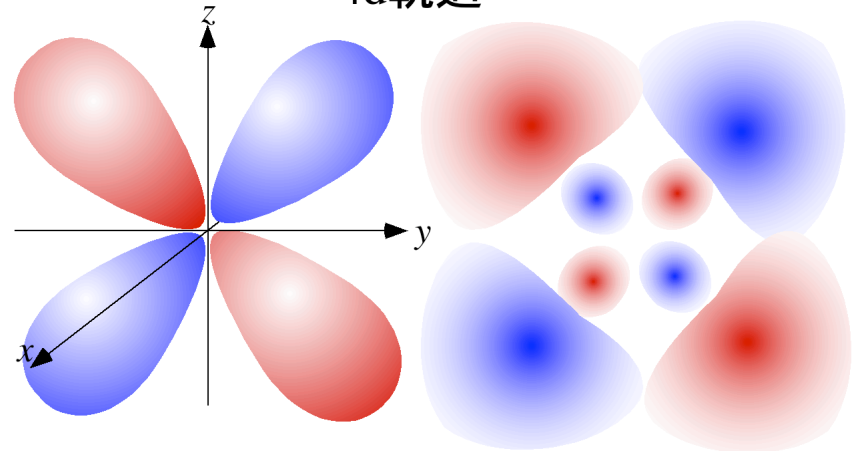
$\Psi^2(r, \theta, \phi)$

$\Psi(r, \theta, \phi)$

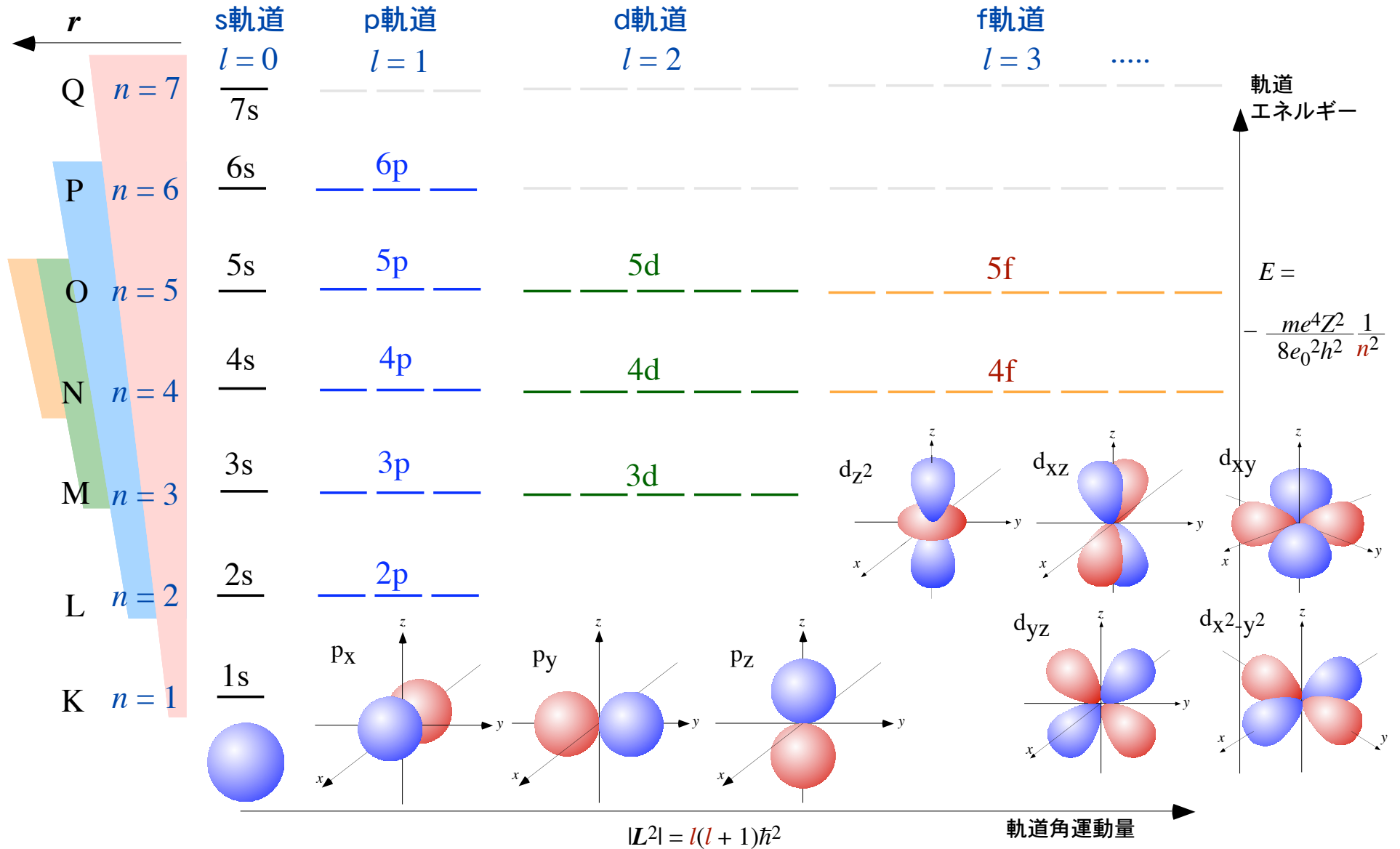
3d軌道



4d軌道



水素原子の軌道



(参考) 波動関数の一覧

$$\rho_0 = \frac{Zr}{a_0} \quad \begin{matrix} \text{(ボーア半径)} \\ a_0 = 0.53 \text{ \AA} \end{matrix}$$

	n	l	m	
1s	1	0	0	$\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_0}$
2s	2	0	0	$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \rho_0) e^{-\rho_0/2}$
2p	2	1	0	$\Psi_{2pz} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0) e^{-\rho_0/2} \cos \theta \quad \leftarrow \frac{z}{r}$
			± 1	$\Psi_{2px} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0) e^{-\rho_0/2} \sin \theta \cos \phi \quad \leftarrow \frac{x}{r}$
			± 1	$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0) e^{-\rho_0/2} \sin \theta \sin \phi \quad \leftarrow \frac{y}{r}$
3s	3	0	0	$\Psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\rho_0 + 2\rho_0^2) e^{-\rho_0/3}$
3p	3	1	0	$\Psi_{3pz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\rho_0 - \rho_0^2) e^{-\rho_0/3} \cos \theta$
			± 1	$\Psi_{3px} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\rho_0 - \rho_0^2) e^{-\rho_0/3} \sin \theta \cos \phi$
			± 1	$\Psi_{3py} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\rho_0 - \rho_0^2) e^{-\rho_0/3} \sin \theta \sin \phi$

(参考) 波動関数の一覧 (続)

$$\rho_0 = \frac{Zr}{a_0} \quad \begin{matrix} \text{(ボーア半径)} \\ a_0 = 0.53 \text{ \AA} \end{matrix}$$

n	l	m	
3d	2	0	$\Psi_{3dz^2} = \frac{1}{81\sqrt{6}\pi} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3} (3\cos^2\theta - 1)$ $\sim 3 \frac{z^2}{r^2} - 1$
	2	± 1	$\Psi_{3dxz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3} \cos\theta \sin\theta \cos\phi$ $\sim \frac{z}{r} \frac{x}{r}$
		± 1	$\Psi_{3dyz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3} \cos\theta \sin\theta \sin\phi$ $\sim \frac{z}{r} \frac{y}{r}$
	2	± 2	$\Psi_{3dxy} = \frac{1}{81\sqrt{2}\pi} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3} \sin^2\theta \sin 2\phi$ $\sim \sin^2\theta (2\cos\phi \sin\phi)$ $\sim \frac{x}{r} \frac{y}{r}$
			$\Psi_{3dx^2-y^2} = \frac{1}{81\sqrt{2}\pi} \left(\frac{Z}{a_0}\right)^{3/2} (\rho_0^2) e^{-\rho_0/3} \sin^2\theta \cos 2\phi$ $\sim \sin^2\theta (\cos^2\phi - \sin^2\phi)$ $\sim \frac{x^2}{r^2} - \frac{y^2}{r^2}$

多電子原子に続く