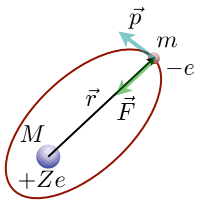
水素原子 (水素様原子)

エネルギー固有値・波動関数・主量子数・角運動量・
方位量子数・ 磁気量子数

水素様原子

- 原子核＋電子 1 個



$$\vec{F} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}\frac{\vec{r}}{r}$$

$$r \equiv |\vec{r}|$$

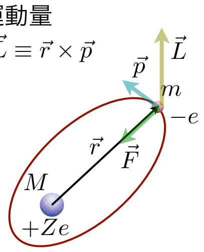
$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

重要

水素様原子（古典力学）

角運動量

$$\vec{L} \equiv \vec{r} \times \vec{p}$$



運動方程式

$$\frac{d}{dt}\vec{p} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}\frac{\vec{r}}{r}$$

$$\frac{d}{dt}(\vec{r}\times\vec{p}) = \frac{d\vec{r}}{dt}\times\vec{p} + \vec{r}\times\frac{d\vec{p}}{dt}$$

$$= \frac{1}{m}(\vec{p}\times\vec{p}) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}\frac{(\vec{r}\times\vec{r})}{r}$$

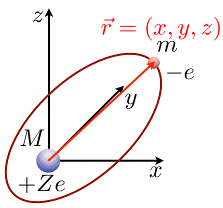
$$= 0$$

$$\frac{d}{dt}\vec{L} = 0$$ 角運動量の保存則

水素様原子（量子力学）

ポテンシャルエネルギー

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$



$$r = \sqrt{x^2 + y^2 + z^2}$$

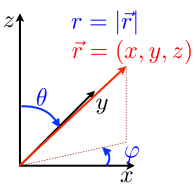
ハミルトニアン

$$\mathcal{H} = \frac{\vec{p}^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

シュレディンガー方程式

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\vec{r}) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}\psi(\vec{r}) = E\psi(\vec{r})$$

極座標



直交座標		極座標
(x, y, z)		(r, θ, φ)
$-\infty \le x \le \infty$		$0 \le r \le \infty$
$-\infty \le y \le \infty$	➡	$0 \le \theta \le \pi$
$-\infty \le z \le \infty$		$0 \le \varphi \le 2\pi$

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

$$\begin{cases} r = \sqrt{x^2+y^2+z^2} \\ \theta = \arctan\dfrac{\sqrt{x^2+y^2}}{z} \\ \varphi = \arctan\dfrac{y}{x} \end{cases}$$

極座標での微積分

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

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

$$\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz\, f(x,y,z)$$

$$= \int_0^{\infty}r^2dr\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\varphi F(r,\theta,\varphi)$$

$$F(r,\theta,\varphi) = f(r\sin\theta\cos\varphi, r\sin\theta\sin\varphi, r\cos\theta)$$

中心力ポテンシャル

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

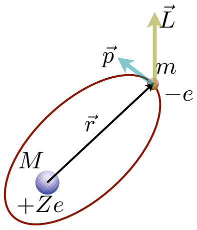
$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$
$$-\frac{\hbar^2}{2mr^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}+V(r)$$

ポテンシャルが原点からの距離だけの関数（中心力ポテンシャル）のときはいつでもこの変換を行なうことができる

角運動量演算子

◦ 角運動量 $\vec{L} \equiv \vec{r}\times\vec{p}$



$$\vec{r} = (x,\, y,\, z)$$
$$\vec{p} = (p_x,\, p_y,\, p_z) = \left(\frac{\hbar}{i}\frac{\partial}{\partial x},\, \frac{\hbar}{i}\frac{\partial}{\partial y},\, \frac{\hbar}{i}\frac{\partial}{\partial z}\right)$$
$$\vec{L} = (L_x,\, L_y,\, L_z)$$

$$L_x = yp_z - zp_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$L_y = zp_x - xp_z = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$L_z = xp_y - yp_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

参考

角運動量演算子の極座標形式

$$L_x = yp_z - zp_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$
$$L_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$
$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$
$$\vec{L}^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$$
$$= -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{1}{\sin^2\theta}\frac{L_z^2}{\hbar^2}\right\}$$

角運動量とハミルトニアン

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$
$$-\frac{\hbar^2}{2mr^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}+V(r)$$

$$\vec{L}^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$$

古典力学の遠心力ポテンシャルに相当

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\boxed{\frac{\vec{L}^2}{2mr^2}}+V(r)$$

シュレディンガー方程式

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\vec{L}^2}{2mr^2}+V(r)$$
$$\vec{L}^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{1}{\sin^2\theta}\frac{L_z^2}{\hbar^2}\right\}$$
$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

$$\mathcal{H}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) = R(r)P(\cos\theta)\Phi(\varphi)$$

角運動量の固有値・固有関数

L_z の固有値・固有関数

$$L_z\Phi(\varphi) = \lambda\Phi(\varphi)$$
$$\frac{\hbar}{i}\frac{\partial}{\partial\varphi}\Phi(\varphi) = \lambda\Phi(\varphi)$$
$$\Phi(\varphi) = Ce^{\frac{i}{\hbar}\lambda\varphi}$$

境界条件は $\Phi(\varphi+2\pi) = \Phi(\varphi)$

$$\Phi(\varphi+2\pi) = Ce^{\frac{i}{\hbar}\lambda(\varphi+2\pi)}$$
$$= Ce^{\frac{i}{\hbar}\lambda\varphi}e^{2\pi i\frac{\lambda}{\hbar}}$$
$$= Ce^{\frac{i}{\hbar}\lambda\varphi}$$

$$e^{2\pi i\frac{\lambda}{\hbar}} = 1 \Rightarrow 2\pi\frac{\lambda}{\hbar} = 2\pi m$$

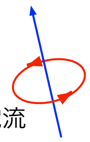
$$\lambda = \hbar m$$
$$\Phi_m(\varphi) = Ce^{im\varphi}$$
$$\int_0^{2\pi}\Phi_m^*(\varphi)\Phi_m(\varphi)d\varphi$$
$$= |C|^2\int_0^{2\pi}d\varphi$$
$$= 2\pi|C|^2 = 1$$

$$L_z\Phi_m(\varphi) = \hbar m\Phi_m(\varphi)$$
$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}$$
$$m = 0,\ \pm1,\ \pm2,\ \pm3\cdots$$

重要

角運動量と磁気量子数

L_z の固有値・固有関数



$$L_z\Phi_m(\varphi) = \hbar m\Phi_m(\varphi)$$

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

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

磁気量子数

角運動量の固有値・固有関数

$\vec{L}^2$ の固有値・固有関数

$$-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{L_z^2}{\hbar^2}\right\}Y(\theta,\varphi) = \lambda Y(\theta,\varphi)$$

条件は $0 \le \theta \le \pi$ で正則

$Y(\theta,\varphi) = P(\cos\theta)\Phi_m(\varphi)$ $\quad \xi = \cos\theta$ とおくと

$$L_z\Phi_m(\varphi) = \hbar m\Phi_m(\varphi) \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3\cdots$$

$$-\left\{\frac{\partial}{\partial\xi}\left((1-\xi^2)\frac{\partial}{\partial\xi}\right) - \frac{m^2}{1-\xi^2}\right\}P(\xi) = \frac{\lambda}{\hbar^2}P(\xi)$$

ただし、$-1 \le \xi \le 1$

角運動量の固有値・固有関数

$$-\left\{\frac{\partial}{\partial\xi}\left((1-\xi^2)\frac{\partial}{\partial\xi}\right) - \frac{m^2}{1-\xi^2}\right\}P(\xi) = \frac{\lambda}{\hbar^2}P(\xi)$$ は

$\dfrac{\lambda}{\hbar^2} = \ell(\ell+1) \quad \ell = 0, 1, 2, 3, \cdots$ かつ $|m| \le \ell$ のときだけ

$-1 \le \xi \le 1$ で正則な解(ルジャンドルの陪多項式)をもつ

$m = -\ell, , \cdots, 0, 1, \cdots \ell - 1, \ell$ $\qquad 2\ell + 1$ 重縮退

一つの ℓ に対して $2\ell + 1$ 通りの m の値が存在する

ℓ	m							縮退
0	0							なし
1	−1	0	1					3重
2	−2	−1	0	1	2			5重
3	−3	−2	−1	0	1	2	3	7重

参考

ルジャンドルの陪多項式

$$P_\ell(\xi) = \frac{1}{2^\ell}\frac{d^\ell}{d\xi^\ell}(\xi^2-1)^\ell$$

$$P_\ell^{|m|}(\xi) = (1-\xi^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{d\xi^{|m|}}P_\ell(\xi)$$

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

$$P_0^0(\xi) = 1$$
$$P_1^0(\xi) = \xi$$
$$P_1^1(\xi) = \sqrt{1-\xi^2}$$
$$P_2^0(\xi) = \frac{3}{2}\xi^2 - \frac{1}{2}$$
$$P_2^1(\xi) = 3\xi\sqrt{1-\xi^2}$$
$$P_2^2(\xi) = 3(1-\xi^2)$$

$$\int_{-1}^{1} P_\ell^{|m|}(\xi)P_{\ell'}^{|m|}(\xi)d\xi = \frac{2}{2\ell+1}\frac{(\ell+|m|)!}{(\ell-|m|)!}\delta_{\ell,\ell'}$$

角運動量の固有値・固有関数

$\vec{L}^2$ $\; L_z$ の固有値・固有関数

$$\frac{\lambda}{\hbar^2} = \ell(\ell+1) \quad (\ell = 0, 1, 2, 3, \cdots) \;\Rightarrow \lambda = \hbar^2\ell(\ell+1)$$

$$Y(\theta,\varphi) = P(\cos\theta)\Phi_m(\varphi)$$

$$\Rightarrow Y_{\ell,m}(\theta,\varphi) = C_{\ell,m}P_\ell^{|m|}(\cos\theta)e^{im\varphi}$$

球面調和関数

$\vec{L}^2 Y_{\ell,m}(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_{\ell,m}(\theta,\varphi) \qquad \ell = 0, 1, 2, 3, \cdots$

方位量子数

$L_z Y_{\ell,m}(\theta,\varphi) = \hbar m Y_{\ell,m}(\theta,\varphi) \qquad m = 0, \pm 1, \pm 2, \cdots, \pm\ell$

磁気量子数

参考

球面調和関数

$$Y_{\ell,m}(\theta,\varphi) = (-1)^{\frac{m+|m|}{2}}\frac{1}{\sqrt{2\pi}}\sqrt{\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}}P_\ell^{|m|}(\cos\theta)e^{im\varphi}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_{\ell,m}^*(\theta,\varphi)Y_{\ell',m'}(\theta,\varphi)\sin\theta d\theta d\varphi = \delta_{\ell,\ell'}\delta_{m,m'}$$

$$Y_{0,0}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} \qquad Y_{2,0}(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

$$Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{2,\pm 2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$$

$$Y_{1,\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi} \qquad Y_{2,\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$$

重要

方位量子数の異なる状態

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

$\ell = 0 \Rightarrow Y_{0,0} = \text{const.}$ **s** 状態(縮退無し)

p 状態 (3重縮退) $\ell = 1 \Rightarrow$

$$\left\{ \begin{array}{l} Y_{1,0} \propto \cos\theta = \dfrac{z}{r} \quad \mathbf{p}_z\text{状態} \\ \left. \begin{array}{l} Y_{1,1} \propto \sin\theta e^{i\varphi} \\ Y_{1,-1} \propto \sin\theta e^{-i\varphi} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} Y_{1,1} + Y_{1,-1} \propto \sin\theta\cos\varphi = \dfrac{x}{r} \quad \mathbf{p}_x\text{状態} \\ Y_{1,1} - Y_{1,-1} \propto \sin\theta\sin\varphi = \dfrac{y}{r} \quad \mathbf{p}_y\text{状態} \end{array} \right. \end{array} \right.$$

$\ell = 2$ **d** 状態(5重縮退)

$\ell = 3$ **f** 状態(7重縮退)

ハミルトニアンの固有値・固有関数

$$\left\{ -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\vec{L}^2}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \right\} \psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

$\psi(r,\theta,\varphi) = R(r)Y_{\ell,m}(\theta,\varphi)$ とおくと $\vec{L}^2 Y_{\ell,m} = \hbar^2\ell(\ell+1)Y_{\ell,m}$ より

$$\left[-\frac{\hbar^2}{2m}\left\{ \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2} \right\} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \right] R(r) = ER(r)$$

条件は$r=0$で正則かつ，境界条件 $\lim_{r\to\infty} R(r) = 0$ を満たす

重要

動径方向のシュレディンガー方程式

$$\left[-\frac{\hbar^2}{2m}\left\{ \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2} \right\} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \right] R(r) = ER(r)$$

$$\frac{\hbar^2}{m} = \text{エネルギー} \times \text{長さ}^2$$

$$\frac{e^2}{4\pi\varepsilon_0} = \text{エネルギー} \times \text{長さ}$$

ボーア半径

$$\text{長さ} = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 5.3\times 10^{-11}[\text{m}] = 0.053\ [\text{nm}] = 0.53\ [\text{Å}]$$

$$\text{エネルギー} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B} = 43.6\times 10^{-19}[\text{J}] = 27.2\ [\text{eV}]$$

動径方向のシュレディンガー方程式

$$\left[-\frac{\hbar^2}{2m}\left\{ \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2} \right\} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \right] R(r) = ER(r)$$

$$a_B = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \quad \text{ボーア半径}$$

$$E_0 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B}$$

$\varepsilon = \dfrac{E}{E_0} \quad \rho = \dfrac{r}{a_B}$ とおくと

$$\left[\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) + 2\left(\varepsilon + \frac{Z}{\rho}\right) - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) = 0$$

$$\left[\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) + 2\left(\varepsilon + \frac{Z}{\rho}\right) - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) = 0$$

$R(\rho) = \rho^\ell u(\rho)$ とおくと

$$\frac{\partial^2 u}{\partial\rho^2} + \frac{2(\ell+1)}{\rho}\frac{\partial u}{\partial\rho} + 2\left(\varepsilon + \frac{Z}{\rho}\right)u = 0$$

$\rho\to\infty$ の極限では $\dfrac{\partial^2 u}{\partial\rho^2} + 2\varepsilon u = 0$

$\rho\to\infty$ で $u(\rho)\to 0$ となるためには $\varepsilon < 0 \quad u(\rho) \sim e^{-\sqrt{-2\varepsilon}\rho}$

$\alpha = \sqrt{-2\varepsilon} \quad x = 2\alpha\rho \quad u(\rho) = e^{-\alpha\rho}y(x)$ とおくと

$$x\frac{\partial^2 y}{\partial x^2} + [2(\ell+1) - x]\frac{\partial y}{\partial x} + \left[\frac{Z}{\alpha} - (\ell+1)\right] y = 0$$

ラゲールの陪微分方程式

ラゲールの陪微分方程式

$$x\frac{\partial^2 y}{\partial x^2} + [2(\ell+1) - x]\frac{\partial y}{\partial x} + \left[\frac{Z}{\alpha} - (\ell+1)\right] y = 0 \quad \text{は}$$

$$\frac{Z}{\alpha} = n \quad (n = 1, 2, 3, \cdots)$$

のときのみ無限遠で有界な解 をもつ.

$$y(x) = L_{n+\ell}^{2\ell+1}(x) \quad \text{ラゲールの陪多項式}$$

ただし、

$\ell < n$

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

でなければならない

参考

ラゲールの陪多項式

$$\frac{Z}{\alpha} = n \quad (n = 1, 2, 3, \cdots)$$

$$y(x) = L_{n+\ell}^{2\ell+1}(x)$$

$$\ell < n$$

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

n	ℓ	$L_{n+\ell}^{2\ell+1}(x)$ n
1	0	$L_1^1(x) = -1$
2	0	$L_2^1(x) = 2x - 4$
	1	$L_3^3(x) = -6$
3	0	$L_3^0(x) = -3x^2 + 19x - 18$
	1	$L_4^3(x) = 12x - 16$
	2	$L_5^5(x) = -5$

$$L_{n+\ell}^{2\ell+1}(x) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{\{(n+\ell)!\}^2}{(n+\ell-1-k)!(2\ell+1+k)!} x^k$$

重要

エネルギー固有値

$$a_B = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \qquad E_0 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B} \qquad \varepsilon = \frac{E}{E_0} \qquad \alpha = \sqrt{-2\varepsilon}$$

$$\frac{Z}{\alpha} = n \qquad (n = 1, 2, 3, \cdots)$$

$$E = E_0\varepsilon = -\frac{E_0}{2}\alpha^2 = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_B}\left(\frac{Z}{n}\right)^2$$

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z^2}{n^2} \qquad (n = 1, 2, 3, \cdots)$$ 主量子数

$$E_R = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 13.6 \text{ [eV]} \qquad E_n = -\frac{E_R Z^2}{n^2}$$

リュドベリー定数

動径波動関数

$$\rho = \frac{r}{a_B} \qquad R(\rho) = \rho^\ell u(\rho) \qquad u(\rho) = e^{-\alpha\rho} y(x) \qquad x = 2\alpha\rho$$

$$\frac{Z}{\alpha} = n \qquad y(x) = L_{n+\ell}^{2\ell+1}(x)$$

$$R_{n,\ell}(r) = -\sqrt{\left(\frac{2Z}{na_B}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} \left(\frac{2Zr}{na_B}\right)^\ell e^{-\frac{Z}{n}\frac{r}{a_B}} L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_B}\right)$$

$Z = 1$ のとき

$$R_{1,0}(r) = \left(\frac{1}{a_B}\right)^{\frac{3}{2}} 2e^{-\frac{r}{a_B}}$$

$$R_{2,0}(r) = \left(\frac{1}{2a_B}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_B}\right) e^{-\frac{r}{2a_B}}$$

$$R_{2,1}(r) = \left(\frac{1}{2a_B}\right)^{\frac{3}{2}} \frac{1}{\sqrt{3}} \frac{r}{a_B} e^{-\frac{r}{2a_B}}$$

重要　重要

水素様原子のまとめ

$$\mathcal{H}\psi_{n,\ell,m}(r,\theta,\varphi) = E_n \psi_{n,\ell,m}(r,\theta,\varphi)$$

$$\psi_{n,\ell,m}(r,\theta,\varphi) = R_{n,\ell}(r) Y_{\ell,m}(\theta,\varphi)$$

$$E_n = -\frac{E_R Z^2}{n^2} \quad n = 1, 2, 3, 4, \cdots$$ 主量子数　n^2重縮退

リュドベリー定数　ボーア半径

$$E_R = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B} = 13.6\text{[eV]} \qquad a_B = 0.053\text{[nm]} = 0.53\text{[Å]}$$

$$\vec{L}^2\psi_{n,\ell,m}(r,\theta,\varphi) = \hbar^2\ell(\ell+1)\psi_{n,\ell,m}(r,\theta,\varphi)$$

$$L_z\psi_{n,\ell,m}(r,\theta,\varphi) = \hbar m \psi_{n,\ell,m}(r,\theta,\varphi)$$

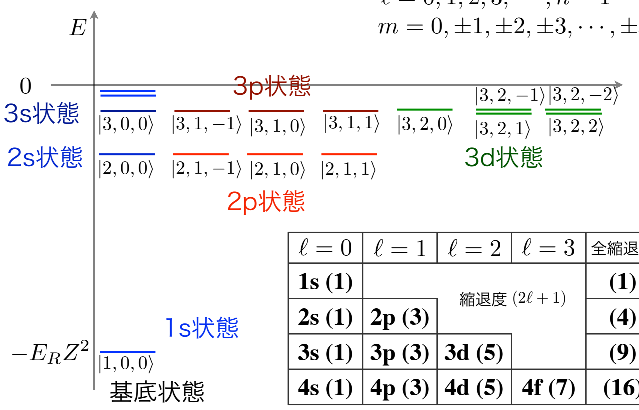
$$\ell = 0, 1, 2, 3, \cdots, n-1$$ 副量子数（方位量子数）　$2\ell+1$重縮退

重要　$$m = 0, \pm1, \pm2, \pm3, \cdots, \pm\ell$$ 磁気量子数　重要

$$E_n = -\frac{E_R Z^2}{n^2} \qquad |n,\ell,m\rangle \quad n = 1, 2, 3, 4, \cdots$$

$$\ell = 0, 1, 2, 3, \cdots, n-1$$

$$m = 0, \pm1, \pm2, \pm3, \cdots, \pm\ell$$



$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	全縮退度
1s (1)	縮退度 $(2\ell+1)$			**(1)**
2s (1)	**2p (3)**			**(4)**
3s (1)	**3p (3)**	**3d (5)**		**(9)**
4s (1)	**4p (3)**	**4d (5)**	**4f (7)**	**(16)**

波動関数の例

- 水素(Z=1)の場合

$$|1,0,0\rangle = \sqrt{\frac{1}{\pi a_B^3}} e^{-\frac{r}{a_B}} \equiv |1s\rangle$$

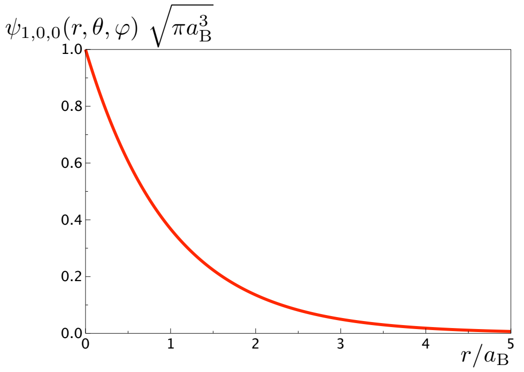
$$|2,0,0\rangle = \sqrt{\frac{1}{32\pi a_B^3}} e^{-\frac{r}{2a_B}} \left(2 - \frac{r}{a_B}\right) \equiv |2s\rangle$$

$$|2,1,0\rangle = \sqrt{\frac{1}{32\pi a_B^3}} e^{-\frac{r}{2a_B}} \frac{r}{a_B}\cos\theta \equiv |2p_z\rangle$$

$$|2,1,1\rangle = \sqrt{\frac{1}{64\pi a_B^3}} e^{-\frac{r}{2a_B}} \frac{r}{a_B}\sin\theta e^{i\varphi} \qquad \frac{1}{\sqrt{2}}(|2,1,1\rangle + |2,1,-1\rangle) \equiv |2p_x\rangle$$

$$|2,1,-1\rangle = \sqrt{\frac{1}{64\pi a_B^3}} e^{-\frac{r}{2a_B}} \frac{r}{a_B}\sin\theta e^{-i\varphi} \qquad \frac{1}{\sqrt{2}i}(|2,1,1\rangle - |2,1,-1\rangle) \equiv |2p_y\rangle$$

波動関数（Z=1の場合）



基底状態での平均値(Z=1)

$$\langle 1s|r|1s\rangle$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\sqrt{\frac{1}{\pi a_B^3}}e^{-\frac{r}{a_B}}\,r\,\sqrt{\frac{1}{\pi a_B^3}}e^{-\frac{r}{a_B}}\,r^2\sin\theta\, dr d\theta d\varphi$$

$$= 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}r^3 e^{-\frac{2r}{a_B}}dr$$

$$x = -\frac{2r}{a_B}$$

$$= 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}\left(\frac{a_B}{2}x\right)^3 e^{-x}\frac{a_B}{2}dx$$

$$= \frac{1}{4}a_B\int_0^{\infty}x^3 e^{-x}dx \;=\frac{3}{2}a_B$$

$$\int_0^{\infty}x^n \mathrm{e}^{-x}\mathrm{d}x = n!$$

基底状態での平均値(Z=1)

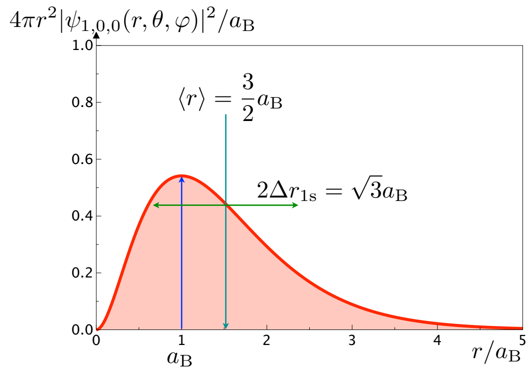
$$\langle 1s|r^2|1s\rangle = 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}r^4 e^{-\frac{2r}{a_B}}dr$$

$$= 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}\left(\frac{a_B}{2}x\right)^4 e^{-x}\frac{a_B}{2}dx$$

$$= \frac{a_B^2}{8}\int_0^{\infty}x^4 e^{-x}dx \;= 3a_B^2$$

$$\Delta r_{1s} = \sqrt{\langle 1s|r^2|1s\rangle - \langle 1s|r|1s\rangle^2} = \sqrt{3a_B^2 - \left(\frac{3}{2}a_B\right)^2} = \frac{\sqrt{3}}{2}a_B$$

確率密度（Z=1の場合）



基底状態での平均値(Z=1)

$$\langle 1s|\frac{1}{r}|1s\rangle = 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}r e^{-\frac{2r}{a_B}}dr$$

$$= 4\pi\int_0^{\infty}\frac{1}{\pi a_B^3}\left(\frac{a_B}{2}x\right)e^{-x}\frac{a_B}{2}dx$$

$$= \frac{1}{a_B}\int_0^{\infty}x e^{-x}dx$$

$$= \frac{1}{a_B}$$

基底状態での平均値(Z=1)

$$E_n = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_B}\frac{1}{n^2}$$

$$\mathcal{H}|1s\rangle = E_1|1s\rangle$$

$$\langle E\rangle_{1s} = \langle 1s|\mathcal{H}|1s\rangle = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_B}$$

$$\langle V\rangle_{1s} = \langle 1s|-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}|1s\rangle = -\frac{e^2}{4\pi\varepsilon_0}\langle 1s|\frac{1}{r}|1s\rangle = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B}$$

$$E = T + V$$

$$\langle T\rangle_{1s} = \langle E\rangle_{1s} - \langle V\rangle_{1s} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_B} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_B} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_B}$$