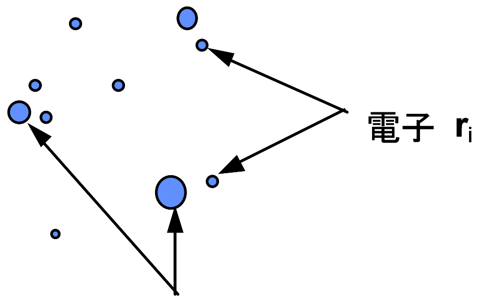
水素型原子

☆Schrödinger 方程式



Schrödinger 方程式（非定常）　$i\hbar \frac{\partial \psi}{\partial t} = H\psi$

一般の Hamiltonian

$$H = -\sum_k \frac{\hbar^2}{2M_k} \nabla_k{}^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i{}^2 + \sum_{k,l} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|} - \sum_{k,i} \frac{Z_k e^2}{|\mathbf{R}_k - \mathbf{r}_i|} + \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

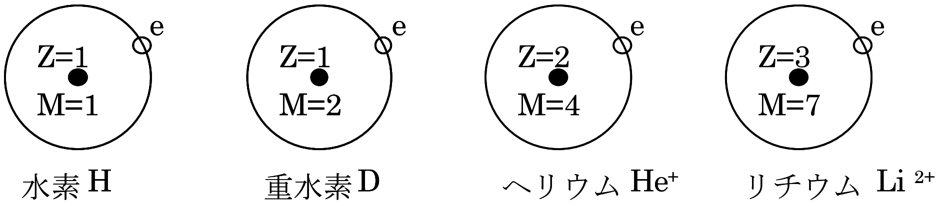
原子核の電荷+$Z_k e$，質量 M_k

電子の電荷 e，質量 m_e

注意：SI 単位のためには $\frac{1}{4\pi\varepsilon_0}$ がクーロン力の項に必要

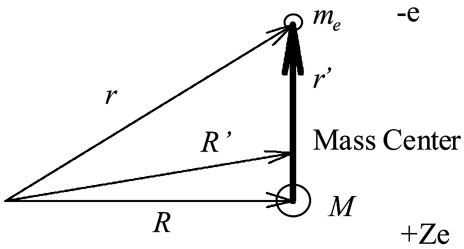
$$H = -\sum_k \frac{\hbar^2}{2M_k} \nabla_k{}^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i{}^2 + \sum_{k,l} \frac{Z_k Z_l e^2}{4\pi\varepsilon_0 |\mathbf{R}_k - \mathbf{R}_l|} - \sum_{k,i} \frac{Z_k e^2}{4\pi\varepsilon_0 |\mathbf{R}_k - \mathbf{r}_i|} + \sum_{i,j} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

☆水素型原子(2 粒子系)



$$H=-\frac{\hbar^2}{2M}\nabla^2{}_{\mathbf{R}}-\frac{\hbar^2}{2m_e}\nabla_{\mathbf{r}}{}^2-\frac{Ze^2}{|\mathbf{r}-\mathbf{R}|}$$ ：定常問題

座標変換：



質量中心の位置 $\mathbf{R}'=(m_e\mathbf{r}+M\mathbf{R})/(m_e+M)$

相対位置 $\mathbf{r}'=\mathbf{r}-\mathbf{R}$

全質量 $M_{Total}=m_e+M$

換算質量(Reduced Mass) $m=\dfrac{m_eM}{m_e+M}$

$m_e/M=1837$,　$m \sim m_e$

さて，このように座標変換を行うと，

$$\frac{1}{m_e}\nabla^2{}_r+\frac{1}{M}\nabla^2{}_R=\frac{1}{m}\nabla^2{}_{r'}+\frac{1}{M_{Total}}\nabla^2{}_{R'}$$

この証明：

x 成分に関して

$$X'=(m_ex+MX)/(m_e+M)$$

$$x'=x-X$$

$$\frac{\partial}{\partial x}=\frac{\partial X'}{\partial x}\frac{\partial}{\partial X'}+\frac{\partial x'}{\partial x}\frac{\partial}{\partial x'}=\frac{m_e}{m_e+M}\frac{\partial}{\partial X'}+\frac{\partial}{\partial x'}$$

$$\frac{\partial}{\partial X}=\frac{M}{m_e+M}\frac{\partial}{\partial X'}-\frac{\partial}{\partial x'}$$

よって，

$$\frac{1}{m_e}\frac{\partial^2}{\partial x^2}+\frac{1}{M}\frac{\partial^2}{\partial X^2}=\frac{1}{m_e}\left(\frac{m_e}{m_e+M}\frac{\partial}{\partial X'}+\frac{\partial}{\partial x'}\right)^2+\frac{1}{M}\left(\frac{M}{m_e+M}\frac{\partial}{\partial X'}-\frac{\partial}{\partial x'}\right)^2$$

$$=\frac{1}{m_e}\left(\left(\frac{m_e}{m_e+M}\right)^2\frac{\partial^2}{\partial X'^2}+2\frac{m_e}{m_e+M}\frac{\partial}{\partial X'}\frac{\partial}{\partial x'}+\frac{\partial^2}{\partial x'^2}\right)$$

$$+\frac{1}{M}\left(\left(\frac{M}{m_e+M}\right)^2\frac{\partial^2}{\partial X'^2}-2\frac{M}{m_e+M}\frac{\partial}{\partial X'}\frac{\partial}{\partial x'}+\frac{\partial^2}{\partial x'^2}\right)$$

$$=\frac{1}{m}\frac{\partial^2}{\partial x'^2}+\frac{1}{M_{Total}}\frac{\partial^2}{\partial X'^2}$$

よって,

$$i\hbar\frac{\partial\psi_1}{\partial t}=-\frac{\hbar^2}{2M_{Total}}\nabla^2{}_{\mathbf{R}'}\psi_1-\frac{\hbar^2}{2m}\nabla^2{}_{r'}\psi_1-\frac{Ze^2}{|\mathbf{r}'|}\psi_1$$

$\psi_1(\boldsymbol{r}', \boldsymbol{R}', t)$? $|\psi_1(\mathbf{r}',\mathbf{R}',t)|^2 d^3\mathbf{r}' d^3\mathbf{R}'$: 体積 d^3R に重心を d^3r に相対位置を見いだす確率

ここで, $\mathbf{r}\leftarrow\mathbf{r}', \mathbf{R}\leftarrow\mathbf{R}'$ と書くことにする.

$$i\hbar\frac{\partial\psi_1}{\partial t}=-\frac{\hbar^2}{2M_{Total}}\nabla^2{}_{\mathbf{R}}\psi_1-\frac{\hbar^2}{2m}\nabla^2{}_{r}\psi_1-\frac{Ze^2}{|\mathbf{r}|}\psi_1$$

さらに, 変数分離 $\psi_1(\mathbf{r},\mathbf{R},t)=\psi(\mathbf{r},t)\Psi(\mathbf{R},t)$ を仮定する.
これを代入して,

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2M_{Total}}\nabla^2\Psi$$ 重心運動 質量Mの自由粒子

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi-\frac{Ze^2}{r}\psi$$ 相対運動

重心運動:
平面波

$$\Psi=\exp\frac{i}{\hbar}(\mathbf{P}\cdot\mathbf{R}-E_p t)$$

ただし, $E_p=\frac{p^2}{2M}$: 並進運動エネルギー, $\mathbf{P}=(p_x,p_y,p_z)$: 運動量ベクトル

Ψ=const **--->** **PR**: const.

ドブロイ波(de Borglie)

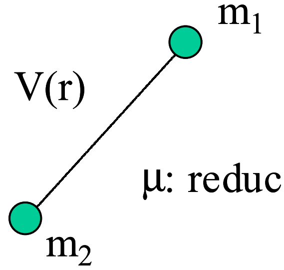
相対運動：

$$\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi-\frac{Ze^2}{r}\psi$$

$$=-\frac{\hbar^2}{2m}\nabla^2\psi+V(r)\psi$$

$$Here,\ V(r)\equiv-\frac{Ze^2}{r}$$

注意：2 原子分子の振動・回転の相対運動の S.E.の導出プロセスもここまで全く同様となる. 電子と原子核を２つの原子核と考えればよい.



定常状態の場合には,

$$E\psi=-\frac{\hbar^2}{2m}\nabla^2\psi+V(r)\psi$$

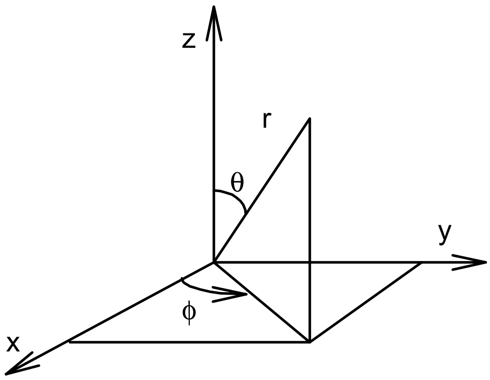
$$\frac{\hbar^2}{2m}\nabla^2\psi+\{E-V(r)\}\psi=0$$

$$\nabla^2\psi+\frac{2m}{\hbar^2}\{E-V(r)\}\psi=0$$

$$\nabla^2\psi+f(r)\psi=0$$

$$Here,\ f(r)\equiv\frac{2m}{\hbar^2}\{E-V(r)\}$$

極座標での Laplacian は,



$$\nabla^2\psi \equiv \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

注意　右辺第一項

$$= \frac{1}{r}\left[\frac{\partial}{\partial r}\left(\psi + r\frac{\partial\psi}{\partial r}\right)\right] = \frac{1}{r}\left[2\frac{\partial\psi}{\partial r} + r\frac{\partial^2\psi}{\partial r^2}\right] = \frac{1}{r^2}\left[2r\frac{\partial\psi}{\partial r} + r^2\frac{\partial^2\psi}{\partial r^2}\right] = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right]$$

とも書ける．

$$\therefore \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + f(r)\psi = 0$$

$\psi(r,\theta,\phi) = R(r)S(\theta,\phi)$ と分離できる．代入してψで割り r^2 をかける．

$$r^2\frac{1}{Rr}\frac{\partial^2}{\partial r^2}(rR) + \frac{1}{S}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial S}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 S}{\partial\phi^2}\right] + r^2 f(r) = 0$$

$$r^2\frac{1}{Rr}\frac{\partial^2}{\partial r^2}(rR) + r^2 f(r) = -\frac{1}{S}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial S}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 S}{\partial\phi^2}\right] = \alpha$$

角度によらない　　　　　　　　　　r によらない

$$\frac{1}{r}\frac{d^2}{dr^2}(rR) + \left\{f(r) - \frac{\alpha}{r^2}\right\}R = 0 \qquad \text{動径方程式}$$

$$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial S}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2 S}{\partial\phi^2} = \alpha S \qquad \text{角度方程式}$$

$$-\Delta_{\theta,\phi}S = \alpha S$$

$$Here,\ \Delta_{\theta,\phi} \equiv \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

注意：f(r)は角度方程式には入らない

つまり，f(r)の形によらずに角度方程式はこれを解けばよい．

さらに変数分離 $S(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ とする．角度方程式に代入して $\sin^2\theta$を掛け，S で割る．

$$\left[-\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-\alpha\right]\sin^2\theta=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-\beta$$

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

$$\frac{\partial^2\Phi}{\partial\phi^2}=-\beta\Phi$$

$\Phi_m(\phi)=e^{im\phi}$ $m=\cdots-2,-1,0,1,2,\cdots$ のときに周期関数となる.

周期関数 $\beta=m^2(=0,1,4,9,\cdots)$

sinθ=0 のとき(θ=0, π), Θの正則特異点となる.

$\alpha=l(l+1)$ $l=|m|,|m|+1,|m|+2,\cdots$

m=0: l = 0, 1, 2, 3, …

m=1: l = 1, 2, 3, …

m=2: l = 2, 3, 4, …

逆に：

l = 0 → m=0

l = 1 → m=-1, 0, 1

l = 2 → m=-2, -1, 0, 1,2

…

$2\ell+1$ 重の縮退

l: 軌道角運動量

m: 磁気量子数

と呼ばれる.

角運動量の量子力学的表現については，ここを参照

$$\hat{L}^2Y_{lm}(\theta,\phi)=L^2Y_{lm}(\theta,\phi)$$

球面調和関数（表面調和関数）Spherical harmonics

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

ルジャンドル陪関数 Associated Legendre polynomial

$$P_l^m(x) \equiv \frac{(-1)^m}{2^l\, l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l \qquad -l \le m \le l$$

実際の関数形の例

$Y_{00} = \sqrt{\frac{1}{4\pi}}$
$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$,　$Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$
$Y_{20} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$,　$Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$,　$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}$

動径方程式

$$\frac{1}{r}\frac{d^2}{dr^2}(rR)+\left\{f(r)-\frac{l(l+1)}{r^2}\right\}R=0$$

これは，f(r)による．

$$f(r)=\frac{2m}{\hbar^2}\left(E-V(r)\right)$$

$$=\frac{2m}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)$$

$$\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}(rR)+\left\{E+\frac{Ze^2}{r}-\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right\}R=0$$

$rR(r)\equiv\chi(r)$ とおく

$$\frac{\hbar^2}{2m}\frac{d^2}{dr^2}(\chi)+\left\{E+\frac{Ze^2}{r}-\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right\}\chi=0$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}\chi-\frac{Ze^2}{r}\chi+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\chi=E\chi$$

遠心力

有効ポテンシャルを受けて直線上を運動する質量 m の質点

ただし， $\chi(0)=0,\ \chi(\infty)=$ **有限**

これが解けて，エネルギー固有値がすべての l(l=0,1,2,3,...)について

一連の固有値 E_{nl} と固有関数 $\chi_{nl}(r)$ が求まったとすると，

$$\psi_{nlm}(\mathbf{r},t)=R_{nl}(r)Y_{lm}(\theta,\phi)\exp(\frac{E_{nl}}{i\hbar}t)=\frac{\chi_{nl}(r)}{r}Y_{lm}(\theta,\phi)\exp(\frac{E_{nl}}{i\hbar}t)$$

の解を持つ．ここで，$\psi_{nlm}(\mathbf{r},t)$ は，

H（エネルギー）の固有値が E_{nl} で，

L^2（角運動量の２乗）の固有値が $\hbar^2 l(l+1)$ で，

L_z（角運動量の z 成分）の固有値が $\hbar^2 m$ の同時固有関数である．

完全交換系：３つで固有関数が一意に定まる．

さて，

正の E は，すべて固有値になりうる　－＞散乱状態

E<0 の場合は，離散エネルギー　－＞束縛状態　：　これについて解く．

$E--\frac{\hbar^2}{2m}\lambda^2$ とおいて，λを求める．

$$\frac{d^2}{dr^2}\chi+\frac{2m}{\hbar^2}\frac{Ze^2}{r}\chi-\frac{l(l+1)}{r^2}\chi=\lambda^2\chi$$

ここで，第２項の係数は,

$$\frac{2m}{\hbar^2}Ze^2 = 2Z\frac{me^2}{\hbar^2} = 2Z\frac{m_e e^2}{\hbar^2}\frac{m}{m_e} = 2Z\frac{1}{a_0\eta}$$ と変形できる.

$\eta = \frac{m_e}{m}$， $a_0 = \frac{\hbar^2}{m_e e^2}$ ：ボーア半径=0.529Å

$m = \frac{m_e M}{m_e + M}$ なので， $\eta = \frac{m_e}{m} = \frac{m_e + M}{M} = 1 + \frac{m_e}{M} = \begin{cases} 1.000549 : \text{水素原子} \\ 1.000274 : \text{重水素} \end{cases}$

よって，動径方程式は

$$\frac{d^2}{dr^2}\chi + \frac{2Z}{a_0\eta}\frac{1}{r}\chi - \frac{l(l+1)}{r^2}\chi = \lambda^2\chi$$

$$\frac{d^2}{dr^2}\chi + A\frac{1}{r}\chi - \frac{B}{r^2}\chi = \lambda^2\chi \qquad A \equiv \frac{2Z}{a_0\eta}, \qquad B \equiv l(l+1)$$

See Oxford p108, 109

解は,

$$\lambda = \frac{A}{2(s_0 + n')} \qquad s_0 = \frac{1}{2} + \sqrt{\frac{1}{4} + B}$$

$$n' = 0,1,2,...$$

$$\chi(r) = \exp(-\lambda r)\left(c_{s0}r^{s0} + ... + c_{s0+n'}r^{s0+n'}\right)$$

$$\{s(s+1) - B\}c_{s+1} = A\frac{1}{s_0 + n'}(s - s_0 - n')c_s$$

今の場合は,

$s_0 = \frac{1}{2} + \sqrt{\frac{1}{4} + l(l+1)} = l + 1$ なので,

$$\lambda = \frac{A}{2(s_0 + n')} = \frac{1}{2(l + 1 + n')}\frac{2Z}{a_0\eta} = \frac{1}{n}\frac{Z}{a_0\eta} = \frac{1}{n}\frac{1}{r_0}$$

便宜上： $\frac{1}{r_0} \equiv \frac{Z}{\eta a_0}$ とおく.

であり， $n \equiv l + 1 + n'$ をエネルギー量子数または，主量子数と呼ぶ.（$n = l + 1, l + 2, ...$）

n’: 動径量子数，n: 主量子数（エネルギー量子数）

$$E_{nl} = -\frac{\hbar^2}{2m}\lambda^2 = -\frac{\hbar^2}{2m}\frac{1}{n^2}\frac{Z^2}{a_0{}^2\eta^2} = -\frac{\hbar^2 Z^2}{2\eta m_e a_0{}^2}\frac{1}{n^2}$$

水素原子であれば，$E_{nl} = 13.6eV\dfrac{1}{n^2}$ となる．

$$l = \begin{matrix} 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ s & p & d & f & g & h & i \end{matrix}$$

さて，動径関数の形は，

$$\{s(s+1) - l(l+1)\}c_{s+1} = \frac{1}{r_0}\frac{2}{n}(s-n)c_s$$

$$\chi(r) = \exp(-\frac{r}{nr_0})\left(c_{l+1}r^{l+1} + ... + c_n r^n\right)$$

具体的には，

n=1, l=0 では，$\chi_{10}(r) = \exp(-\dfrac{r}{r_0})(c_1 r)$

n=2, l=0 では，$\chi_{20}(r) = \exp(-\dfrac{r}{2r_0})(c_1 r + c_2 r^2)$

$$\{1(1+1) - 0(0+1)\}c_2 = \frac{1}{r_0}\frac{2}{2}(1-2)c_1 \quad \therefore c_2 = -\frac{1}{2r_0}c_1$$

$$\chi_{20}(r) = c_1\exp(-\frac{r}{2r_0})(r - \frac{1}{2r_0}r^2)$$

n=2, l=1 では，$\chi_{21}(r) = \exp(-\dfrac{r}{2r_0})(c_1 r + c_2 r^2)$

$$\{1(1+1) - 1(1+1)\}c_2 = \frac{1}{r_0}\frac{2}{2}(1-2)c_1 \quad \therefore c_1 = 0$$

$$\chi_{21}(r) = c_2\exp(-\frac{r}{2r_0})(r^2)$$

n=3, l=0 では，$\chi_{30}(r) = \exp(-\dfrac{r}{3r_0})\left(c_1 r + c_2 r^2 + c_3 r^3\right)$

$$\{1(1+1) - 0(0+1)\}c_2 = \frac{1}{r_0}\frac{2}{3}(1-3)c_1 \quad \therefore c_2 = -\frac{2}{3}\frac{1}{r_0}c_1$$

$$\{2(2+1) - 0(0+1)\}c_3 = \frac{1}{r_0}\frac{2}{3}(2-3)c_2 \quad \therefore c_3 = -\frac{1}{9}\frac{1}{r_0}c_2 = \frac{2}{27}\frac{1}{{r_0}^2}c_1$$

$$\chi_{30}(r) = c_1\exp(-\frac{r}{3r_0})(r - \frac{2}{3}\frac{1}{r_0}r^2 + \frac{2}{27}\frac{1}{{r_0}^2}r^3)$$

$$= \frac{c_1}{3}\exp(-\frac{r}{3r_0})(3r - 2\frac{1}{r_0}r^2 + \frac{2}{9}\frac{1}{{r_0}^2}r^3)$$

.....

$$r' = \frac{r}{r_0}$$

$$R_{10} = 2\left(\frac{1}{r_0}\right)^{3/2} \exp\left(-\frac{r}{r_0}\right) = 2\left(\frac{1}{r_0}\right)^{3/2} \exp(-r')$$

$$R_{20} = 2\left(\frac{1}{2r_0}\right)^{3/2} \left(1-\frac{r}{2r_0}\right)\exp\left(-\frac{r}{2r_0}\right) = \frac{1}{\sqrt{2}}\left(\frac{1}{r_0}\right)^{3/2} \left(1-\frac{r'}{2}\right)\exp\left(-\frac{r'}{2}\right)$$

$$R_{21} = \frac{2}{\sqrt{3}}\left(\frac{1}{2r_0}\right)^{5/2} r\exp\left(-\frac{r}{2r_0}\right) = \frac{1}{2\sqrt{6}}\left(\frac{1}{r_0}\right)^{3/2} r'\exp\left(-\frac{r'}{2}\right)$$

$$R_{30} = \frac{2}{3}\left(\frac{1}{3r_0}\right)^{3/2} \left(3-2\frac{r}{r_0}+\frac{2}{9}\frac{r^2}{r_0^{\ 2}}\right)\exp\left(-\frac{r}{3r_0}\right) = \frac{2}{9\sqrt{3}}\left(\frac{1}{r_0}\right)^{3/2} \left(3-2r'+\frac{2}{9}r'^2\right)\exp\left(-\frac{r'}{3}\right)$$

$$R_{31} = \frac{\sqrt{8}}{3}\left(\frac{1}{3r_0}\right)^{5/2} \left(2-\frac{r}{3r_0}\right)r\exp\left(-\frac{r}{3r_0}\right) = \frac{2\sqrt{2}}{27\sqrt{3}}\left(\frac{1}{r_0}\right)^{3/2} \left(2-\frac{r'}{3}\right)r'\exp\left(-\frac{r'}{3}\right)$$

$$R_{32} = \sqrt{\frac{8}{45}}\left(\frac{1}{3r_0}\right)^{7/2} r^2\exp\left(-\frac{r}{3r_0}\right) = \frac{2\sqrt{2}}{81\sqrt{15}}\left(\frac{1}{r_0}\right)^{3/2} r'^2\exp\left(-\frac{r'}{3}\right)$$

波動関数$\psi_{nlm}(r,\theta,\phi)$で表される状態にいる電子を体積要素$dV = r^2\sin\theta d\theta d\phi dr$の中に見いだす確率は,

$$\begin{aligned}\omega_{nlm}(r,\theta,\phi)dV &= \left|\psi_{nlm}(r,\theta,\phi)\right|^2 dV \\ &= \left|\psi_{nlm}(r,\theta,\phi)\right|^2 r^2\sin\theta d\theta d\phi dr \\ &= \left|\psi_{nlm}(r,\theta,\phi)\right|^2 r^2 dr d\Omega \\ &= R_{nl}^{\ 2}(r)\left|Y_{lm}(\theta,\phi)\right|^2 r^2 dr d\Omega\end{aligned}$$

これを dΩについて積分すると, 電子が半径 r と r+dr の球殻の間に存在する確率$\omega_{nl}(r)dr$を得る.

動径関数の表現

$$R_{10}(r_0)^{3/2} = 2\exp(-r')$$

$$R^2{}_{10} r^2 = \left(\frac{1}{r_0}\right)^3 4\exp(-2r')r^2 = \left(\frac{1}{r_0}\right)^3 4\exp(-2r')r'^2\, r_0{}^2 = \left(\frac{1}{r_0}\right) 4\exp(-2r')r'^2$$

$$R^2{}_{10} r^2 r_0 = 4\exp(-2r')r'^2$$

波動関数の極大

R_{nl}	r_{max}	$R_{ln}{}^2(r_{max})$
R_{10}	0	4
R_{20}	0	1/2
R_{21}	2	$\frac{1}{6e^2}$ =0.061313
R_{30}	0	$\frac{4}{27}$ =0.14814
R_{31}	$3(2-\sqrt{2})$ =1.757	$\left\{\frac{4(2-\sqrt{2})e^{-2+\sqrt{2}}}{9\sqrt{3}}\right\}^2$ =0.00700
R_{32}	6	$\frac{128}{1215e^4}$ =0.00193

$$\psi_{100} = R_{10}Y_{00} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\sqrt{\frac{1}{\pi}}\exp(-r')\right\}$$

$$\psi_{200} = R_{20}Y_{00} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\sqrt{\frac{1}{8\pi}}\left(1-\frac{r'}{2}\right)\exp\left(-\frac{r'}{2}\right)\right\}$$

$$\psi_{210} = R_{21}Y_{10} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\frac{1}{4\sqrt{2\pi}}r'\exp\left(-\frac{r'}{2}\right)\cos\theta\right\}$$

$$\psi_{21\pm1} = R_{21}Y_{1\pm1} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\mp\frac{1}{4\sqrt{\pi}}r'\exp\left(-\frac{r'}{2}\right)\sin\theta\, e^{\pm i\phi}\right\}$$

$$\psi_{300} = R_{30}Y_{00} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\frac{1}{9\sqrt{3\pi}}\left(3-2r'+\frac{2}{9}r'^2\right)\exp\left(-\frac{r'}{3}\right)\right\}$$

$$\psi_{310} = R_{31}Y_{10} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\frac{\sqrt{2}}{27\sqrt{\pi}}\left(2-\frac{r'}{3}\right)r'\exp\left(-\frac{r'}{3}\right)\cos\theta\right\}$$

$$\psi_{31,\pm1=}R_{31}Y_{1,\pm1} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\mp\frac{1}{27\sqrt{\pi}}\left(2-\frac{r'}{3}\right)r'\exp\left(-\frac{r'}{3}\right)\sin\theta\, e^{\pm i\phi}\right\}$$

$$\psi_{320} = R_{32}Y_{10} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\frac{1}{81\sqrt{6\pi}}r'^2\exp\left(-\frac{r'}{3}\right)\left(3\cos^2\theta-1\right)\right\}$$

$$\psi_{32,\pm1} = R_{32}Y_{2,\pm1} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\mp\frac{1}{81\sqrt{\pi}}r'^2\exp\left(-\frac{r'}{3}\right)\sin\theta\cos\theta e^{\pm i\phi}\right\}$$

$$\psi_{32,\pm2} = R_{32}Y_{2,\pm2} = \left(\frac{1}{r_0}\right)^{3/2}\left\{\frac{1}{162\sqrt{\pi}}r'^2\exp\left(-\frac{r'}{3}\right)\sin^2\theta\, e^{\pm2i\phi}\right\}$$

電子密度の断面図

☆原子スペクトル

準位 E_2 から E_1 に遷移するときに放出される photon のエネルギー

$$E_{nl} = -\frac{\hbar^2}{2m}\lambda^2 = -\frac{\hbar^2}{2m}\frac{1}{n^2}\frac{Z^2}{{a_0}^2\eta^2} = -\frac{\hbar^2 Z^2}{2\eta m_e {a_0}^2}\frac{1}{n^2}$$

$$h\nu = E_2 - E_1$$

波数

$$\frac{\nu}{c} = \frac{E_2 - E_1}{hc} = \frac{1}{ch}\frac{\hbar^2 Z^2}{2\eta m_e {a_0}^2}\left\{\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right\}$$

$$\frac{\nu}{c} = \frac{1}{ch}\frac{\hbar^2 Z^2}{2\eta m_e {a_0}^2}\left\{\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right\}$$

$$= \frac{\hbar}{4\pi m_e {a_0}^2 c}\frac{Z^2}{\eta}\left\{\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right\}$$

$$= R_\infty \frac{Z^2}{\eta}\left\{\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right\}$$

リュードベリ定数(Rydberg wave number of infinite mass)

$$R_\infty = \frac{\hbar}{4\pi m_e {a_0}^2 c} = 109737.318 cm^{-1}$$

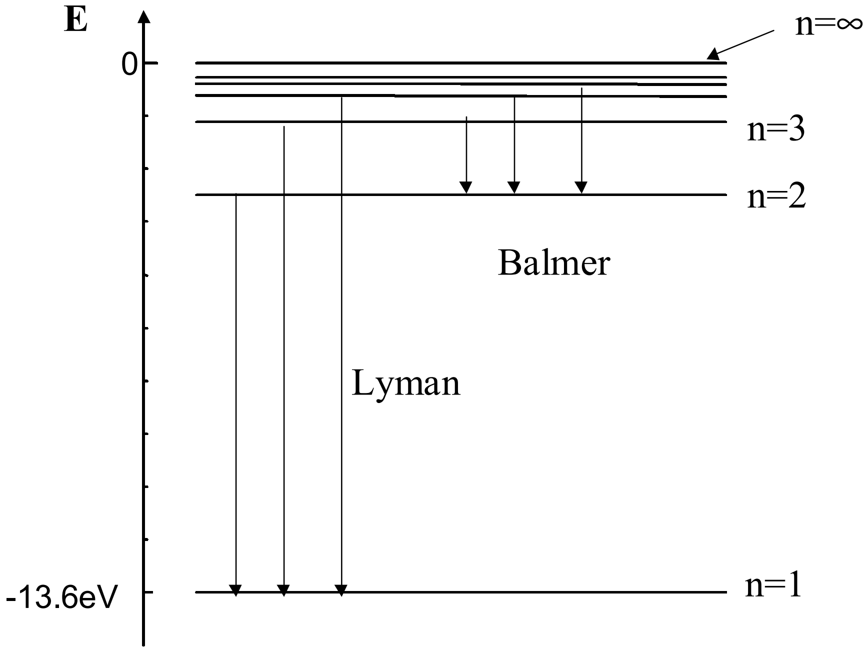
水素原子：Z=1

$$\eta = \frac{m_e}{m} = \frac{m_e + M}{M} = 1 + \frac{m_e}{M} = \begin{cases} 1.000549 : \text{水素原子} \\ 1.000274 : \text{重水素} \end{cases}$$

$$R_H = \frac{R_\infty}{\eta_H} = 109677.59\ cm^{-1}$$

$$\frac{\nu}{c} = R_\infty \frac{1}{\eta}\left\{\frac{1}{1^2} - \frac{1}{{n_2}^2}\right\} \quad , n_2 = 2,3,4,... \qquad \text{ライマン系列}$$

$n_1 = 1$	$n_1 = 2$	$n_1 = 3$	$n_1 = 4$	$n_1 = 5$
ライマン	バルマー	パッシェン	ブラケット	プント
Lyman	Balmer	Ritz-Pashen	Brackett	Pfund


E
0
-13.6eV
n=∞
n=3
n=2
n=1
Balmer
Lyman