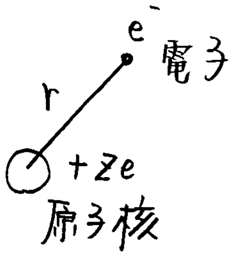
4.2. "水素"原子 の 束縛状態



$$V(r) = -\frac{Ze^2}{r}$$

$$\psi(\mathbf{r}) = R_\ell(r)\,Y_{\ell m}(\hat{\mathbf{r}})$$

$$\downarrow$$

$$\left[\underline{\frac{d^2}{dr^2}} + \underline{\frac{2}{r}\frac{d}{dr}} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{r} - \underline{\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}}\right)\right] R_\ell(r) = 0.$$

$$\rho \equiv \sqrt{\frac{8\mu|E|}{\hbar^2}}\; r \quad \to \quad \frac{1}{r} = \sqrt{\frac{8\mu|E|}{\hbar^2}} \cdot \frac{1}{\rho}$$

$$\downarrow$$

$$\left[\frac{8\mu|E|}{\hbar^2}\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) + \underbrace{\frac{2\mu}{\hbar^2}\left(\underset{\underset{-|E|}{\parallel}}{E} + \sqrt{\frac{8\mu|E|}{\hbar^2}} \cdot \frac{Ze^2}{\rho}\right)}_{\frac{2\mu}{\hbar^2}|E|\left(\underset{\underset{4\lambda}{\parallel}}{\left(\sqrt{\frac{8\mu}{\hbar^2|E|}} \cdot Ze^2\right)}\frac{1}{\rho} - 1\right)}\right] R_\ell(\rho) = 0$$

$$\downarrow$$

$$\boxed{\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)\right] R_\ell(\rho) = 0}$$

$$\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} = Z \cdot \underset{\underset{\alpha = \frac{1}{137}}{\parallel}}{\left(\frac{e^2}{\hbar c}\right)} \sqrt{\frac{\mu c^2}{2|E|}}$$

$1\,eV \sim 1.6\times10^{-19}\,J$

(note) 電磁気の単位系

$$V(r) = \begin{cases} -\dfrac{e^2}{r} & (\text{cgs ガウス}) \\ -\dfrac{1}{4\pi\varepsilon_0}\,\dfrac{e^2}{r} & (\text{SI}) \end{cases}$$

２つの単位系では電荷 e の次元が違う。

微細構造定数

$$\alpha = \begin{cases} \dfrac{e^2}{\hbar c} & (\text{cgs ガウス}) \\ \dfrac{1}{4\pi\varepsilon_0}\cdot\dfrac{e^2}{\hbar c} & (\text{SI}) \end{cases}$$

を使えば，どちらの場合も

$$V(r) = -\hbar c\cdot\alpha\cdot\frac{1}{r}$$

$$\alpha \sim \frac{1}{137}$$

$$\hbar c \sim 197.3 \ (\text{MeV}\cdot\text{fm})$$
$$= 1973 \ (\text{eV}\cdot\text{Å})$$

- ρ → ∞ での振るまい

$$\frac{d^2}{d\rho^2} R_\ell - \frac{1}{4} R_\ell = 0$$

$$\Downarrow \quad R_\ell(\rho) \sim e^{-\frac{\rho}{2}}$$

- ρ → 0 での振るまい

$$\frac{d^2}{d\rho^2} R_\ell + \frac{2}{\rho}\frac{d}{d\rho} R_\ell - \frac{\ell(\ell+1)}{\rho^2} R_\ell = 0$$

$$\Downarrow \quad R_\ell \sim \rho^\ell$$

$$\left(R_\ell'' - \frac{2}{\rho} R_\ell' = \ell(\ell-1)\rho^{\ell-2} + 2\ell\rho^{\ell-2} = \ell(\ell+1)\rho^{\ell-2} \right)$$

⇓

$$\boxed{R_\ell(\rho) = e^{-\frac{\rho}{2}} \underline{G(\rho)} = e^{-\frac{\rho}{2}} \underline{\rho^\ell H(\rho)} \quad \text{とおいてみる。}}$$

↓

$$R_\ell' = -\frac{1}{2} e^{-\frac{\rho}{2}} G + e^{-\frac{\rho}{2}} G'$$

$$R_\ell'' = \frac{1}{4} e^{-\frac{\rho}{2}} G - e^{-\frac{\rho}{2}} G' + e^{-\frac{\rho}{2}} G''$$

$$\Downarrow \quad \left[\cancel{\frac{1}{4}} G - G' + G'' - \frac{1}{\rho} G + \frac{2}{\rho} G' - \frac{\ell(\ell+1)}{\rho^2} G + \left(\frac{\lambda}{\rho} - \cancel{\frac{1}{4}} \right) G \right] \times e^{-\frac{\rho}{2}} = 0$$

$$\Downarrow \quad G'' - \left(1 - \frac{2}{\rho}\right) G' + \left(\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right) G = 0.$$

$$\sum_{k=0}^{\infty} a_k k(k-1)\rho^{k-2} = 2a_2 + 6a_3\rho + \cdots$$

$$\sum_{k=0}^{\infty} a_{k+1}\cdot k(k+1)\rho^{k-1} = 2a_2 + 6a_3\rho + \cdots$$

$$G(\rho) = \rho^{\ell} H(\rho)$$

$\downarrow$

$$G' = \ell\rho^{\ell-1}H + \rho^{\ell}H'$$

$$G'' = \ell(\ell-1)\rho^{\ell-2}H + 2\ell\rho^{\ell-1}H' + \rho^{\ell}H''$$

$\downarrow$

$$\cancel{\ell(\ell-1)\rho^{\ell-2}}H + 2\ell\rho^{\ell-1}H' + \rho^{\ell}H'' \underline{-\ell\rho^{\ell-1}}H - \rho^{\ell}H'$$

$$+ 2\ell\cancel{\rho^{\ell-2}}H + 2\rho^{\ell-1}H' - \cancel{\ell(\ell+1)\rho^{\ell-2}}H$$

$$+ \frac{\lambda-1}{\rho}\rho^{\ell}H = 0$$

$\downarrow$

$$\boxed{H'' + \left(\frac{2\ell+2}{\rho} - 1\right)H' + \frac{\lambda-\ell-1}{\rho}H = 0}$$

$$H(\rho) = \sum_{k=0}^{\infty} a_k\rho^k$$ と展開してみる

$\downarrow$

$$\sum_{k=0}^{\infty} a_k\left[\underline{k(k-1)\rho^{k-2}} + k\left(\underline{\frac{2\ell+2}{\rho}} - 1\right)\rho^{k-1} + (\lambda-\ell-1)\rho^{k-1}\right] = 0$$

$k \to k+1$ $k \to k+1$

$\downarrow$

$$\sum_{k=0}^{\infty}\Big(a_{k+1}\underline{(k+1)}\cdot k\cdot\rho^{k-1} + \underline{(k+1)}(2\ell+2)\rho^{k-1}a_{k+1}$$

$$-k a_k\rho^{k-1} + (\lambda-\ell-1)\rho^{k-1}a_k\Big) = 0$$

$$\left[\begin{array}{l} H'' = \sum_{k=0}^{\infty} k(k-1)a_k\rho^{k-2} = \sum_{k=0}^{\infty} k(k+1)a_{k+1}\rho^{k-1} \\ \frac{1}{\rho}H' = \sum_{k=0}^{\infty} k a_k\rho^{k-2} = \sum_{k=0}^{\infty}(k+1)a_{k+1}\rho^{k-1} \end{array}\right.$$

↓

$$\sum_{k=0}^{\infty} \rho^{k-1}\left[(k+1)(k+2l+2)a_{k+1}+(\lambda-l-1-k)a_k\right]=0$$

↓

$$\boxed{(k+1)(k+2l+2)a_{k+1}+(\lambda-l-1-k)a_k=0}$$

漸化式

(note) $$\frac{a_{k+1}}{a_k}=-\frac{\lambda-l-1-k}{(k+1)(k+2l+2)} \rightarrow \frac{1}{k}$$

↓ $a_k \sim \frac{1}{k!}$

↓

もし　kのシリーズが無限に続けば

$$H(\rho)=\sum_{k=0}^{\infty} a_k \rho^k \sim \sum_{k=0}^{\infty} \frac{\rho^k}{k!} = e^{\rho}$$

この時

$$R_l(\rho) \sim \rho^l e^{\rho} \cdot e^{-\frac{\rho}{2}} = \rho^l e^{\frac{\rho}{2}} \quad (発散)$$

→ このようにならないためには和がどこかで止まる必要がある。

↓

$\boxed{\lambda = l+1+n_r}$ という条件が満たされれば

$$a_k = 0 \quad (k \geq n_r+1)$$

$$\sum_{k=0}^{n_r} a_k \rho^k = L_{n-\ell-1}^{(2\ell+1)}(\rho)$$ ラゲール陪多項式

$$n = \ell + 1 + n_r$$

$$\frac{a_{k+1}}{a_k} = -\frac{\lambda - \ell - 1 - k}{(k+1)(k+2\ell+2)}$$

$$L_m^{(\alpha)}(\rho) = \sum_{k=0}^{m} \binom{m+\alpha}{m-k} \frac{(-\rho)^k}{k!}$$

(note) $b_k \equiv \binom{m+\alpha}{m-k} \frac{(-1)^k}{k!}$ として

$\alpha = 2\ell+1,\ m = n-\ell-1$ のとき

$$\frac{b_{k+1}}{b_k} = \frac{\cancel{(m+\alpha)!}}{(\alpha+k+1)!\,(m-k-1)!} \cdot \frac{(\alpha+k)!\,(m-k)!}{\cancel{(m+\alpha)!}}$$

$$\times \frac{k!}{(k+1)!} \cdot \frac{(-1)^{k+1}}{(-1)^k}$$

$$= -\frac{1}{k+1} \cdot \frac{m-k}{\alpha+k+1}$$

$$= -\frac{n-\ell-1-k}{(k+1)(k+2\ell+2)} = \frac{a_{k+1}}{a_k}$$

$L_0^{(\alpha)}(x) = 1$
$L_1^{(\alpha)}(x) = -x + \alpha + 1$
$L_2^{(\alpha)}(x) = \frac{x^2}{2} - (\alpha+2)\,x + \frac{(\alpha+1)(\alpha+2)}{2}$ など

$$\rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}\, r$$

$n = n_r + \ell + 1$ とおくと

- $n \geq \ell + 1$
- n は整数
- エネルギーは

$$\lambda = \overset{= \alpha}{\frac{Ze^2}{\hbar c}} \sqrt{\frac{\mu c^2}{2|E|}} = n$$

$$\Downarrow$$

$$E = -|E| = -\frac{(Z\alpha)^2}{2n^2} \cdot \mu c^2$$

$$\rho = \sqrt{\frac{8\mu}{\hbar^2} \cdot \frac{(Z\alpha)^2}{2n^2} \cdot \mu c^2}\ r = \frac{2\mu c\, Z\alpha}{n\hbar} \cdot r$$

$$= \boxed{\frac{2Z}{n a_0} r}; \quad a_0 \equiv \frac{\hbar}{\mu c \alpha}$$

（ボーア半径）

▨ スペクトル

エネルギーは n にしかよらない。

↔ 同じ n を持つ ℓ, m の組は同じエネルギーを持つ。

- 基底状態 ($n = 1$)

$$n_r = \ell = 0$$

$$E = -\frac{(Z\alpha)^2}{2} \cdot \mu c^2$$

$\mu c^2 = 0.51$ MeV, $Z = 1$ とすると

$$E = -\frac{1}{2} \cdot \left(\frac{1}{137}\right)^2 \cdot 0.51 = 1.36 \times 10^{-5}\ \text{MeV}$$

$$= 13.6\ \text{eV}$$

波動関数： $R_{\underbrace{10}_{\uparrow\, n\ell}}(r) \propto e^{-\frac{\rho}{2}} = e^{-Zr/a_0}$

・第1励起状態 (n=2)

$$n_r + l + 1 = 2 \rightarrow \begin{array}{l} n_r = 1,\ l = 0\ ;\quad m = 0 \\ n_r = 0\ ,\ l = 1\ ;\quad m = 0, \pm 1 \end{array}$$

4つの状態が同じエネルギーを持つ

$$E = -\frac{(Z\alpha)^2}{8} \cdot \mu c^2 = \frac{1}{4} \cdot E_{n=0}$$

波動関数

i) $n_r = 1,\ l = 0$

$$\begin{cases} \frac{a_1}{a_0} = -\frac{1}{2} \\ a_n = 0 \quad (n > 2) \end{cases} \rightarrow H(\rho) \propto (1 - \frac{\rho}{2})$$

$$\Updownarrow$$

$$\psi(r) \propto \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}\ Y_{00}(\hat{r})$$

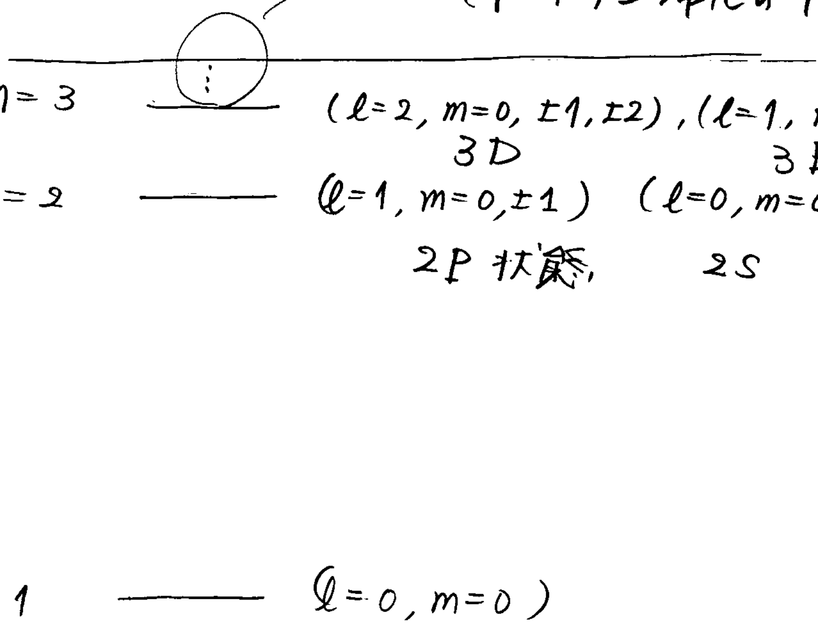
ii) $n_r = 0,\ l = 1 \quad \rightarrow \quad H(\rho) = \mathrm{const.}$

$$\psi(r) \propto r e^{-\frac{Zr}{2a_0}}\ Y_{1m}(\hat{r})$$

・第2励起状態 (n=3)

$$n_r + l + 1 = 3 \rightarrow \begin{array}{ll} n_r = 2,\ l = 0, & m = 0 \\ n_r = 1\ ,\ l = 1, & m = 0, \pm 1 \\ n_r = 0,\ l = 2, & m = 0, \pm 1, \pm 2 \end{array}$$

9つの状態がエネルギー的に「縮退」



無限個の束縛状態
($\frac{1}{r}$ ポテンシャルの特徴)

$E = 0$

$n = 3$ $(\ell=2, m=0, \pm1, \pm2)$, $(\ell=1, m=0, \pm1)$, $(\ell=0, m=0)$

3D 3P 3S

$n = 2$ $(\ell=1, m=0, \pm1)$ $(\ell=0, m=0)$

2P 状態, 2S

$n = 1$ $(\ell=0, m=0)$

1S 状態

一般に，与えられた n に対し

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

各 ℓ に対し $-\ell \leq m \leq \ell$

の状態がエネルギー的に縮退.

波動関数は $R_{n\ell}(\rho) = L_{n-\ell-1}^{(2\ell+1)}(\rho) \cdot e^{-\frac{\rho}{2}} \rho^{\ell}$

ラゲール陪多項式

$$L_n^{(\alpha)}(\rho) = \sum_{m=0}^{n} \binom{n+\alpha}{n-m} \frac{(-\rho)^m}{m!}$$