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3次元ポテンシャル場におけるSchrödinger方程式

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

$$+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\equiv\nabla^2$$

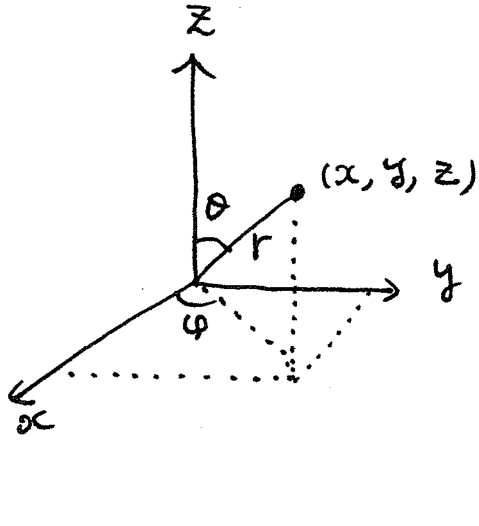
球対称ポテンシャル

$$V(x,y,z)=V(r)$$

$$r^2=x^2+y^2+z^2$$

e.g. 水素原子

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



極座標表示

$$\psi(x,y,z)\longrightarrow\psi(r,\theta,\varphi)$$

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

1階, 2階微分・・・・

ポテンシャルが球対称

$\longrightarrow$ θ,φ に依存しない

$\longrightarrow$ ~~ψ~~ ψ を r (動径)方向と θ,φ (角度)方向に変数分離することが可能

$$\psi(r,\theta,\varphi)\equiv R(r)\,Y(\theta,\varphi)$$

②

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Yに対する微分方程式

$Y_{\ell m}(\theta, \varphi)$: 球面調和関数 (公式集を見よ)

→ 角運動量の量子化　s p d f

ℓ : 方位量子数　0, 1, 2, 3, ...

m : 磁気量子数　$-\ell, -\ell+1, \cdots 0, \ell-1, \ell$

Rに対する微分方程式

→ 水素原子 (陽子1コ, 電子1コ)

の場合にのみ厳密に解ける.

$$-\frac{\hbar^2}{2m}\underbrace{\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)}_{\text{↳どーする?}}R(r) + V(r)R(r) = ER(r)$$

$$r = (x^2+y^2+z^2)^{\frac{1}{2}} \qquad ①$$

$$\frac{\partial}{\partial x}R(r) = \frac{\partial}{\partial r}R(r) \times \frac{\partial r}{\partial x} \qquad ②$$

$$\frac{\partial r}{\partial x} = \frac{1}{2}(x^2+y^2+z^2)^{-\frac{1}{2}} \times 2x = \frac{x}{r}$$

$$\therefore \frac{\partial}{\partial x}R(r) = \cancel{\frac{\partial}{\partial x}}\ \frac{\partial}{\partial r}R(r) \times \frac{x}{r}$$

Rの2階微分

$$\frac{\partial}{\partial x}\frac{\partial}{\partial x}R(r) = \frac{\partial}{\partial x}\left[\frac{\partial}{\partial r}R(r) \times \frac{x}{r}\right]$$

$$= \frac{\partial^2}{\partial r^2}R(r) \times \frac{\partial r}{\partial x}\frac{x}{r} + \frac{\partial}{\partial r}R(r)\frac{\partial}{\partial x}\left(\frac{x}{r}\right)$$

$$= \frac{\partial^2}{\partial r^2}R(r)\frac{x^2}{r^2} + \frac{\partial}{\partial r}R(r)\left\{\frac{1}{r} + \frac{\partial r}{\partial x}\frac{\partial}{\partial r}\left(\frac{x}{r}\right)\right\}$$

$$= \frac{x^2}{r^2}\frac{\partial^2}{\partial r^2}R(r) + \frac{\partial}{\partial r}R(r)\left(\frac{1}{r} - \frac{x}{r}\frac{x}{r^2}\right)$$

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$$\therefore \frac{\partial^2}{\partial x^2}R(r) = \frac{1}{r}\frac{\partial}{\partial r}R(r) - \frac{x^2}{r^3}\frac{\partial}{\partial r}R(r) + \frac{x^2}{r^2}\frac{\partial^2}{\partial r^2}R(r)$$

→ yとzも同様

$$\nabla^2 R(r) = \frac{3}{r}\frac{\partial}{\partial r}R(r) - \frac{(x^2+y^2+z^2)}{r^3}\frac{\partial}{\partial r}R(r) + \frac{(x^2+y^2+z^2)}{r^2}\frac{\partial^2}{\partial r^2}R(r)$$

$$= \frac{2}{r}\frac{\partial}{\partial r}R(r) + \frac{\partial^2}{\partial r^2}R(r)$$

よって解くべき方程式は

$$-\frac{\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}\right)R(r) + V(r)R(r) = ER(r)$$

→ θ, φ は考えていないので S軌道のみ

$\frac{\partial}{\partial r}, \frac{\partial^2}{\partial r^2}$ → 1次元のshooting法がそのまま使える

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

両辺に $r(\delta r)^2$を掛けて、$R(r+\delta r)$、$R(r)$, $R(r-\delta r)$ の項でまとめると

$$R(r+\delta r) = \frac{r\left[\frac{2m}{\hbar^2}(\delta r)^2\{V(r) - E\} + 2\right]R(r) + (-r+\delta r)R(r-\delta r)}{r+\delta r}$$

→ プログラムで解く.

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原子単位系 $\quad 4\pi\varepsilon_0 = 1$

$$\begin{cases} \hbar = 1 \\ m = 1 \\ e^2 = 1 \end{cases} \Rightarrow$$

長さの単位 a_B (ボーア半径)
$= 0.529\,\text{Å}$

エネルギーの単位 E_H (ハートリー)
$= \underbrace{13.6058}_{} \times 2\ \text{eV}$

水素1S軌道の
束縛エネルギー

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

nのみに依存
(l, mに依らない)

$$E_n = -\frac{1}{2}\frac{1}{n^2} \quad \text{(Hartree)}$$