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４．水素類似原子
Hydrogen-like atom

４－１　水素類似原子のハミルトニアン
Hamiltonian of hydrogen-like atom

原点に位置する水素類似原子のハミルトニアンは

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r} \\ &= -\frac{\hbar^2}{2m_\mathrm{e}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r} \\ &= -\frac{\hbar^2}{2m_\mathrm{e}}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\end{aligned} \qquad (4.1.1)$$

と表される。ただし，Z は原子番号で $r=\sqrt{x^2+y^2+z^2}$ とする。$\Delta=\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ はラプラシアンと呼ばれる。また

プランク定数：$h = 6.62606896(33)\times 10^{-34}$ $[\mathrm{J\cdot s}]$

ディラック定数：$\hbar = \frac{h}{2\pi} = 1.05457168(18)\times 10^{-34}$ $[\mathrm{J\cdot s}]$

真空の誘電率：$\varepsilon_0 = \frac{1}{\mu_0 c^2} = 8.854187817\cdots\times 10^{-12}$ $[\mathrm{F\cdot m^{-1}}]$

真空中の光速：$c = 299792485$ $[\mathrm{m\cdot s^{-1}}]$

真空の透磁率：$\mu_0 = 4\pi\times 10^{-7}$ $[\mathrm{N\cdot A^{-2}}] = 1.2566370614\cdots\times 10^{-6}$ $[\mathrm{N\cdot A^{-2}}]$

電気素量：$e = 1.602176462(63)\times 10^{-19}$ $[\mathrm{C}]$

電子の静止質量：$m_\mathrm{e} = 9.10938188(72)\times 10^{-31}$ $[\mathrm{kg}]$

などである。

－－

付録４－１　水素類似原子のハミルトニアンの導出

極座標（球座標）(r,θ,φ)

$$\begin{Bmatrix} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{Bmatrix} \Leftrightarrow \begin{Bmatrix} r=\sqrt{x^2+y^2+z^2} \\ \theta = \arctan\frac{\sqrt{x^2+y^2}}{z} \\ \varphi = \arctan\frac{y}{x} \end{Bmatrix}$$

を使うと，

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta}+\frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi}$$
$$=\frac{x}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial r}+\frac{x}{\sqrt{x^2+y^2}z}\frac{1}{1+\frac{x^2+y^2}{z^2}}\frac{\partial}{\partial \theta}-\frac{y}{x^2}\frac{1}{1+\frac{y^2}{x^2}}\frac{\partial}{\partial \varphi}$$
$$=\frac{x}{r}\frac{\partial}{\partial r}+\frac{xz}{r^2\sqrt{x^2+y^2}}\frac{\partial}{\partial \theta}-\frac{y}{x^2+y^2}\frac{\partial}{\partial \varphi}$$
$$=\frac{r\sin\theta\cos\varphi}{r}\frac{\partial}{\partial r}+\frac{r^2\sin\theta\cos\varphi\cos\theta}{r^3\sin\theta}\frac{\partial}{\partial \theta}-\frac{r\sin\theta\sin\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial \varphi}$$
$$=\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}$$
$$\frac{\partial}{\partial y}=\frac{\partial r}{\partial y}\frac{\partial}{\partial r}+\frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta}+\frac{\partial \varphi}{\partial y}\frac{\partial}{\partial \varphi}$$
$$=\frac{y}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial r}+\frac{y}{\sqrt{x^2+y^2}z}\frac{1}{1+\frac{x^2+y^2}{z^2}}\frac{\partial}{\partial \theta}+\frac{1}{x}\frac{1}{1+\frac{y^2}{x^2}}\frac{\partial}{\partial \varphi}$$
$$=\frac{y}{r}\frac{\partial}{\partial r}+\frac{yz}{r^2\sqrt{x^2+y^2}}\frac{\partial}{\partial \theta}+\frac{x}{x^2+y^2}\frac{\partial}{\partial \varphi}$$
$$=\frac{r\sin\theta\sin\varphi}{r}\frac{\partial}{\partial r}+\frac{r^2\sin\theta\sin\varphi\cos\theta}{r^3\sin\theta}\frac{\partial}{\partial \theta}+\frac{r\sin\theta\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial \varphi}$$
$$=\sin\theta\sin\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial \theta}-\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}$$
$$\frac{\partial}{\partial z}=\frac{\partial r}{\partial z}\frac{\partial}{\partial r}+\frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta}+\frac{\partial \varphi}{\partial z}\frac{\partial}{\partial \varphi}$$
$$=\frac{z}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial r}-\frac{\sqrt{x^2+y^2}}{z^2}\frac{1}{1+\frac{x^2+y^2}{z^2}}\frac{\partial}{\partial \theta}$$
$$=\frac{z}{r}\frac{\partial}{\partial r}-\frac{r\sin\theta}{r^2}\frac{\partial}{\partial \theta}$$
$$=\frac{r\cos\theta}{r}\frac{\partial}{\partial r}-\frac{r\sin\theta}{r^2}\frac{\partial}{\partial \theta}$$
$$=\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial \theta}$$

から，

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\left(\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)^2$$
$$+\left(\sin\theta\sin\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial \theta}+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)^2$$
$$+\left(\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial \theta}\right)^2$$

$$=\sin\theta\cos\varphi\frac{\partial}{\partial r}\left(\sin\theta\cos\varphi\frac{\partial}{\partial r}\right)+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}\left(\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}\right)+\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\left(\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)$$
$$+\sin\theta\cos\varphi\frac{\partial}{\partial r}\left(\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}\right)+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta}\left(\sin\theta\cos\varphi\frac{\partial}{\partial r}\right)$$

$$-\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}\left(\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\left(\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}\right)$$

$$-\sin\theta\cos\varphi\frac{\partial}{\partial r}\left(\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\left(\sin\theta\cos\varphi\frac{\partial}{\partial r}\right)$$

$$+\sin\theta\sin\varphi\frac{\partial}{\partial r}\left(\sin\theta\sin\varphi\frac{\partial}{\partial r}\right)+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\left(\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\right)+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\left(\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$+\sin\theta\sin\varphi\frac{\partial}{\partial r}\left(\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\sin\varphi\frac{\partial}{\partial r}\right)$$

$$+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\left(\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\left(\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\right)$$

$$+\sin\theta\sin\varphi\frac{\partial}{\partial r}\left(\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\left(\sin\theta\sin\varphi\frac{\partial}{\partial r}\right)$$

$$+\cos\theta\frac{\partial}{\partial r}\left(\cos\theta\frac{\partial}{\partial r}\right)+\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)$$

$$-\cos\theta\frac{\partial}{\partial r}\left(\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial r}\right)$$

$$=\sin^2\theta\cos^2\varphi\frac{\partial^2}{\partial r^2}+\frac{\cos\theta\cos^2\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{\sin\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$+\sin\theta\cos\theta\cos^2\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\cos^2\varphi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)$$

$$-\frac{\cos\theta\sin\varphi\cos\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)-\frac{\cos\theta\sin\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\theta}\right)$$

$$-\sin\varphi\cos\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\varphi}\right)-\frac{\sin\varphi}{r}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial r}\right)$$

$$+\sin^2\theta\sin^2\varphi\frac{\partial^2}{\partial r^2}+\frac{\cos\theta\sin^2\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$+\sin\theta\cos\theta\sin^2\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\sin^2\varphi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)$$

$$+\frac{\cos\theta\sin\varphi\cos\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)+\frac{\cos\theta\cos\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\theta}\right)$$

$$+\sin\varphi\cos\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\varphi}\right)+\frac{\cos\varphi}{r}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial r}\right)$$

$$+\cos^2\theta\frac{\partial^2}{\partial r^2}+\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$-\sin\theta\cos\theta\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial r}\right)$$

整理して

$$=\sin^2\theta\cos^2\varphi\frac{\partial^2}{\partial r^2}+\sin^2\theta\sin^2\varphi\frac{\partial^2}{\partial r^2}+\cos^2\theta\frac{\partial^2}{\partial r^2}$$

$$+\frac{\cos\theta\cos^2\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\sin^2\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$+\frac{\sin\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)+\frac{\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$+\sin\theta\cos\theta\cos^2\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)+\sin\theta\cos\theta\sin^2\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)-\sin\theta\cos\theta\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\theta}\right)$$

$$+\frac{\cos\theta\cos^2\varphi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)+\frac{\cos\theta\sin^2\varphi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial r}\right)$$

$$-\frac{\cos\theta\sin\varphi\cos\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)+\frac{\cos\theta\sin\varphi\cos\varphi}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$-\frac{\cos\theta\sin\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\cos\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\theta}\right)$$

$$-\sin\varphi\cos\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\varphi}\right)+\sin\varphi\cos\varphi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial\varphi}\right)$$

$$-\frac{\sin\varphi}{r}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial r}\right)+\frac{\cos\varphi}{r}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial r}\right)$$

まとめられところをまとめて

$$=\frac{\partial^2}{\partial r^2}+\frac{\cos\theta}{r^2}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$+\frac{\sin\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)+\frac{\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$+\frac{\cos\theta}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial r}\right)-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial r}\right)$$

$$-\frac{\cos\theta\sin\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial\theta}\right)+\frac{\cos\theta\cos\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\theta}\right)$$

$$-\frac{\sin\varphi}{r}\frac{\partial}{\partial\varphi}\left(\cos\varphi\frac{\partial}{\partial r}\right)+\frac{\cos\varphi}{r}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial r}\right)$$

さらに計算を進めて

$$=\frac{\partial^2}{\partial r^2}-\frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta}+\frac{\cos^2\theta}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta}+\frac{\sin^2\theta}{r^2}\frac{\partial^2}{\partial\theta^2}$$

$$+\frac{\sin\varphi\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}+\frac{\sin^2\varphi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}-\frac{\sin\varphi\cos\varphi}{r^2\sin^2\theta}\frac{\partial}{\partial\varphi}+\frac{\cos^2\varphi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

$$+\frac{\cos^2\theta}{r}\frac{\partial}{\partial r}+\frac{\sin\theta\cos\theta}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}+\frac{\sin^2\theta}{r}\frac{\partial}{\partial r}-\frac{\sin\theta\cos\theta}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}$$

$$+\frac{\cos\theta\sin^2\varphi}{r^2\sin\theta}\frac{\partial}{\partial\theta}-\frac{\cos\theta\sin\varphi\cos\varphi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\varphi}+\frac{\cos\theta\cos^2\varphi}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{\cos\theta\sin\varphi\cos\varphi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\varphi}$$

$$+\frac{\sin^2\varphi}{r}\frac{\partial}{\partial r}-\frac{\sin\varphi\cos\varphi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\varphi}+\frac{\cos^2\varphi}{r}\frac{\partial}{\partial r}+\frac{\sin\varphi\cos\varphi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\varphi}$$

またまとめて

$$=\frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r}\frac{\partial}{\partial r}$$

$$=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\left(\sin\theta\frac{\partial^2}{\partial\theta^2}+\cos\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

$$=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

結局，ラプラシアンが

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

と書けて，ハミルトニアンは

$$\begin{aligned}\hat{H}&=-\frac{\hbar^2}{2m_{\mathrm{e}}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}\\&=-\frac{\hbar^2}{2m_{\mathrm{e}}}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{Ze^2}{4\pi\varepsilon_0 r}\end{aligned}$$

と書ける。