7-3 Schrödinger 方程式の極座標表示

極座標（3次元）：
$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases}$$

この時，微分演算子 ∇^2 は

$$\boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}$$ である

（覚えること！）

（証）
$$\underline{\nabla = \mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \mathbf{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}}$$

また
$$\begin{cases} d\mathbf{e}_r = \mathbf{e}_\theta\, d\theta + \sin\theta\,\mathbf{e}_\varphi\, d\varphi \\ d\mathbf{e}_\theta = -\mathbf{e}_r\, d\theta + \cos\theta\,\mathbf{e}_\varphi\, d\varphi \\ d\mathbf{e}_\varphi = -\sin\theta\,\mathbf{e}_r\, d\theta - \cos\theta\,\mathbf{e}_\theta\, d\varphi \end{cases}$$

ここで $\boxed{\mathbf{e}_r\cdot\mathbf{e}_\theta = \mathbf{e}_\theta\cdot\mathbf{e}_\varphi = \mathbf{e}_\varphi\cdot\mathbf{e}_r = 0}$ である

（直交系）

定義より

$$\boxed{\begin{aligned} d\mathbf{e}_r &= \frac{\partial\mathbf{e}_r}{\partial r}dr + \frac{\partial\mathbf{e}_r}{\partial\theta}d\theta + \frac{\partial\mathbf{e}_r}{\partial\varphi}d\varphi \\ d\mathbf{e}_\theta &= \frac{\partial\mathbf{e}_\theta}{\partial r}dr + \frac{\partial\mathbf{e}_\theta}{\partial\theta}d\theta + \frac{\partial\mathbf{e}_\theta}{\partial\varphi}d\varphi \\ d\mathbf{e}_\varphi &= \frac{\partial\mathbf{e}_\varphi}{\partial r}dr + \frac{\partial\mathbf{e}_\varphi}{\partial\theta}d\theta + \frac{\partial\mathbf{e}_\varphi}{\partial\varphi}d\varphi \end{aligned}}$$

よって
$$\begin{cases} \dfrac{\partial \mathbf{e}_r}{\partial r} = 0, & \dfrac{\partial \mathbf{e}_r}{\partial \theta} = \mathbf{e}_\theta, & \dfrac{\partial \mathbf{e}_r}{\partial \varphi} = \sin\theta\, \mathbf{e}_\varphi \\ \dfrac{\partial \mathbf{e}_\theta}{\partial r} = 0, & \dfrac{\partial \mathbf{e}_\theta}{\partial \theta} = -\mathbf{e}_r, & \dfrac{\partial \mathbf{e}_\theta}{\partial \varphi} = \cos\theta\, \mathbf{e}_\varphi \\ \dfrac{\partial \mathbf{e}_\varphi}{\partial r} = 0, & \dfrac{\partial \mathbf{e}_\varphi}{\partial \theta} = -\sin\theta\, \mathbf{e}_r, & \dfrac{\partial \mathbf{e}_\varphi}{\partial \varphi} = -\cos\theta\, \mathbf{e}_\theta \end{cases}$$

これらより

$$\nabla^2 = \left[\mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right]\left[\mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right]$$

$$= \frac{\partial^2}{\partial r^2} + \underbrace{\mathbf{e}_r \frac{\partial}{\partial r}\left(\mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta}\right)}_{=0} + \underbrace{\mathbf{e}_r \frac{\partial}{\partial r}\left(\mathbf{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)}_{=0} + \underbrace{\mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta}\left(\mathbf{e}_r \frac{\partial}{\partial r}\right)}_{=\frac{1}{r}\frac{\partial}{\partial r}}$$

$$+ \underbrace{\mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta}\left(\mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta}\right)}_{=\frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}} + \underbrace{\mathbf{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta}\left(\mathbf{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)}_{=0} + \underbrace{\mathbf{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\left(\mathbf{e}_r \frac{\partial}{\partial r}\right)}_{=\frac{1}{r}\frac{\partial}{\partial r}}$$

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

整理すると

$$\boxed{\begin{aligned} \nabla^2 &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \varphi^2} \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \varphi^2} \end{aligned}}$$

[極座標表示のSchrödinger方程式]

$$\boxed{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\right]\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r})}$$

ここで角運動量演算子 $\mathbb{L}$ を導入する。

$$\boxed{\hat{\mathbb{L}} \equiv \mathbf{r}\times\hat{\mathbf{p}} = -i\hbar\,\mathbf{r}\times\nabla}$$

この時

$$\boxed{\hat{\mathbb{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}$$

が示される。(第8章で詳しくみる)

この時、Schrödinger方程式は

$$\boxed{\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{\mathbb{L}}^2}{2mr^2}+V(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})}$$

と書ける。

これは <u>変数分離型</u> の微分方程式

変数分離型： $\underline{\psi(r) = R(r)\, Y(\theta,\varphi)}$ とおくと

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)\right]Y(\theta,\varphi) + \frac{1}{2mr^2}R(r)\left(\hat{\mathbb{L}}^2 Y(\theta,\varphi)\right)$$

$$+ V(r)R(r)Y(\theta,\varphi) = E\,R(r)Y(\theta,\varphi)$$

これを $R(r)\,Y(\theta,\varphi)$ で割算すると

$$\boxed{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)\right]\frac{1}{R(r)} + \frac{1}{2mr^2}\left(\hat{\mathbb{L}}^2 Y(\theta,\varphi)\right)\frac{1}{Y(\theta,\varphi)} + V(r) = E}$$

これは r, と(θ,φ) の変数が分離している

ここで $\boxed{\hat{\mathbb{L}}^2 Y(\theta,\varphi) = \lambda\, Y(\theta,\varphi)}$ とおく

（ λ は $\hat{\mathbb{L}}^2$ の固有値 ）

この時 Schrödinger 方程式は

$$\boxed{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \frac{\lambda}{2mr^2}R(r) + V(r)R(r) = E\,R(r)}$$

となる.