参考　具体的なラプラシアンの計算

$\frac{\partial^2\varphi}{\partial x^2}$は、

$$
\begin{aligned}
\frac{\partial^2\varphi}{\partial x^2} &= \frac{\partial}{\partial x}\frac{\partial\varphi}{\partial x} \\
&= \frac{\partial\frac{\partial\varphi}{\partial x}}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\frac{\partial\varphi}{\partial x}}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\frac{\partial\varphi}{\partial x}}{\partial\phi}\frac{\partial\phi}{\partial x} \\
&= \frac{\partial(\sin\theta\cos\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial\varphi}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi})}{\partial r}\sin\theta\cos\phi \\
&+ \frac{\partial(\sin\theta\cos\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial\varphi}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi})}{\partial\theta}\frac{\cos\theta\cos\phi}{r} \\
&- \frac{\partial(\sin\theta\cos\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial\varphi}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi})}{\partial\phi}\frac{\sin\phi}{r\sin\theta} \\
&= \Big[\sin\theta\cos\phi\frac{\partial^2\varphi}{\partial r^2} + \cos\theta\cos\phi\big(-\frac{1}{r^2}\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\partial^2\varphi}{\partial\theta\partial r}\big) \\
&\quad - \frac{\sin\phi}{\sin\theta}\big(-\frac{1}{r^2}\frac{\partial\varphi}{\partial\phi} + \frac{1}{r}\frac{\partial^2\varphi}{\partial\phi\partial r}\big)\Big]\sin\theta\cos\phi \\
&+ \Big[\cos\phi\big(\cos\theta\frac{\partial\varphi}{\partial r} + \sin\theta\frac{\partial^2\varphi}{\partial r\partial\theta}\big) + \frac{1}{r}\cos\phi\big(-\sin\theta\frac{\partial\varphi}{\partial\theta} + \cos\theta\frac{\partial^2\varphi}{\partial^2\theta}\big) \\
&\quad - \frac{1}{r}\sin\phi\big(-\frac{\cos\theta}{\sin^2\theta}\frac{\partial\varphi}{\partial\phi} + \frac{1}{\sin\theta}\frac{\partial^2\varphi}{\partial\phi\partial\theta}\big)\Big]\frac{\cos\theta\cos\phi}{r} \\
&+ \Big[-\sin\theta\big(-\sin\phi\frac{\partial\varphi}{\partial r} + \cos\phi\frac{\partial^2\varphi}{\partial r\partial\phi}\big) - \frac{1}{r}\cos\theta\big(-\sin\phi\frac{\partial\varphi}{\partial\theta} + \cos\phi\frac{\partial^2\varphi}{\partial\theta\partial\phi}\big) \\
&\quad + \frac{1}{r}\frac{1}{\sin\theta}\big(\cos\phi\frac{\partial\varphi}{\partial\phi} + \sin\phi\frac{\partial^2\varphi}{\partial\phi^2}\big)\Big]\frac{\sin\phi}{r\sin\theta} \\
&= \sin^2\theta\cos^2\phi\frac{\partial^2\varphi}{\partial r^2} + \big(\cos^2\theta\cos^2\phi + \sin^2\phi\big)\frac{1}{r}\frac{\partial\varphi}{\partial r} \\
&+ \frac{1}{r^2}\Big[\big(-2\cos\theta\sin\theta\cos^2\phi + \frac{\cos\theta}{\sin\theta}\sin^2\phi\big)\frac{\partial\varphi}{\partial\theta} + \cos^2\theta\cos^2\phi\frac{\partial^2\varphi}{\partial\theta^2} \\
&\quad + \big(\sin\phi\cos\phi + \frac{\sin\phi\cos\phi\cos^2\theta}{\sin^2\theta} + \frac{\cos\phi\sin\phi}{\sin^2\theta}\big)\frac{\partial\varphi}{\partial\phi} + \frac{\sin^2\phi}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\Big] \\
&+ \frac{2}{r}\Big[\cos\theta\sin\theta\cos^2\phi\frac{\partial^2\varphi}{\partial r\partial\theta} - \sin\phi\cos\phi\frac{\partial^2\varphi}{\partial r\partial\phi} - \frac{1}{r}\frac{\cos\theta}{\sin\theta}\sin\phi\cos\phi\frac{\partial^2\varphi}{\partial\theta\partial\phi}\Big]
\end{aligned}
\tag{9.20}
$$

となります。同様にして$\frac{\partial^2\varphi}{\partial y^2}$は、

$$
\begin{aligned}
\frac{\partial^2 \varphi}{\partial y^2} &= \frac{\partial}{\partial y}\frac{\partial \varphi}{\partial y} \\
&= \frac{\partial \frac{\partial \varphi}{\partial y}}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial \frac{\partial \varphi}{\partial y}}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial \frac{\partial \varphi}{\partial y}}{\partial \phi}\frac{\partial \phi}{\partial y} \\
&= \frac{\partial\left(\sin\theta\sin\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi}\right)}{\partial r}\sin\theta\sin\phi \\
&\quad + \frac{\partial\left(\sin\theta\sin\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi}\right)}{\partial \theta}\frac{\cos\theta\sin\phi}{r} \\
&\quad + \frac{\partial\left(\sin\theta\sin\phi\frac{\partial\varphi}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial\varphi}{\partial\phi}\right)}{\partial \phi}\frac{\cos\phi}{r\sin\theta} \\
&= \Bigg[\sin\theta\sin\phi\frac{\partial^2\varphi}{\partial r^2} + \cos\theta\sin\phi\left(-\frac{1}{r^2}\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\partial^2\varphi}{\partial\theta\partial r}\right) \\
&\quad + \frac{\cos\phi}{\sin\theta}\left(-\frac{1}{r^2}\frac{\partial\varphi}{\partial\phi} + \frac{1}{r}\frac{\partial^2\varphi}{\partial\phi\partial r}\right)\Bigg]\sin\theta\sin\phi \\
&\quad + \Bigg[\sin\phi\left(\cos\theta\frac{\partial\varphi}{\partial r} + \sin\theta\frac{\partial^2\varphi}{\partial r\partial\theta}\right) + \frac{1}{r}\sin\phi\left(-\sin\theta\frac{\partial\varphi}{\partial\theta} + \cos\theta\frac{\partial^2\varphi}{\partial\theta^2}\right) \\
&\quad\quad + \frac{1}{r}\cos\phi\left(-\frac{\cos\theta}{\sin^2\theta}\frac{\partial\varphi}{\partial\phi} + \frac{1}{\sin\theta}\frac{\partial^2\varphi}{\partial\phi\partial\theta}\right)\Bigg]\frac{\cos\theta\sin\phi}{r} \\
&\quad + \Bigg[\sin\theta\left(\cos\phi\frac{\partial\varphi}{\partial r} + \sin\phi\frac{\partial^2\varphi}{\partial r\partial\phi}\right) + \frac{1}{r}\cos\theta\left(\cos\phi\frac{\partial\varphi}{\partial\theta} + \sin\phi\frac{\partial^2\varphi}{\partial\theta\partial\phi}\right) \\
&\quad\quad + \frac{1}{r}\frac{1}{\sin\theta}\left(-\sin\phi\frac{\partial\varphi}{\partial\phi} + \cos\phi\frac{\partial^2\varphi}{\partial\phi^2}\right)\Bigg]\frac{\cos\phi}{r\sin\theta} \\
&= \sin^2\theta\sin^2\phi\frac{\partial^2\varphi}{\partial r^2} + \left(\cos^2\theta\sin^2\phi + \cos^2\phi\right)\frac{1}{r}\frac{\partial\varphi}{\partial r} \\
&\quad + \frac{1}{r^2}\Bigg[\left(-2\cos\theta\sin\theta\sin^2\phi + \frac{\cos\theta}{\sin\theta}\cos^2\phi\right)\frac{\partial\varphi}{\partial\theta} + \cos^2\theta\sin^2\phi\frac{\partial^2\varphi}{\partial\theta^2} \\
&\quad\quad - \left(\cos\phi\sin\phi + \frac{\cos\phi\sin\phi\cos^2\theta}{\sin^2\theta} + \frac{\sin\phi\cos\phi}{\sin^2\theta}\right)\frac{\partial\varphi}{\partial\phi} + \frac{\cos^2\phi}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\Bigg] \\
&\quad + \frac{2}{r}\left[\cos\theta\sin\theta\sin^2\phi\frac{\partial^2\varphi}{\partial r\partial\theta} + \sin\phi\cos\phi\frac{\partial^2\varphi}{\partial r\partial\phi} + \frac{1}{r}\frac{\cos\theta}{\sin\theta}\sin\phi\cos\phi\frac{\partial^2\varphi}{\partial\theta\partial\phi}\right]
\end{aligned}
\tag{9.21}
$$

となります。同様にして$\frac{\partial^2\varphi}{\partial z^2}$は、

$$\frac{\partial^2\varphi}{\partial z^2} = \frac{\partial}{\partial z}\frac{\partial\varphi}{\partial z}$$
$$= \frac{\partial\frac{\partial\varphi}{\partial z}}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial\frac{\partial\varphi}{\partial z}}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial\frac{\partial\varphi}{\partial z}}{\partial\phi}\frac{\partial\phi}{\partial z}$$
$$= \frac{\partial\left(\cos\theta\frac{\partial\varphi}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial\varphi}{\partial\theta}\right)}{\partial r}\cos\theta - \frac{\partial\left(\cos\theta\frac{\partial\varphi}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial\varphi}{\partial\theta}\right)}{\partial\theta}\frac{\sin\theta}{r}$$
$$= \left[\cos\theta\frac{\partial^2\varphi}{\partial r^2} - \sin\theta\left(-\frac{1}{r^2}\frac{\partial\varphi}{\partial\theta} + \frac{1}{r}\frac{\partial^2\varphi}{\partial\theta\partial r}\right)\right]\cos\theta$$
$$+ \left[\left(\sin\theta\frac{\partial\varphi}{\partial r} - \cos\theta\frac{\partial^2\varphi}{\partial r\partial\theta}\right) + \frac{1}{r}\left(\cos\theta\frac{\partial\varphi}{\partial\theta} + \sin\theta\frac{\partial^2\varphi}{\partial\theta^2}\right)\right]\frac{\sin\theta}{r}$$
$$= \cos^2\theta\frac{\partial^2\varphi}{\partial r^2} + \sin^2\theta\frac{1}{r}\frac{\partial\varphi}{\partial r} + \frac{1}{r^2}\left[2\sin\theta\cos\theta\frac{\partial\varphi}{\partial\theta} + \sin^2\theta\frac{\partial^2\varphi}{\partial\theta^2}\right] - \frac{2}{r}\cos\theta\ \sin\theta\ \frac{\partial^2\varphi}{\partial r\partial\theta} \tag{9.22}$$

となります。これで直交座標x, y, z座標での２階微分を極座標r, θ, ϕで表すことができたので、直交座標で表されたラプラシアンにφをかけた式を極座標で表すと、式（9.20）、(9.21)、(9.22）を使い、微分の項ごとにまとめていくと、以下のようになります。

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2}$$
$$= \left(\sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi + \cos^2\theta\right)\frac{\partial^2\varphi}{\partial r^2}$$
$$+ \left(\cos^2\theta\cos^2\phi + \sin^2\phi + \cos^2\theta\sin^2\phi + \cos^2\phi + \sin^2\theta\right)\frac{1}{r}\frac{\partial\varphi}{\partial r}$$
$$+ \left(\sin\phi\cos\phi + \frac{\sin\phi\cos\phi\cos^2\theta}{\sin^2\theta} + \frac{\cos\phi\sin\phi}{\sin^2\theta}\right.$$
$$\left.-\sin\phi\cos\phi - \frac{\sin\phi\cos\phi\cos^2\theta}{\sin^2\theta} - \frac{\cos\phi\sin\phi}{\sin^2\theta}\right)\frac{1}{r^2}\frac{\partial\varphi}{\partial\phi}$$
$$+ \left(\frac{\sin^2\phi}{\sin^2\theta} + \frac{\cos^2\phi}{\sin^2\theta}\right)\frac{1}{r^2}\frac{\partial^2\varphi}{\partial\phi^2}$$
$$+ \left(-2\cos\theta\sin\theta\cos^2\phi + \frac{\cos\theta}{\sin\theta}\sin^2\phi\right.$$
$$\left.-2\cos\theta\sin\theta\sin^2\phi + \frac{\cos\theta}{\sin\theta}\cos^2\phi + 2\sin\theta\cos\theta\right)\frac{1}{r^2}\frac{\partial\varphi}{\partial\theta}$$
$$+ \left(\cos^2\theta\cos^2\phi + \cos^2\theta\sin^2\phi + \sin^2\theta\right)\frac{1}{r^2}\frac{\partial^2\varphi}{\partial\theta^2}$$
$$+ \frac{2}{r}\left[\left(\cos\theta\sin\theta\cos^2\phi + \cos\theta\sin\theta\sin^2\phi - \cos\theta\sin\theta\right)\frac{\partial^2\varphi}{\partial r\partial\theta}\right.$$
$$\left.+ \left(-\sin\phi\cos\phi + \sin\phi\cos\phi\right)\frac{\partial^2\varphi}{\partial r\partial\phi} + \left(-\frac{1}{r}\frac{\cos\theta}{\sin\theta}\sin\phi\cos\phi + \frac{1}{r}\frac{\cos\theta}{\sin\theta}\sin\phi\cos\phi\right)\frac{\partial^2\varphi}{\partial\theta\partial\phi}\right]$$
$$= \frac{\partial^2\varphi}{\partial r^2} + \frac{2}{r}\frac{\partial\varphi}{\partial r} + \frac{1}{r^2}\left(\frac{\cos\theta}{\sin\theta}\frac{\partial\varphi}{\partial\theta} + \frac{\partial^2\varphi}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\right) \tag{9.23}$$

つまり、極座標で表されたラプラシアンにφをかけた式$\Delta\varphi$は、

$$\Delta\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} = \frac{\partial^2\varphi}{\partial r^2} + \frac{2}{r}\frac{\partial\varphi}{\partial r} + \frac{1}{r^2}\left(\frac{\cos\theta}{\sin\theta}\frac{\partial\varphi}{\partial\theta} + \frac{\partial^2\varphi}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\right) \tag{9.24}$$

となります。また、

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\varphi}{\partial\theta}) = \frac{1}{\sin\theta}(\cos\theta\frac{\partial\varphi}{\partial\theta} + \sin\theta\frac{\partial^2\varphi}{\partial\theta^2}) = \frac{\cos\theta}{\sin\theta}\frac{\partial\varphi}{\partial\theta} + \frac{\partial^2\varphi}{\partial\theta^2} \tag{9.25}$$

なので、極座標で表されたラプラシアンφにをかけた$\Delta\varphi$を、

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} = \frac{\partial^2\varphi}{\partial r^2} + \frac{2}{r}\frac{\partial\varphi}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\varphi}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\right) \tag{9.26}$$

と書くこともあります。これで式（9.17）が得られました。

❖球対称ポテンシャルにおける極座標シュレーディンガー方程式の変数分離

この極座標で表されたシュレーディンガー方程式は一般には解くことは困難です。しかし、第5章で見たように原子、原子核などさまざまな場合において、ポテンシャルは角度依存性がなく、**球対称**$V(r)$でした。実はポテンシャルが球対称$V(r)$ならば、本書で何度も出てきた変数分離法によって簡単になることが知られています。そこで、本書ではポテンシャルは球対称$V(r)$である場合のみを考えましょう。

極座標シュレーディンガー方程式でポテンシャルを球対称$V(r)$と置いた式、

$$-\frac{\hbar^2}{2m}\left[\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\varphi}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}\right)\right] + V(r)\varphi = E\varphi \tag{9.27}$$