『詳解　量子化学の基礎 第 2 版』
『詳解　量子化学の基礎 』
で省略している演習問題の解答のいくつか

1 解答 9 初版：87 頁／第 2 版：87 頁

まずは，$\partial^2/\partial x^2$ からはじめる。$\partial/\partial x$ は，

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{8.16}$$

であるから，これより以下のように計算される。

$$\begin{aligned}
\frac{\partial^2}{\partial x^2} &= \frac{\partial}{\partial x}\times\frac{\partial}{\partial x}\\
&= \left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\\
&\qquad\qquad\times\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\\
&= \sin\theta\cos\phi\frac{\partial}{\partial r}\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆\\
&\quad + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆☆\\
&\quad - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆☆☆\\
&= \sin^2\theta\cos^2\phi\frac{\partial^2}{\partial r^2} - \frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\frac{\partial}{\partial\theta} + \frac{\sin\theta\cos\theta\cos^2\phi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}\\
&\qquad + \frac{\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial\phi} - \frac{\sin\phi\cos\phi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\phi} \qquad \text{☆を展開した}\\
&\quad + \frac{\cos^2\theta\cos^2\phi}{r}\frac{\partial}{\partial r} + \frac{\sin\theta\cos\theta\cos^2\phi}{r}\frac{\partial}{\partial\theta}\frac{\partial}{\partial r} - \frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\frac{\partial}{\partial\theta}\\
&\qquad + \frac{\cos^2\theta\cos^2\phi}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\cos^2\theta\sin\phi\cos\phi}{r^2\sin^2\theta}\frac{\partial}{\partial\phi} - \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} \qquad \text{☆☆を展開した}\\
&\quad + \frac{\sin^2\phi}{r}\frac{\partial}{\partial r} - \frac{\sin\phi\cos\phi}{r}\frac{\partial}{\partial\phi}\frac{\partial}{\partial r} + \frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\\
&\qquad - \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta} + \frac{\sin\phi\cos\phi}{r^2\sin^2\theta}\frac{\partial}{\partial\phi} + \frac{\sin^2\phi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad \text{☆☆☆を展開した}\\
&= \sin^2\theta\cos^2\phi\frac{\partial^2}{\partial r^2} + \frac{\cos^2\theta\cos^2\phi}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\sin^2\phi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\
&\quad + \left(\frac{\cos^2\theta\cos^2\phi + \sin^2\phi}{r}\right)\frac{\partial}{\partial r} + \left(-\frac{2\sin\theta\cos\theta\cos^2\phi}{r^2} + \frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta}\\
&\quad + \underbrace{\left(\frac{\sin\phi\cos\phi}{r^2} + \frac{\sin\phi\cos\phi + \cos^2\theta\sin\phi\cos\phi}{r^2\sin^2\theta}\right)}_{=\frac{2\sin\phi\cos\phi}{r^2\sin^2\theta}}\frac{\partial}{\partial\phi} + \frac{\sin\theta\cos\theta\cos^2\phi}{r}\left(\frac{\partial}{\partial r}\frac{\partial}{\partial\theta} + \frac{\partial}{\partial\theta}\frac{\partial}{\partial r}\right)\\
&\quad - \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} + \frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta}\right) - \frac{\sin\phi\cos\phi}{r}\left(\frac{\partial}{\partial\phi}\frac{\partial}{\partial r} + \frac{\partial}{\partial r}\frac{\partial}{\partial\phi}\right) \qquad \text{整理した}
\end{aligned}$$

これより，(8.23) 式が得られた。

次に，$\partial^2/\partial y^2$ を導く。$\partial/\partial y$ は，

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{8.17}$$

であるから，これより以下のように計算される。

$$\begin{aligned}
\frac{\partial^2}{\partial y^2} &= \frac{\partial}{\partial y}\times\frac{\partial}{\partial y}\\
&= \left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\\
&\qquad\qquad \times\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\\
&= \sin\theta\sin\phi\frac{\partial}{\partial r}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆\\
&\quad + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆☆\\
&\quad + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \qquad ☆☆☆\\
&= \sin^2\theta\sin^2\phi\frac{\partial^2}{\partial r^2} - \frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\frac{\partial}{\partial\theta} + \frac{\sin\theta\cos\theta\sin^2\phi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}\\
&\qquad - \frac{\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial\phi} + \frac{\sin\phi\cos\phi}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\phi} \qquad \text{☆を展開した}\\
&\quad + \frac{\cos^2\theta\sin^2\phi}{r}\frac{\partial}{\partial r} + \frac{\sin\theta\cos\theta\sin^2\phi}{r}\frac{\partial}{\partial\theta}\frac{\partial}{\partial r} - \frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\frac{\partial}{\partial\theta}\\
&\qquad + \frac{\cos^2\theta\sin^2\phi}{r^2}\frac{\partial^2}{\partial\theta^2} - \frac{\cos^2\theta\sin\phi\cos\phi}{r^2\sin^2\theta}\frac{\partial}{\partial\phi} + \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} \qquad \text{☆☆を展開した}\\
&\quad + \frac{\cos^2\phi}{r}\frac{\partial}{\partial r} + \frac{\sin\phi\cos\phi}{r}\frac{\partial}{\partial\phi}\frac{\partial}{\partial r} + \frac{\cos\theta\cos^2\phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\\
&\qquad + \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta} - \frac{\sin\phi\cos\phi}{r^2\sin^2\theta}\frac{\partial}{\partial\phi} + \frac{\cos^2\phi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad \text{☆☆☆を展開した}\\
&= \sin^2\theta\sin^2\phi\frac{\partial^2}{\partial r^2} + \frac{\cos^2\theta\sin^2\phi}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\cos^2\phi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \left(\frac{\cos^2\theta\sin^2\phi + \cos^2\phi}{r}\right)\frac{\partial}{\partial r}\\
&\quad + \left(-\frac{2\sin\theta\cos\theta\sin^2\phi}{r^2} + \frac{\cos\theta\cos^2\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta}\\
&\quad - \underbrace{\left(\frac{\sin\phi\cos\phi + \cos^2\theta\sin\phi\cos\phi}{r^2\sin^2\theta} + \frac{\sin\phi\cos\phi}{r^2}\right)}_{\dfrac{\sin\phi\cos\phi}{r^2\sin^2\theta}}\frac{\partial}{\partial\phi} + \frac{\sin\theta\cos\theta\sin^2\phi}{r}\left(\frac{\partial}{\partial r}\frac{\partial}{\partial\theta} + \frac{\partial}{\partial\theta}\frac{\partial}{\partial r}\right)\\
&\quad + \frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} + \frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta}\right) + \frac{\sin\phi\cos\phi}{r}\left(\frac{\partial}{\partial\phi}\frac{\partial}{\partial r} + \frac{\partial}{\partial r}\frac{\partial}{\partial\phi}\right) \qquad \text{整理した}
\end{aligned}$$

これより，(8.24) 式が得られた。

2 解答 10 初版：89 頁／第 2 版：89 頁

$$
\begin{aligned}
\hat{\ell}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\
&\quad - i\hbar\Bigg[\underbrace{r\cos\theta}_{(8.3)\text{ 式}}\underbrace{\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)}_{(8.16)\text{ 式}} - \underbrace{r\sin\theta\cos\phi}_{(8.1)\text{ 式}}\underbrace{\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)}_{(8.18)\text{ 式}}\Bigg] \\
&\quad - i\hbar\Bigg[r\sin\theta\cos\theta\cos\phi\frac{\partial}{\partial r} + \cos^2\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\cos\theta\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi} \\
&\qquad\qquad - r\sin\theta\cos\theta\cos\phi\frac{\partial}{\partial r} + \sin^2\theta\cos\phi\frac{\partial}{\partial\theta}\Bigg] \\
&= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)
\end{aligned}
$$

$$
\begin{aligned}
\hat{\ell}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \\
&= -i\hbar\Bigg[\underbrace{r\sin\theta\cos\phi}_{(8.1)\text{ 式}}\underbrace{\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)}_{(8.17)\text{ 式}} \\
&\qquad\qquad - \underbrace{r\sin\theta\sin\phi}_{(8.2)\text{ 式}}\underbrace{\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)}_{(8.16)\text{ 式}}\Bigg] \\
&= -i\hbar\Bigg[r\sin^2\theta\sin\phi\cos\phi\frac{\partial}{\partial r} + \sin\theta\cos\theta\sin\phi\cos\phi\frac{\partial}{\partial\theta} + \cos^2\phi\frac{\partial}{\partial\phi} \\
&\qquad\qquad - r\sin^2\theta\sin\phi\cos\phi\frac{\partial}{\partial r} - \sin\theta\cos\theta\sin\phi\cos\phi\frac{\partial}{\partial\theta} + \sin^2\phi\frac{\partial}{\partial\phi}\Bigg] \\
&= -i\hbar\frac{\partial}{\partial\phi}
\end{aligned}
$$

3 解答 25 初版：225 頁／第 2 版：237 頁

$$
\begin{aligned}
J &= \begin{vmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{vmatrix} \\
&= \sin\theta\cos\phi \begin{vmatrix} r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ -r\sin\theta & 0 \end{vmatrix} \\
&\quad - \sin\theta\sin\phi \begin{vmatrix} r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ -r\sin\theta & 0 \end{vmatrix} \\
&\quad + \cos\theta \begin{vmatrix} r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ r\cos\theta\sin\phi & r\sin\theta\cos\phi \end{vmatrix} \\
&= r^2\sin^3\theta\cos^2\phi + r^2\sin\theta^3\sin^2\phi + \cos\theta\left(r^2\sin\theta\cos\theta\cos^2\phi + r^2\sin\theta\cos\theta\sin^2\phi\right) \\
&= r^2\sin^3\theta + r^2\cos^2\theta\sin\theta \\
&= r^2\sin\theta\left(\sin^2\theta + \cos^2\theta\right) \\
&= r^2\sin\theta
\end{aligned}
$$

4 解答 26 初版：226 頁／第 2 版：238 頁

(14.55) 式の 4 行目から 5 行目への積分

$$\frac{R^2}{2}\left\{\int_1^\infty \xi e^{-R\xi}\mathrm{d}\xi \int_{-1}^1 e^{-R\eta}\mathrm{d}\eta + \int_1^\infty e^{-R\xi}\mathrm{d}\xi \int_{-1}^1 \eta e^{-R\eta}\mathrm{d}\eta\right\} \qquad \text{(14.55) 式の 4 行目}$$

$$= \frac{R^2}{2}\left\{\left[-\frac{e^{-R\xi}}{R}\left(\xi+\frac{1}{R}\right)\right]_1^\infty \times \left[-\frac{e^{-R\eta}}{R}\right]_{-1}^1 + \left[-\frac{e^{-R\xi}}{R}\right]_1^\infty \times \left[-\frac{e^{-R\eta}}{R}\left(\eta+\frac{1}{R}\right)\right]_{-1}^1\right\} \qquad \text{(C.73) 式より}$$

$$= \frac{R^2}{2}\left\{\left[-\frac{e^{-R\xi}\xi}{R} - \frac{e^{-R\xi}}{R^2}\right]_1^\infty \times \left[-\frac{e^{-R\eta}}{R}\right]_{-1}^1 + \left[-\frac{e^{-R\xi}}{R}\right]_1^\infty \times \left[-\frac{e^{-R\eta}}{R}\left(\eta+\frac{1}{R}\right)\right]_{-1}^1\right\} \qquad \text{少し展開した}$$

$$= \frac{R^2}{2}\left\{\left((0-0) - \left(-\frac{e^{-R}}{R} - \frac{e^{-R}}{R^2}\right)\right) \times \left(-\frac{e^{-R}}{R} + \frac{e^{R}}{R}\right)\right.$$

$$\left. + \left(0+\frac{e^{-R}}{R}\right) \times \left(-\frac{e^{-R}}{R}\left(1+\frac{1}{R}\right) + \frac{e^{R}}{R}\left(-1+\frac{1}{R}\right)\right)\right\} \qquad \text{上限と下限を代入}$$

⋮

あとはひたすら整理して

⋮

$$= \frac{1-(1+R)e^{-2R}}{R} \qquad \text{(14.55) 式の 5 行目}$$

(14.55) 式の 3 行目から 4 行目への積分

$$\frac{R^2}{2}\left\{\int_1^\infty \xi e^{-R\xi}\mathrm{d}\xi \int_{-1}^1 \mathrm{d}\eta - \int_1^\infty e^{-R\xi}\mathrm{d}\xi \int_{-1}^1 \eta\mathrm{d}\eta\right\} \qquad \text{(14.55) 式の 3 行目}$$

$$= \frac{R^2}{2}\left\{\left[-\frac{e^{-R\xi}}{R}\left(\xi+\frac{1}{R}\right)\right]_1^\infty \times \underbrace{\Big[\eta\Big]_{-1}^1}_{=2} - \left[\frac{e^{-R\xi}}{-R}\right]_1^\infty \times \underbrace{\left[\frac{\eta^2}{2}\right]_{-1}^1}_{=0}\right\} \qquad \text{(C.73) 式より}$$

$$= R^2\left[-\frac{\xi e^{-R\xi}}{R} - \frac{e^{-R\xi}}{R^2}\right]_1^\infty \qquad \text{少し展開した}$$

$$= R^2\left\{(0-0) - \left(-\frac{e^{-R}}{R} - \frac{e^{-R}}{R^2}\right)\right\} \qquad \text{上限と下限を代入}$$

$$= (R+1)e^{-R} \qquad \text{(14.55) 式の 4 行目}$$

ただし，上式の (C.73) 式は，第 2 版では (B.73) 式と読み替えてください。

5 解答 32 初版：278 頁／第 2 版：290 頁

$$
\begin{aligned}
\varphi(1,1,1) &= \frac{1}{2}\left(\mathrm{s}+\mathrm{p}_x+\mathrm{p}_y+\mathrm{p}_z\right)\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1+\sqrt{3}\sin\theta\cos\phi+\sqrt{3}\sin\theta\sin\phi+\sqrt{3}\cos\theta\right)\\
&\qquad \text{図 17.3 より}, \phi = 45^\circ \text{だから}, \cos\phi=\sin\phi=\frac{1}{\sqrt{2}}\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1+\frac{\sqrt{3}}{\sqrt{2}}\sin\theta+\frac{\sqrt{3}}{\sqrt{2}}\sin\theta+\sqrt{3}\cos\theta\right)\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1+\sqrt{6}\sin\theta+\sqrt{3}\cos\theta\right)\\
\frac{\partial\varphi(1,1,1)}{\partial\theta} &= \frac{R(r)}{2\sqrt{4\pi}}\left(\sqrt{6}\cos\theta-\sqrt{3}\sin\theta\right)=0\\
&\xrightarrow{\text{すなわち}} \tan\theta=\sqrt{2} \xrightarrow{\text{すなわち}} \theta=\tan^{-1}\sqrt{2}=54.7356^\circ
\end{aligned}
$$

$$
\begin{aligned}
\varphi(-1,-1,1) &= \frac{1}{2}\left(\mathrm{s}-\mathrm{p}_x-\mathrm{p}_y+\mathrm{p}_z\right)\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1-\sqrt{3}\sin\theta\cos\phi-\sqrt{3}\sin\theta\sin\phi+\sqrt{3}\cos\theta\right)\\
&\qquad \text{図 17.3 より}, \phi = 225^\circ \text{だから}, \cos\phi=\sin\phi=-\frac{1}{\sqrt{2}}\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1+\frac{\sqrt{3}}{\sqrt{2}}\sin\theta+\frac{\sqrt{3}}{\sqrt{2}}\sin\theta+\sqrt{3}\cos\theta\right)\\
&= \frac{R(r)}{2\sqrt{4\pi}}\left(1+\sqrt{6}\sin\theta+\sqrt{3}\cos\theta\right)\\
\frac{\partial\varphi(-1,-1,1)}{\partial\theta} &= \frac{R(r)}{2\sqrt{4\pi}}\left(\sqrt{6}\cos\theta-\sqrt{3}\sin\theta\right)=0\\
&\xrightarrow{\text{すなわち}} \tan\theta=\sqrt{2} \xrightarrow{\text{すなわち}} \theta=\tan^{-1}\sqrt{2}=54.7356^\circ
\end{aligned}
$$

以上より，$\varphi(1,1,1)$ と $\varphi(-1,-1,1)$ はそれぞれ，天頂角 $\theta = 54.7356^\circ$ である。また，これらは同一面内にあるから，これらがなす角は $54.7356^\circ \times 2 = 109.4712^\circ$ である。