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物理化学Ⅳ（加藤将樹） 宿題レポート　その１

途中の過程も書くこと．紙面が足りない場合はレポート用紙等を付け足してホッチキス等で綴じること．

（締め切り：次回授業 (4/24) 開始時に集めます）

問題 1 次の量を極座標 (r, θ, ϕ) で表しなさい．

$$\text{(a)}\ \frac{\partial x}{\partial r},\ \text{(b)}\ h_3 \left(\equiv \sqrt{\left(\frac{\partial x}{\partial \phi}\right)^2 + \left(\frac{\partial y}{\partial \phi}\right)^2 + \left(\frac{\partial z}{\partial \phi}\right)^2} \right),\ \text{(c)}\ \Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

問題 2 水素原子の主量子数 n が $1 \sim 3$ の全ての定常状態について，波動関数を書き下しなさい．(テキスト p.101 1-5(1))

物理化学Ⅳ（加藤将樹） 宿題レポート　その１ (解答例)

問題１　極座標表示に際して，

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

を準備しておく．ここから，

$$\begin{cases} r = \sqrt{x^2+y^2+z^2} \\ \cos\theta = \dfrac{z}{\sqrt{x^2+y^2+z^2}} \\ \tan\phi = \dfrac{y}{x} \end{cases}$$

である．

(a)

$$\frac{\partial x}{\partial r} = \sin\theta\cos\phi$$

(b)

$$\frac{\partial x}{\partial \phi} = -r\sin\theta\sin\phi,\ \frac{\partial y}{\partial \phi} = r\sin\theta\cos\phi,\ \frac{\partial z}{\partial \phi} = 0$$

よって，

$$\begin{aligned} h_3 &= \sqrt{\left(\frac{\partial x}{\partial \phi}\right)^2 + \left(\frac{\partial y}{\partial \phi}\right)^2 + \left(\frac{\partial z}{\partial \phi}\right)^2} \\ &= \sqrt{(-r\sin\theta\sin\phi)^2 + (r\sin\theta\cos\phi)^2 + 0^2} \\ &= \sqrt{r^2\sin^2\theta(\sin^2\phi+\cos^2\phi)^2} \\ &= \sqrt{r^2\sin^2\theta} \end{aligned}$$

ここで，$0 < \theta < \pi$ より

$$= r\sin\theta$$

(c) まず，偏微分の公式から x，y，z の偏微分は r，θ，ϕ を用いて次のように書ける．

$$\begin{cases} \dfrac{\partial}{\partial x} = \dfrac{\partial r}{\partial x}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial x}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \phi}{\partial x}\dfrac{\partial}{\partial \phi} \\ \dfrac{\partial}{\partial y} = \dfrac{\partial r}{\partial y}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial y}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \phi}{\partial y}\dfrac{\partial}{\partial \phi} \\ \dfrac{\partial}{\partial z} = \dfrac{\partial r}{\partial z}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial z}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \phi}{\partial z}\dfrac{\partial}{\partial \phi} \end{cases}$$

ここで，準備しておいた式から

$$\begin{cases} \dfrac{\partial r}{\partial x} = \dfrac{x}{\sqrt{x^2+y^2+z^2}} = \sin\theta\cos\phi \\ -\sin\theta\dfrac{\partial \theta}{\partial x} = -\dfrac{xz}{\left(\sqrt{x^2+y^2+z^2}\right)^3} \iff \dfrac{\partial \theta}{\partial x} = \dfrac{\cos\theta\cos\phi}{r} \\ \dfrac{1}{\cos^2\phi}\dfrac{\partial \phi}{\partial x} = -\dfrac{y}{x^2} \iff \dfrac{\partial \phi}{\partial x} = -\dfrac{\sin\phi}{r\sin\theta} \end{cases}$$

$$\begin{cases} \dfrac{\partial r}{\partial y} = \dfrac{y}{\sqrt{x^2+y^2+z^2}} = \sin\theta\sin\phi \\ -\sin\theta\dfrac{\partial \theta}{\partial y} = -\dfrac{yz}{\left(\sqrt{x^2+y^2+z^2}\right)^3} \iff \dfrac{\partial \theta}{\partial y} = \dfrac{\cos\theta\sin\phi}{r} \\ \dfrac{1}{\cos^2\phi}\dfrac{\partial \phi}{\partial y} = \dfrac{1}{x} \iff \dfrac{\partial \phi}{\partial y} = \dfrac{\cos\phi}{r\sin\theta} \end{cases}$$

$$\begin{cases} \dfrac{\partial r}{\partial z} = \dfrac{z}{\sqrt{x^2+y^2+z^2}} = \cos\theta \\ -\sin\theta\dfrac{\partial \theta}{\partial z} = \dfrac{x^2+y^2+z^2-z^2}{\left(\sqrt{x^2+y^2+z^2}\right)^3} \iff \dfrac{\partial \theta}{\partial z} = -\dfrac{\sin\theta}{r} \\ \dfrac{1}{\cos^2\phi}\dfrac{\partial \phi}{\partial z} = 0 \iff \dfrac{\partial \phi}{\partial z} = 0 \end{cases}$$

よって，次のページからそれぞれの値を代入していく．

先ほど求めた 1 次偏微分は次のようになる.

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

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

$$\frac{\partial}{\partial z}=\frac{\partial r}{\partial z}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta}+\frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}=\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$$

つぎに, x についての 2 次偏微分を求める.

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

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

ここで上式右辺第一項について計算する.

$$\text{右辺第一項}=\sin\theta\cos\phi\frac{\partial}{\partial r}\left(\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$=\sin\theta\cos\phi\left(\sin\theta\cos\phi\frac{\partial^2}{\partial r^2}-\frac{\cos\theta\cos\phi}{r^2}\frac{\partial}{\partial\theta}+\frac{\cos\theta\cos\phi}{r}\frac{\partial^2}{\partial r\partial\theta}+\frac{\sin\phi}{r^2\sin\theta}\frac{\partial}{\partial\phi}-\frac{\sin\phi}{r\sin\theta}\frac{\partial^2}{\partial r\partial\phi}\right)$$

同様に右辺第二項は

$$\text{右辺第二項}=\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$=\frac{\cos\theta\cos\phi}{r}\left(\cos\theta\cos\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial\theta\partial r}-\frac{\sin\theta\cos\phi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\theta\cos\phi}{r}\frac{\partial^2}{\partial\theta^2}+\frac{\sin\phi\cos\theta}{r\sin^2\theta}\frac{\partial}{\partial\phi}-\frac{\sin\phi}{r\sin\theta}\frac{\partial^2}{\partial\theta\partial\phi}\right)$$

右辺第三項は

$$\text{右辺第三項}=-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\left(\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$=-\frac{\sin\phi}{r\sin\theta}\left(-\sin\theta\sin\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial\phi\partial r}-\frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\theta\cos\phi}{r}\frac{\partial^2}{\partial\phi\partial\theta}-\frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}-\frac{\sin\phi}{r\sin\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

つぎに y についての二次偏微分を求める.

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

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

$$\text{右辺第一項} = \sin\theta\sin\phi\frac{\partial}{\partial r}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$= \sin\theta\sin\phi\left(\sin\theta\sin\phi\frac{\partial^2}{\partial r^2} - \frac{\cos\theta\sin\phi}{r^2}\frac{\partial}{\partial\theta} + \frac{\cos\theta\sin\phi}{r}\frac{\partial^2}{\partial r\partial\theta} - \frac{\cos\phi}{r^2\sin\theta}\frac{\partial}{\partial\phi} + \frac{\cos\phi}{r\sin\theta}\frac{\partial^2}{\partial r\partial\phi}\right)$$

右辺第二項は

$$\text{右辺第二項} = \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$= \frac{\cos\theta\sin\phi}{r}\left(\cos\theta\sin\phi\frac{\partial}{\partial r} + \sin\theta\sin\phi\frac{\partial^2}{\partial\theta\partial r} - \frac{\sin\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\theta\sin\phi}{r}\frac{\partial^2}{\partial\theta^2} - \frac{\cos\phi\cos\theta}{r\sin^2\theta}\frac{\partial}{\partial\phi} + \frac{\cos\phi}{r\sin\theta}\frac{\partial^2}{\partial\theta\partial\phi}\right)$$

右辺第三項は

$$\text{右辺第三項} = \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$
$$= \frac{\cos\phi}{r\sin\theta}\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \sin\theta\sin\phi\frac{\partial^2}{\partial\phi\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\theta\sin\phi}{r}\frac{\partial^2}{\partial\phi\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} + \frac{\cos\phi}{r\sin\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

つぎに z についての二次偏微分を求める.

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

右辺第一項は

$$\text{右辺第一項} = \cos\theta\frac{\partial}{\partial r}\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)$$
$$= \cos\theta\left(\cos\theta\frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta} - \frac{\sin\theta}{r}\frac{\partial^2}{\partial r\partial\theta}\right)$$

右辺第二項は

$$\text{右辺第二項} = -\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)$$
$$= -\frac{\sin\theta}{r}\left(-\sin\theta\frac{\partial}{\partial r} + \cos\theta\frac{\partial^2}{\partial\theta\partial r} - \frac{\cos\theta}{r}\frac{\partial}{\partial\theta} - \frac{\sin\theta}{r}\frac{\partial^2}{\partial\theta^2}\right)$$

よって，まとめると

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

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

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

ここからは，非常に複雑になるので，各項右側の演算子が同じもののみを計算する．

$\dfrac{\partial}{\partial r}$ を持つ項を計算する．

$$\frac{\partial}{\partial r}\text{を持つ項}=\frac{\cos^2\theta\cos^2\phi}{r}+\frac{\sin^2\phi}{r}+\frac{\cos^2\theta\sin^2\phi}{r}+\frac{\cos^2\theta}{r}+\frac{\sin^2\theta}{r}=\frac{2}{r}$$

$\dfrac{\partial}{\partial\theta}$ を持つ項を計算する．

$$\frac{\partial}{\partial\theta}\text{を持つ項}=-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}+\frac{\cos\theta\sin^2\phi}{r^2\sin\theta}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}$$
$$-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}+\frac{\cos\theta\cos^2\phi}{r^2\sin\theta}+\frac{\sin\theta\cos\theta}{r^2}+\frac{\sin\theta\cos\theta}{r^2}$$

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

$\dfrac{\partial}{\partial\phi}$ を持つ項を計算する．

$$\frac{\partial}{\partial\phi}\text{を持つ項}=\frac{\sin\phi\cos\phi}{r^2}+\frac{\sin\phi\cos^2\theta\cos\phi}{r^2\sin^2\theta}+\frac{\sin\phi\cos\phi}{r^2\sin^2\theta}-\frac{\sin\phi\cos\phi}{r^2}-\frac{\sin\phi\cos^2\theta\cos\phi}{r^2\sin^2\theta}-\frac{\sin\phi\cos\phi}{r^2\sin^2\theta}=0$$

$\dfrac{\partial^2}{\partial r^2}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial r^2}\text{を持つ項}=\sin^2\theta\cos^2\phi+\sin^2\theta\sin^2\phi+\cos^2\theta=1$$

$\dfrac{\partial^2}{\partial\theta^2}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\theta^2}\text{を持つ項}=\frac{\cos^2\theta\cos^2\phi}{r^2}+\frac{\cos^2\theta\sin^2\phi}{r^2}+\frac{\sin^2\theta}{r^2}=\frac{1}{r^2}$$

$\dfrac{\partial^2}{\partial\phi^2}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\phi^2}\text{を持つ項}=\frac{\sin^2\phi}{r^2\sin^2\theta}+\frac{\cos^2\phi}{r^2\sin^2\theta}=\frac{1}{r^2\sin^2\theta}$$

$\dfrac{\partial^2}{\partial r\partial\theta}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial r\partial\theta}\text{を持つ項}=\frac{\sin\theta\cos\theta\cos^2\phi}{r}+\frac{\sin\theta\cos\theta\sin^2\phi}{r}-\frac{\sin\theta\cos\theta}{r}=0$$

$\dfrac{\partial^2}{\partial r\partial\phi}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial r\partial\phi}\text{を持つ項}=-\frac{\sin\phi\cos\phi}{r}+\frac{\sin\phi\cos\phi}{r}=0$$

$\dfrac{\partial^2}{\partial\theta\partial r}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\theta\partial r}\text{を持つ項}=\frac{\sin\theta\cos\theta\cos^2\phi}{r}+\frac{\sin\theta\cos\theta\sin^2\phi}{r}-\frac{\sin\theta\cos\theta}{r}=0$$

$\dfrac{\partial^2}{\partial\theta\partial\phi}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\theta\partial\phi}\text{を持つ項} = -\frac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta} + \frac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta} = 0$$

$\dfrac{\partial^2}{\partial\phi\partial r}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\phi\partial r}\text{を持つ項} = -\frac{\sin\phi\cos\phi}{r} + \frac{\sin\phi\cos\phi}{r} = 0$$

$\dfrac{\partial^2}{\partial\phi\partial\theta}$ を持つ項を計算する．

$$\frac{\partial^2}{\partial\phi\partial\theta}\text{を持つ項} = -\frac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta} + \frac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta} = 0$$

以上の結果から，ラプラシアン ∇^2 を極座標に変換すると

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\end{aligned}$$

これをテキストのように表現すると

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

のようになる．

問題2

Schrödinger 方程式を極座標で表す．問題1 (c) の結論を使うと，次のように書ける．ただし，波動関数を $\Psi = \Psi(r, \theta, \phi)$，換算質量を $\mu = \dfrac{m_p m_e}{m_p + m_e}$ とする．また，ポテンシャル $V(r)$ は陽子と電子の相互作用であるから，$V(r) = -\dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r}$ である．

$$\left[-\frac{\hbar^2}{2\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}+V(r)\right]\Psi = E\Psi$$

これを整理すると，

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi = 0$$

となる．ここで，$\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ のように分離できると仮定する．すると上式は

$$Y(\theta,\phi)\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+R(r)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+R(r)\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R(r)Y(\theta,\phi) = 0$$

この両辺を $R(r)Y(\theta,\phi)$ で割ると，

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{1}{Y(\theta,\phi)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{Y(\theta,\phi)}\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right) = 0$$

となる．この式を変形する．

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right) = -\frac{1}{Y(\theta,\phi)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)-\frac{1}{Y(\theta,\phi)}\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}$$

この式は，左辺を変数 r のみの式，右辺を θ, ϕ のみの式である．すると両辺は定数 λ に等しいはずである．よって，

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right) = \lambda \qquad \cdots (1)$$

$$-\frac{1}{Y(\theta,\phi)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)-\frac{1}{Y(\theta,\phi)}\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2} = \lambda \qquad \cdots (2)$$

(1) を解く．すると，

$$R_{n,l}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2}{na_0}\right)^3}\left(\frac{2\rho}{n}\right)^l e^{-\rho/n}L_{n+l}^{2l+1}(2\rho/n)$$

である．ここで，

$$\rho = \frac{r}{a_0},\ a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2},\ L_k^s(x) = \frac{d^s}{dx^s}e^x\frac{d^k}{dx^k}(x^k e^{-x})$$

である．このとき，n は主量子数，l は方位量子数で $0 \leq l \leq n-1$ の範囲の値しかとることはできない．

(2) を解く．すると，

$$Y_{l,m}(\theta,\phi) = (-1)^{(m+|m|)/2}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$P_l^{|m|}(z) = (1-z^2)^{|m|/2}\frac{d^{|m|}P_l^0(z)}{dz^{|m|}}$$

である．ここで，

$$z = \cos\theta,\ P_l^0 = \frac{1}{2^l l!}\frac{d^l}{dz^l}(z^2-1)^l$$

となる．このとき，m は磁気量子数で，$-l \leq m \leq l$ の範囲の値しかとることはできない．これらを用いて，定常状態における主量子数 n が $1 \sim 3$ までの波動関数を全て求める．

$n=1$ のとき，

$$R_{1,l}(r) = -\sqrt{\frac{l!}{2[(1+l)!]^3}\left(\frac{2}{a_0}\right)^3}(2\rho)^l e^{-\rho} L_{1+l}^{2l+1}(2\rho)$$

波動関数 $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ より波動関数は，

$$\Psi(r,\theta,\phi) = -\sqrt{\frac{l!}{2[(1+l)!]^3}\left(\frac{2}{a_0}\right)^3}(2\rho)^l e^{-\rho} L_{1+l}^{2l+1}(2\rho)(-1)^{(m+|m|)/2}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

となる．

$n=2$ のとき，

$$R_{2,l}(r) = -\sqrt{\frac{(1-l)!}{4[(2+l)!]^3}\left(\frac{1}{a_0}\right)^3}\rho^l e^{-\rho/2} L_{2+l}^{2l+1}(\rho)$$

波動関数 $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ より波動関数は，

$$\Psi(r,\theta,\phi) = -\sqrt{\frac{(1-l)!}{4[(2+l)!]^3}\left(\frac{1}{a_0}\right)^3}\rho^l e^{-\rho/2} L_{2+l}^{2l+1}(\rho)(-1)^{(m+|m|)/2}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

となる．

$n=3$ のとき，

$$R_{3,l}(r) = -\sqrt{\frac{(2-l)!}{6[(3+l)!]^3}\left(\frac{2}{3a_0}\right)^3}\left(\frac{2\rho}{3}\right)^l e^{-\rho/3} L_{3+l}^{2l+1}(2\rho/3)$$

波動関数 $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ より波動関数は，

$$\Psi(r,\theta,\phi) = -\sqrt{\frac{(2-l)!}{6[(3+l)!]^3}\left(\frac{2}{3a_0}\right)^3}\left(\frac{2\rho}{3}\right)^l e^{-\rho/3} L_{3+l}^{2l+1}(2\rho/3)(-1)^{(m+|m|)/2}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

となる．