同理
$$\frac{\partial r}{\partial y}=\frac{y}{r},\qquad \frac{\partial r}{\partial z}=\frac{z}{r} \tag{6.48}$$

又
$$-\sin\theta\frac{\partial\theta}{\partial x}=\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}\cos\theta=\frac{\partial}{\partial x}\cos\theta=z\frac{\partial}{\partial x}(\frac{1}{r})$$
$$=-\frac{z}{r^2}\frac{\partial r}{\partial x}=-\frac{zx}{r^3}=-\frac{1}{r}\cdot\frac{z}{r}\cdot\frac{x}{r}=-\frac{1}{r}\cos\theta\sin\theta\cos\boldsymbol{\varphi} \tag{6.48}$$

所以
$$\frac{\partial\theta}{\partial x}=\frac{\cos\theta\cos\boldsymbol{\varphi}}{r} \tag{6.50}$$

同理
$$-\sin\theta\frac{\partial\theta}{\partial y}=\frac{1}{r}\cos\theta\sin\theta\sin\varphi,\qquad -\sin\theta\frac{\partial\theta}{\partial z}=\frac{1}{r}(1-\cos^2\theta) \tag{6.51}$$

故
$$\frac{\partial\theta}{\partial y}=\frac{\cos\theta\sin\varphi}{r},\qquad \frac{\partial\theta}{\partial z}=-\frac{\sin\theta}{r} \tag{6.52}$$

而
$$\sec^2\boldsymbol{\varphi}\frac{\partial\varphi}{\partial x}=\frac{\partial}{\partial x}\tan\varphi=y\frac{\partial}{\partial x}(\frac{1}{x})=-\frac{y}{x^2} \tag{6.53}$$

因此
$$\frac{\partial\varphi}{\partial x}=-\frac{y}{x^2}\cos^2\boldsymbol{\varphi} \tag{6.54}$$

同理
$$\frac{\partial\boldsymbol{\varphi}}{\partial y}=-\frac{\cos^2\boldsymbol{\varphi}}{x},\qquad \frac{\partial\boldsymbol{\varphi}}{\partial z}=0 \tag{6.55}$$

利用以上的結果，可將對直角坐標 x, y, z 之偏導數，全部轉成對球面坐標 $r, \theta, \boldsymbol{\varphi}$ 之偏導數：

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\boldsymbol{\theta}}{\partial x}\frac{\partial}{\partial\boldsymbol{\theta}}+\frac{\partial\boldsymbol{\varphi}}{\partial x}\frac{\partial}{\partial\boldsymbol{\varphi}}=\frac{x}{r}\frac{\partial}{\partial r}+\frac{\cos\theta\cos\boldsymbol{\varphi}}{r}\frac{\partial}{\partial\boldsymbol{\theta}}-\frac{y}{x^2}\cos^2\boldsymbol{\varphi}\frac{\partial}{\partial\boldsymbol{\varphi}} \tag{6.56}$$

$$\frac{\partial}{\partial y}=\frac{\partial r}{\partial y}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta}+\frac{\partial\varphi}{\partial y}\frac{\partial}{\partial\varphi}=\frac{y}{r}\frac{\partial}{\partial r}+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}+\frac{\cos^2\boldsymbol{\varphi}}{x}\frac{\partial}{\partial\varphi} \tag{6.57}$$

$$\frac{\partial}{\partial z}=\frac{\partial r}{\partial z}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta}+\frac{\partial\varphi}{\partial z}\frac{\partial}{\partial\varphi}=\frac{z}{r}\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} \tag{6.58}$$

再利用式(6.43)，遂可用 $r, \theta, \boldsymbol{\varphi}$ 表示出角動量在直角坐標分量之運算子形式

$$\hat{L}_x = -i\hbar\,(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

$$= -i\hbar\,(\frac{yz}{r}\frac{\partial}{\partial r} - \frac{y\sin\theta}{r}\frac{\partial}{\partial\theta} - \frac{yz}{r}\frac{\partial}{\partial r} - \frac{z\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} - \frac{z\cos^2\boldsymbol{\varphi}}{x}\frac{\partial}{\partial\varphi})$$

$$= i\hbar\,(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}) \tag{6.59}$$

$$\hat{L}_y = -i\hbar\,(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$$

$$= -i\hbar\,(\frac{xz}{r}\frac{\partial}{\partial r} - \frac{z\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta} - \frac{yz}{x^2}\cos^2\boldsymbol{\varphi}\frac{\partial}{\partial\varphi} - \frac{xz}{r}\frac{\partial}{\partial r} + \frac{x\sin\theta}{r}\frac{\partial}{\partial\theta})$$

$$= i\hbar\,(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}) \tag{6.60}$$

$$\hat{L}_z = -i\hbar\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

$$= -i\hbar\,(\frac{xy}{r}\frac{\partial}{\partial r} + \frac{x\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}$$

$$+ \frac{x\cos^2\boldsymbol{\varphi}}{x}\frac{\partial}{\partial\varphi} - \frac{xy}{r}\frac{\partial}{\partial r} - \frac{y\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta} + \frac{y^2}{x^2}\cos^2\boldsymbol{\varphi}\frac{\partial}{\partial\varphi})$$

$$= -i\hbar\frac{\partial}{\partial\varphi} \tag{6.61}$$

因此得到

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\,(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\boldsymbol{\varphi}^2}) \tag{6.62}$$

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y = \hbar e^{i\varphi}\,(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\boldsymbol{\varphi}}) \tag{6.63}$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y = \hbar e^{-i\varphi}\,(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\boldsymbol{\varphi}}) \tag{6.64}$$

已知 $\hat{\boldsymbol{L}}$ 滿足角動量的定義(6.4)~(6.5)，故由角動量量子化定理 6.1，所作用的狀態空間裡，$\hat{L}^2$ **和** $\hat{L}_z$ **享有共同之固有狀態** $|\ell, m\rangle$ **，並可給出對應之固有值** $\ell(\ell+1)\hbar^2$ **與** $m\hbar$ **。**

$$\hat{L}^2 \; |\ell, m\rangle = \ell(\ell+1)\hbar^2 \; |\ell, m\rangle \qquad (6.65)$$

$$\hat{L}_z \; |\ell, m\rangle = m\hbar \; |\ell, m\rangle \qquad (6.66)$$

將上式投影在位置空間 $|\vec{r}\rangle = |r, \theta, \varphi\rangle$ 後，由式(6.65)與(6.66)得到

$$-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\Psi_{\ell m}(r,\theta,\varphi) = \ell(\ell+1)\hbar^2\,\Psi_{\ell m}(r,\theta,\varphi) \qquad (6.67)$$

$$-i\hbar\frac{\partial}{\partial\varphi}\Psi_{\ell m}(r,\theta,\varphi) = m\hbar\Psi_{\ell m}(r,\theta,\varphi) \qquad (6.68)$$

式中$\Psi_{\ell m}(r,\theta,\varphi)$ 代表狀態 $|\ell, m\rangle$ 在 $|\vec{r}\rangle = |r, \theta, \varphi\rangle$ 上之投影值。令
$\Psi_{\ell m}(r,\theta,\varphi) = f(r)\; Y_\ell^m(\theta,\varphi)$ ，則

$$-\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\,Y_\ell^m(\theta,\varphi) \qquad (6.69)$$

$$-i\hbar\frac{\partial}{\partial\varphi}Y_\ell^m(\theta,\varphi) = m\hbar Y_\ell^m(\theta,\varphi) \qquad (6.70)$$

再令 $Y_\ell^m(\theta,\varphi) = \Theta(\theta)\Phi(\theta)$ ，得

$$-i\hbar\frac{\partial}{\partial\varphi}\Phi(\varphi) = m\hbar\,\Phi(\varphi) \qquad (6.71)$$

故 $$\Phi(\varphi) = e^{im\varphi} \quad \text{或} \quad Y_\ell^m(\theta,\varphi) = \Theta_{\ell m}(\theta)\,e^{im\varphi} \qquad (6.72)$$

因一函數在同一點，不能對應到不同函數值。故可形成 φ 之邊界條件：

$$Y_\ell^m(\theta,\varphi=0) = Y_\ell^m(\theta,\varphi=2\pi) \qquad (6.73)$$

也就是說， $e^0 = e^{im\cdot 2\pi}$ ，或

$$1 = \cos 2m\pi + i\sin 2m\pi \;\Rightarrow\; \boxed{m = 整數 = 0,\ \pm1,\ \pm2,\cdots} \qquad (6.74)$$

但由定理 6. 1　$m = -\ell, -\ell+1, -\ell+2, \cdots, \ell-1, \ell$ ，所以必然地

$$\boxed{\ell = 整數} \qquad (6.75)$$