Aplicação: funções harmônicas esféricas

Começamos considerando a equação de Laplace,

$$\nabla^2 \Psi(\mathbf{r}) = 0.$$

Aí nós escrevemos o operador laplaciano assim:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2},$$

onde $\mathbf{L}$ é o operador momentum angular, definido como

$$\mathbf{L} \equiv \frac{\hbar}{i}\mathbf{r} \times \boldsymbol{\nabla}.$$

Aqui,

$$\hbar \equiv \frac{h}{2\pi},$$

onde h é a constante de Planck. Em mecânica clássica, o momentum angular é dado por

$$\mathbf{L} \equiv \mathbf{r} \times \mathbf{p},$$

onde $\mathbf{p}$ é o momentum linear de uma partícula. Em mecânica quântica, o momentum se torna um operador dado por

$$\mathbf{p} \rightarrow \frac{\hbar}{i}\boldsymbol{\nabla}$$

e aí a definição clássica de momentum angular se torna aquela que escrevemos acima, envolvendo o operador nabla.

1 **Exercício**: Usando a definição acima do operador $\mathbf{L}$ mostre as relações de comutação de suas componentes:

$$\begin{aligned}[L_j, L_k] &\equiv L_j L_k - L_k L_j \\ &= i\hbar \varepsilon_{j,k,l} L_l,\end{aligned}$$

onde os índices repetidos no mesmo termo são somados de 1 a 3.

2 **Exercício**: Defina os operadores $L_\pm$, isto é,

$$L_\pm \equiv L_x \pm i L_y.$$

Demonstre que

$$[L_z, L_\pm] = \pm\hbar L_\pm$$

e

$$\left[\mathbf{L}^2, L_\pm\right] = 0.$$

Também demonstre que

$$\left[\mathbf{L}^2, L_k\right] = 0,$$

para $k = 1, 2, 3$. Note que aqui os índices 1, 2 e 3 sempre correspondem, respectivamente, às componentes x, y e z. Como exercício, verifique todas as relações de comutação acima outra vez, só para seu treinamento.

Em coordenadas esféricas, escrevemos o operador $\mathbf{L}^2$ a partir da definição

$$\mathbf{L} \equiv \frac{\hbar}{i}\mathbf{r}\times\boldsymbol{\nabla},$$

onde usamos

$$\mathbf{r} = r\hat{\mathbf{r}}$$

e

$$\boldsymbol{\nabla} = \hat{\mathbf{r}}\frac{\partial}{\partial r}+\hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\varphi}}\frac{1}{r\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}.$$

Então,

$$\begin{aligned}
\mathbf{L} &= \frac{\hbar}{i}r\hat{\mathbf{r}}\times\left(\hat{\mathbf{r}}\frac{\partial}{\partial r}+\hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\varphi}}\frac{1}{r\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= \frac{\hbar}{i}\left(\hat{\mathbf{r}}\times\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}+\hat{\mathbf{r}}\times\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= \frac{\hbar}{i}\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right).
\end{aligned}$$

E note que,

$$\begin{aligned}
\hat{\mathbf{r}}\times\mathbf{L} &= \frac{\hbar}{i}\left(\hat{\mathbf{r}}\times\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\mathbf{r}}\times\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= \frac{\hbar}{i}\left(-\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= i\hbar\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= i\hbar\left(r\boldsymbol{\nabla}-r\hat{\mathbf{r}}\frac{\partial}{\partial r}\right),
\end{aligned}$$

isto é,

$$\boldsymbol{\nabla} = \hat{\mathbf{r}}\frac{\partial}{\partial r}+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}.$$

Logo, podemos deduzir a expressão acima para o laplaciano em termos do operador momentum angular assim:

$$\begin{aligned}
\boldsymbol{\nabla}\cdot\boldsymbol{\nabla} &= \left(\hat{\mathbf{r}}\frac{\partial}{\partial r}+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\frac{\partial}{\partial r}+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\right)\\
&= \hat{\mathbf{r}}\frac{\partial}{\partial r}\cdot\left(\hat{\mathbf{r}}\frac{\partial}{\partial r}+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\right)+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\cdot\left(\hat{\mathbf{r}}\frac{\partial}{\partial r}+\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\right)\\
&= \hat{\mathbf{r}}\frac{\partial}{\partial r}\cdot\hat{\mathbf{r}}\frac{\partial}{\partial r}+\hat{\mathbf{r}}\frac{\partial}{\partial r}\cdot\left(\frac{1}{i\hbar r}\hat{\mathbf{r}}\times\mathbf{L}\right)\\
&\quad+\frac{1}{i\hbar r}\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\hat{\mathbf{r}}\frac{\partial}{\partial r}-\frac{1}{\hbar^2r^2}\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\\
&= \frac{\partial^2}{\partial r^2}+\frac{1}{i\hbar r}\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\hat{\mathbf{r}}\frac{\partial}{\partial r}-\frac{1}{\hbar^2r^2}\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right).
\end{aligned}$$

Mas,

$$(\hat{\mathbf{r}} \times \mathbf{L}) \cdot \hat{\mathbf{r}} \frac{\partial}{\partial r} = i\hbar \left(\hat{\boldsymbol{\theta}} \frac{\partial}{\partial \theta} + \hat{\boldsymbol{\varphi}} \frac{1}{\text{sen}\theta} \frac{\partial}{\partial \varphi} \right) \cdot (\hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta) \frac{\partial}{\partial r},$$

onde usamos

$$\hat{\mathbf{r}} = \hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta.$$

Sendo assim,

$$\begin{aligned}
(\hat{\mathbf{r}} \times \mathbf{L}) \cdot \hat{\mathbf{r}} \frac{\partial}{\partial r} &= i\hbar \hat{\boldsymbol{\theta}} \frac{\partial}{\partial \theta} \cdot (\hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta) \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\varphi}} \frac{1}{\text{sen}\theta} \frac{\partial}{\partial \varphi} \cdot (\hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta) \frac{\partial}{\partial r} \\
&= i\hbar \hat{\boldsymbol{\theta}} \cdot (\hat{\mathbf{x}} \cos\theta \cos\varphi + \hat{\mathbf{y}} \cos\theta \text{sen}\varphi - \hat{\mathbf{z}} \text{sen}\theta) \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\theta}} \cdot (\hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta) \frac{\partial}{\partial \theta} \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\varphi}} \frac{1}{\text{sen}\theta} \cdot (-\hat{\mathbf{x}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{y}} \text{sen}\theta \cos\varphi) \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\varphi}} \frac{1}{\text{sen}\theta} \cdot (\hat{\mathbf{x}} \text{sen}\theta \cos\varphi + \hat{\mathbf{y}} \text{sen}\theta \text{sen}\varphi + \hat{\mathbf{z}} \cos\theta) \frac{\partial}{\partial \varphi} \frac{\partial}{\partial r},
\end{aligned}$$

ou seja,

$$\begin{aligned}
(\hat{\mathbf{r}} \times \mathbf{L}) \cdot \hat{\mathbf{r}} \frac{\partial}{\partial r} &= i\hbar \hat{\boldsymbol{\theta}} \cdot \hat{\boldsymbol{\theta}} \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{r}} \frac{\partial}{\partial \theta} \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\varphi}} \frac{\text{sen}\theta}{\text{sen}\theta} \cdot \hat{\boldsymbol{\varphi}} \frac{\partial}{\partial r} \\
&\quad + i\hbar \hat{\boldsymbol{\varphi}} \frac{1}{\text{sen}\theta} \cdot \hat{\mathbf{r}} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial r}, \\
&= 2i\hbar \frac{\partial}{\partial r},
\end{aligned}$$

onde aqui usamos

$$\hat{\boldsymbol{\theta}} = \hat{\mathbf{x}} \cos\theta \cos\varphi + \hat{\mathbf{y}} \cos\theta \text{sen}\varphi - \hat{\mathbf{z}} \text{sen}\theta$$

e

$$\hat{\boldsymbol{\varphi}} = -\hat{\mathbf{x}} \text{sen}\varphi + \hat{\mathbf{y}} \cos\varphi.$$

Com isso, vemos que

$$\begin{aligned}
\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} &= \frac{\partial^2}{\partial r^2} + \frac{1}{i\hbar r} 2i\hbar \frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2} (\hat{\mathbf{r}} \times \mathbf{L}) \cdot (\hat{\mathbf{r}} \times \mathbf{L}) \\
&= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2} (\hat{\mathbf{r}} \times \mathbf{L}) \cdot (\hat{\mathbf{r}} \times \mathbf{L}).
\end{aligned}$$

Mas,

$$\begin{aligned} \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) &= \frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\right)\frac{\partial}{\partial r} + \frac{1}{r^2}r^2\frac{\partial^2}{\partial r^2} \\ &= \frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \end{aligned}$$

e, então,

$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right).$$

Resta-nos agora calcular $\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right)$. Para isso, como vimos acima, notamos que

$$\hat{\mathbf{r}}\times\mathbf{L} = i\hbar\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta} + \hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right),$$

dando

$$\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right) = -\hbar^2\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta} + \hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\cdot\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta} + \hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right).$$

Mas aí notamos que

$$\begin{aligned} \frac{\partial}{\partial\theta}\hat{\boldsymbol{\theta}} &= -\hat{\mathbf{x}}\mathrm{sen}\theta\cos\varphi - \hat{\mathbf{y}}\mathrm{sen}\theta\mathrm{sen}\varphi - \hat{\mathbf{z}}\cos\theta \\ &= -\hat{\mathbf{r}} \end{aligned}$$

e

$$\frac{\partial}{\partial\theta}\hat{\boldsymbol{\varphi}} = \mathbf{0}.$$

Também notamos que

$$\begin{aligned} \frac{\partial}{\partial\varphi}\hat{\boldsymbol{\theta}} &= -\hat{\mathbf{x}}\cos\theta\mathrm{sen}\varphi + \hat{\mathbf{y}}\cos\theta\cos\varphi \\ &= \hat{\boldsymbol{\varphi}}\cos\theta \end{aligned}$$

e

$$\begin{aligned} \frac{\partial}{\partial\varphi}\hat{\boldsymbol{\varphi}} &= -\hat{\mathbf{x}}\cos\varphi - \hat{\mathbf{y}}\mathrm{sen}\varphi \\ &= -\hat{\mathbf{r}}\mathrm{sen}\theta - \hat{\boldsymbol{\theta}}\cos\theta. \end{aligned}$$

Usando esses resultados, podemos escrever:

$$\left(\hat{\mathbf{r}}\times\mathbf{L}\right)\cdot\left(\hat{\mathbf{r}}\times\mathbf{L}\right) = -\hbar^2\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\cdot\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta} + \hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)$$

$$
\begin{aligned}
&-\hbar^2\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\cdot\left(\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
= &-\hbar^2\hat{\boldsymbol{\theta}}\cdot\left(\frac{\partial\hat{\boldsymbol{\theta}}}{\partial\theta}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\theta}}\frac{\partial^2}{\partial\theta^2}\right)\\
&-\hbar^2\hat{\boldsymbol{\theta}}\cdot\left(\frac{\partial\hat{\boldsymbol{\varphi}}}{\partial\theta}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}-\hat{\boldsymbol{\varphi}}\frac{\cos\theta}{\mathrm{sen}^2\theta}\frac{\partial}{\partial\varphi}+\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\varphi}\right)\\
&-\hbar^2\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\cdot\left(\frac{\partial\hat{\boldsymbol{\theta}}}{\partial\varphi}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\varphi}\frac{\partial}{\partial\theta}\right)\\
&-\hbar^2\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\cdot\left(\frac{\partial\hat{\boldsymbol{\varphi}}}{\partial\varphi}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}+\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\
= &-\hbar^2\hat{\boldsymbol{\theta}}\cdot\left(-\hat{\mathbf{r}}\frac{\partial}{\partial\theta}+\hat{\boldsymbol{\theta}}\frac{\partial^2}{\partial\theta^2}\right)\\
&-\hbar^2\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\cdot\left(\hat{\boldsymbol{\varphi}}\cos\theta\frac{\partial}{\partial\theta}\right)\\
&-\hbar^2\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\cdot\hat{\boldsymbol{\varphi}}\frac{1}{\mathrm{sen}\theta}\frac{\partial^2}{\partial\varphi^2},
\end{aligned}
$$

isto é,

$$
(\hat{\mathbf{r}}\times\mathbf{L})\cdot(\hat{\mathbf{r}}\times\mathbf{L}) = -\hbar^2\frac{\partial^2}{\partial\theta^2}-\hbar^2\frac{\cos\theta}{\mathrm{sen}\theta}\frac{\partial}{\partial\theta}-\hbar^2\frac{1}{\mathrm{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2}.
$$

De forma análoga, podemos calcular também:

$$
\begin{aligned}
\mathbf{L}^2 &= \mathbf{L}\cdot\mathbf{L}\\
&= -\hbar^2\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\cdot\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= -\hbar^2\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}\cdot\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)+\hbar^2\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\cdot\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}-\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= -\hbar^2\hat{\boldsymbol{\varphi}}\cdot\frac{\partial}{\partial\theta}\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}\right)+\hbar^2\hat{\boldsymbol{\varphi}}\cdot\frac{\partial}{\partial\theta}\left(\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&\quad+\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\frac{\partial}{\partial\varphi}\left(\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\theta}\right)-\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\frac{\partial}{\partial\varphi}\left(\hat{\boldsymbol{\theta}}\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&= -\hbar^2\hat{\boldsymbol{\varphi}}\cdot\left(\frac{\partial}{\partial\theta}\hat{\boldsymbol{\varphi}}\right)\frac{\partial}{\partial\theta}-\hbar^2\hat{\boldsymbol{\varphi}}\cdot\hat{\boldsymbol{\varphi}}\frac{\partial^2}{\partial\theta^2}\\
&\quad+\hbar^2\hat{\boldsymbol{\varphi}}\cdot\left(\frac{\partial}{\partial\theta}\hat{\boldsymbol{\theta}}\right)\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}+\hbar^2\hat{\boldsymbol{\varphi}}\cdot\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\theta}\left(\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right)\\
&\quad+\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\left(\frac{\partial}{\partial\varphi}\hat{\boldsymbol{\varphi}}\right)\frac{\partial}{\partial\theta}+\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\hat{\boldsymbol{\varphi}}\frac{\partial}{\partial\varphi}\frac{\partial}{\partial\theta}\\
&\quad-\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\left(\frac{\partial}{\partial\varphi}\hat{\boldsymbol{\theta}}\right)\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}-\hbar^2\frac{1}{\mathrm{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\hat{\boldsymbol{\theta}}\frac{\partial}{\partial\varphi}\left(\frac{1}{\mathrm{sen}\theta}\frac{\partial}{\partial\varphi}\right),
\end{aligned}
$$

isto é,

$$\begin{aligned}
\mathbf{L}^2 &= -\hbar^2\frac{\partial^2}{\partial\theta^2} \\
&\quad +\hbar^2\hat{\boldsymbol{\varphi}}\cdot(-\hat{\mathbf{r}})\,\frac{1}{\text{sen}\theta}\frac{\partial}{\partial\varphi} \\
&\quad +\hbar^2\frac{1}{\text{sen}\theta}\hat{\boldsymbol{\theta}}\cdot\left(-\hat{\mathbf{r}}\text{sen}\theta-\hat{\boldsymbol{\theta}}\cos\theta\right)\frac{\partial}{\partial\theta} \\
&\quad -\hbar^2\frac{1}{\text{sen}\theta}\hat{\boldsymbol{\theta}}\cdot(\hat{\boldsymbol{\varphi}}\cos\theta)\,\frac{1}{\text{sen}\theta}\frac{\partial}{\partial\varphi}-\hbar^2\frac{1}{\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2},
\end{aligned}$$

ou seja,

$$\mathbf{L}^2 = -\hbar^2\frac{\partial^2}{\partial\theta^2}-\hbar^2\frac{\cos\theta}{\text{sen}\theta}\frac{\partial}{\partial\theta}-\hbar^2\frac{1}{\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2},$$

que é igual a

$$(\hat{\mathbf{r}}\times\mathbf{L})\cdot(\hat{\mathbf{r}}\times\mathbf{L}) = -\hbar^2\frac{\partial^2}{\partial\theta^2}-\hbar^2\frac{\cos\theta}{\text{sen}\theta}\frac{\partial}{\partial\theta}-\hbar^2\frac{1}{\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

Então, como já tínhamos lá em cima,

$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{1}{\hbar^2 r^2}\,(\hat{\mathbf{r}}\times\mathbf{L})\cdot(\hat{\mathbf{r}}\times\mathbf{L})\,,$$

por ser

$$(\hat{\mathbf{r}}\times\mathbf{L})\cdot(\hat{\mathbf{r}}\times\mathbf{L}) = \mathbf{L}^2,$$

concluímos que podemos escrever:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\mathbf{L}^2}{\hbar^2 r^2}.$$

Com a expressão acima para $\mathbf{L}^2$, segue que

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2}\frac{\cos\theta}{\text{sen}\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

Notemos também que

$$\begin{aligned}
\frac{1}{\text{sen}\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right) &= \frac{1}{\text{sen}\theta}\left(\frac{\partial}{\partial\theta}\text{sen}\theta\right)\frac{\partial}{\partial\theta}+\frac{1}{\text{sen}\theta}\text{sen}\theta\frac{\partial^2}{\partial\theta^2} \\
&= \frac{\cos\theta}{\text{sen}\theta}\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}
\end{aligned}$$

e, portanto,

$$\mathbf{L}^2 = -\hbar^2\frac{1}{\text{sen}\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)-\hbar^2\frac{1}{\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2},$$

dando

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\text{sen}\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2},$$

que é exatamente o laplaciano em coordenadas esféricas. Esta também é outra forma de deduzir o laplaciano em coordenadas esféricas.

Por exemplo, na equação de Schrödinger em coordenadas esféricas, digamos, para o átomo de hidrogênio, seja $\psi(r,\theta,\varphi)$ a função de onda do elétron. Então a equação de Schrödinger no centro de massa do átomo é dada por

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi)-\frac{e^2}{r}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi).$$

Note que estamos usando o sistema CGS de unidades e que a carga elétrica do próton deve ser igual e de sinal oposto à carga do elétron, isto é, o próton tem carga $e>0$. A massa reduzida do sistema é escrita μ na equação acima. Assim, pelo método de separação de variáveis, tentemos separar a parte radial da parte angular, escrevendo

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi).$$

Logo,

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\mathbf{L}^2}{\hbar^2 r^2}\right]\psi(r,\theta,\varphi)-\frac{e^2}{r}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi),$$

isto é,

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r,\theta,\varphi)+\frac{\mathbf{L}^2}{2\mu r^2}\psi(r,\theta,\varphi)-\frac{e^2}{r}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi),$$

ou seja,

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)+\frac{1}{Y(\theta,\varphi)}\frac{\mathbf{L}^2}{2\mu r^2}Y(\theta,\varphi)-\frac{e^2}{r} = E,$$

ou ainda,

$$-\frac{\hbar^2}{2\mu}\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)+\frac{1}{Y(\theta,\varphi)}\frac{\mathbf{L}^2}{2\mu}Y(\theta,\varphi)-e^2r = Er^2.$$

Logo,

$$\frac{1}{Y(\theta,\varphi)}\mathbf{L}^2Y(\theta,\varphi) = 2\mu Er^2+2\mu e^2r+\frac{\hbar^2}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right).$$

Introduzindo uma constante de separação, K, obtemos:

$$\frac{1}{Y(\theta,\varphi)}\mathbf{L}^2Y(\theta,\varphi) = K$$

e

$$2\mu Er^2+2\mu e^2r+\frac{\hbar^2}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) = K.$$

A equação radial nós vamos considerar em outra aula.

Vamos agora usar o operador $\mathbf{L}^2$ e resolver a equação angular:

$$\mathbf{L}^2 Y(\theta,\varphi) = KY(\theta,\varphi),$$

isto é,

$$\left[-\hbar^2 \frac{1}{\text{sen}\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right) - \hbar^2\frac{1}{\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] Y(\theta,\varphi) = KY(\theta,\varphi).$$

Para isso, vamos fazer outra separação de variáveis:

$$Y(\theta,\varphi) = Q(\theta)\,\Phi(\varphi).$$

Então, obtemos:

$$\frac{1}{Q(\theta)\,\text{sen}\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)Q(\theta) + \frac{1}{\Phi(\varphi)\,\text{sen}^2\theta}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = -\frac{K}{\hbar^2},$$

ou seja,

$$\frac{\text{sen}\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)Q(\theta) + \frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = -\frac{K}{\hbar^2}\text{sen}^2\theta,$$

ou ainda,

$$\frac{\text{sen}\theta}{Q(\theta)}\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)Q(\theta) + \frac{K}{\hbar^2}\text{sen}^2\theta = -\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi).$$

Logo, introduzindo uma nova constante de separação, C, obtemos:

$$\text{sen}\theta\frac{\partial}{\partial\theta}\left(\text{sen}\theta\frac{\partial}{\partial\theta}\right)Q(\theta) + \frac{K}{\hbar^2}\text{sen}^2\theta Q(\theta) = CQ(\theta)$$

e

$$\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = -C\Phi(\varphi).$$

Mas, obviamente,

$$\Phi(\varphi+2\pi) = \Phi(\varphi)$$

e, assim, como na equação de Schrödinger as funções de onda não precisam ser reais, segue que as soluções possíveis para a equação para $\Phi(\varphi)$ é dada por

$$\Phi_m(\varphi) = \mathcal{N}_m \exp(im\varphi),$$

onde $m \in \mathbb{Z}$. Portanto,

$$C = m^2$$

e equação para $Q(\theta)$ agora fica:

$$\text{sen}\theta\frac{d}{d\theta}\left[\text{sen}\theta\frac{dQ(\theta)}{d\theta}\right]+\frac{K}{\hbar^2}\text{sen}^2\theta Q(\theta) = m^2 Q(\theta).$$

O que acontece se nós mudarmos de variável fazendo

$$x \equiv \cos\theta$$

e reescrevemos a equação acima? O que teremos é algo assim:

$$\begin{aligned}\frac{d}{d\theta} &= \frac{dx}{d\theta}\frac{d}{dx}\\ &= -\text{sen}\theta\frac{d}{dx}.\end{aligned}$$

Seja

$$P(x) \equiv Q(\theta).$$

Então,

$$\text{sen}^2\theta\frac{d}{dx}\left[\text{sen}^2\theta\frac{dP(x)}{dx}\right]+\frac{K}{\hbar^2}\text{sen}^2\theta P(x) = m^2 P(x).$$

Mas,

$$\begin{aligned}\text{sen}^2\theta &= 1-\cos^2\theta\\ &= 1-x^2\end{aligned}$$

e, assim,

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{dP(x)}{dx}\right]+\frac{K}{\hbar^2}P(x) = \frac{m^2}{1-x^2}P(x),$$

isto é,

$$\left(1-x^2\right)\frac{d^2P(x)}{dx^2}-2x\frac{dP(x)}{dx}+\frac{K}{\hbar^2}P(x) = \frac{m^2}{1-x^2}P(x),$$

ou seja,

$$\left(1-x^2\right)\frac{d^2P(x)}{dx^2}-2x\frac{dP(x)}{dx}+\left(\frac{K}{\hbar^2}-\frac{m^2}{1-x^2}\right)P(x) = 0,$$

que é quase a equação associada de Legendre:

$$\left(1-x^2\right)\frac{d^2}{dx^2}P_\ell^m(x)-2x\frac{d}{dx}P_\ell^m(x)+\left[\ell(\ell+1)-\frac{m^2}{1-x^2}\right]P_\ell^m(x) = 0.$$

Por que, no caso do átomo de hidrogênio, devemos ter

$$K = \hbar^2\ell(\ell+1),$$

com $\ell = 0, 1, 2, \ldots$? Eis a questão! É possível demonstrar isso usando as regras de comutação do exercício 12 acima, o que normalmente é feito nos cursos de mecânica quântica. Aqui, entretanto, vamos usar um argumento menos sofisticado. Consideremos o caso em que $m = 0$. Aí teremos a equação de Legendre. Se nós usarmos o método de introdução à física matemática de soluções por série, veremos que, como para $\theta = 0$ e $\theta = \pi$ a série diverge caso ℓ não seja inteiro, temos que escolher os autovalores com $\ell = 0, 1, 2, \ldots$ para que nesses polos da esfera a solução seja finita, ou seja, temos que procurar por soluções polinomiais. Isso vem do fato de que a função de onda em mecânica quântica tem sempre que ser quadraticamente integrável para que a soma total de probabilidade seja igual a 1. Um espaço de funções quadraticamente integrável é chamado de espaço L^2. Logo, nossa resposta fica exatamente que, para a equação radial, temos que escrever:

$$Y_\ell^m(\theta, \varphi) = \mathcal{N}_\ell^m P_\ell^m(\cos\theta)\exp(im\varphi),$$

com $\ell = 0, 1, 2, \ldots$ e $m = 0, \pm1, \pm2, \ldots, \pm\ell$. E, quando usamos a normalização tal que

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \operatorname{sen}\theta Y_{\ell'}^{m'*}(\theta, \varphi) Y_\ell^m(\theta, \varphi) = \delta_{\ell'\ell}\delta_{m'm},$$

as funções ortonormais $Y_\ell^m(\theta, \varphi)$ são chamadas funções harmônicas esféricas. O resultado da normalização é, portanto,

$$Y_\ell^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos\theta)\exp(im\varphi).$$

Lembremos que quando separamos as variáveis angulares da radial e depois quando encontramos os autovalores de $\mathbf{L}^2$, em suma, ficamos com:

$$\mathbf{L}^2 Y_\ell^m(\theta, \varphi) = \hbar^2\ell(\ell+1) Y_\ell^m(\theta, \varphi).$$

3 Exercício: Demonstre que

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

e que, portanto,

$$L_z Y_\ell^m(\theta, \varphi) = \hbar m Y_\ell^m(\theta, \varphi).$$