21.3: Common Operators in Quantum Mechanics

Some common operators occurring in quantum mechanics are collected in the table below:

Observable Name	Symbol	Operator	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	L	$\hat{L}^2$	$\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2$
	L_x	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	L_y	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	L_z	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

In the sections below we analyze in details two main operators for the energy and the angular momentum.

Hamiltonian Operator

The main quantity that quantum mechanics is interested in is the total energy of the system, E. The operator corresponding to this quantity is called *Hamiltonian*:

$$\hat{H}=-\frac{\hbar^2}{2}\sum_i\frac{1}{m_i}\nabla_i^2+V, \tag{21.3.1}$$

where i is an index over all the particles of the system. Using the formalism of operators in conjunction with Equation 21.3.1, we can write the TISEq just simply as:

$$\hat{H}\psi=E\psi. \tag{21.3.2}$$

Comparing Equation 21.3.1 to the classical analog in Equation 18.3.2, we notice how the first term in the Hamiltonian operator represents the corresponding kinetic energy operator, $\hat{K}$, while the second term represents the potential energy operator, $\hat{V}$. For a one-electron system—such as the ones we studied in chapter 20—we can write:

$$\hat{K}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=\frac{\hbar^2}{2m}\nabla^2, \tag{21.3.3}$$

which is universal and applies to all systems. The potential energy operator $\hat{V}$ is what differentiate each system. Using Equation 21.3.2, we can then simply obtain the TISEq for each of the first three models discussed in chapter 20 by simply using:

$$\begin{aligned}\text{Free particle:}\quad & \hat{V}=0,\\ \text{Particle in a box:}\quad & \hat{V}=0 \text{ inside the box, } \hat{V}=\infty \text{ outside the box,}\\ \text{Harmonic oscillator:}\quad & \hat{V}=\frac{1}{2}kx^2.\end{aligned} \tag{21.3.4}$$

While these three cases are trivial to solve, the case of the rigid rotor is more complicated to solve, since the kinetic energy operator needs to be solved in spherical polar coordinates, as we will show in the next section.

Angular Momentum Operator

To write the kinetic energy operator $\hat{K}$ for the rigid rotor, we need to express the Laplacian, ∇^2, in spherical polar coordinates:

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2}, \tag{21.3.5}$$

where $\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ is the radial Laplacian, and $\hat{L}^2$ is the square of the total angular momentum operator, which is:

$$\begin{aligned}\hat{L}^2 &= \hat{L}\cdot\hat{L} = \left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right)\cdot\left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right)\\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2,\end{aligned} \tag{21.3.6}$$

with $\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ the unitary vectors in three-dimensional space. The component along each direction, $\left\{\hat{L}_x,\hat{L}_y,\hat{L}_z\right\}$, are then expressed in cartesian coordinates using to the following formulas:

$$\begin{aligned}\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),\\ \hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),\\ \hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).\end{aligned} \tag{21.3.7}$$

The eigenvalues equation corresponding to the total angular momentum is:

$$\hat{L}^2 Y(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_\ell^{m_\ell}(\theta,\varphi), \tag{21.3.8}$$

where ℓ is the azimuthal quantum number and $Y_\ell^m(\theta,\varphi)$ are the spherical harmonics, both of which we already encountered in chapter 20. Recall once again that each energy level E_ℓ is $(2\ell+1)$-fold degenerate in m_ℓ, since m_ℓ can have values $-\ell,-\ell+1,\ldots,\ell-1,\ell$. This means that there are $(2\ell+1)$ states with the same energy E_ℓ, each characterized by the magnetic magnetic quantum number m_ℓ. This quantum number can be determined using the following eigenvalues equation:

$$\hat{L}_z Y(\theta,\varphi) = \hbar m_\ell Y_\ell^{m_\ell}(\theta,\varphi). \tag{21.3.9}$$

The interpretation of these results is rather complicated, since the angular momenta are quantum operators and they cannot be drawn as vectors like in classical mechanics. Nevertheless, it is common to depict them heuristically as in figure $21.3.1$,[1] where a set of states with quantum numbers $\ell=2$, and $m_\ell=-2,-1,0,1,2$ are reported. Since $|L|=\sqrt{L^2}=\hbar\sqrt{6}$, the vectors are all shown with length $\hbar\sqrt{6}$. The rings represent the fact that L_z is known with certainty, but L_x and L_y are unknown; therefore every classical vector with the appropriate length and z-component is drawn, forming a cone. The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by ℓ and m_ℓ, could be somewhere on this cone but it cannot be defined for a single system.

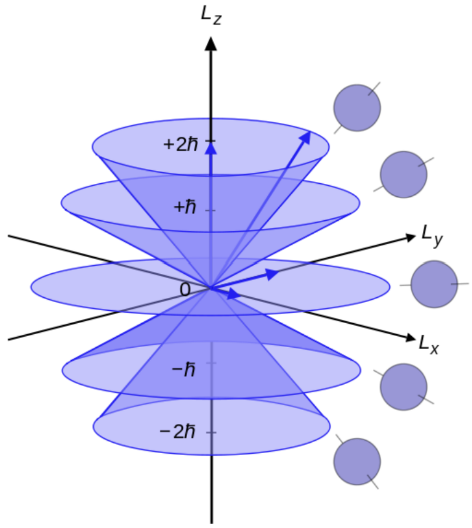

Figure 21.3.1: Illustration of the vector model of orbital angular momentum.

1. This diagram is taken from Wikipedia by user Maschen, and is of public domain