7.4: Angular Momentum Operators and Eigenvalues

Angular momentum is a key component in the physical descriptions of rotating systems. It is important because angular momentum, just like energy and linear momentum, must be conserved in any process. Consequently angular momentum is used to derive selection rules for spectroscopic transitions, determine which states of atoms and molecules can be affected by various perturbations, and identify possible and forbidden mechanisms in chemical reactions. Rotational angular momentum also explains the splitting of spectral lines in electric and magnetic fields and the angular distributions of gas-phase reaction products.

Now that we have the rotational wavefunctions that describe the rotational states, we need the angular momentum operators that enable us to extract the angular momentum properties from the wavefunctions. In this section we develop the operators for total angular momentum and the z-component of angular momentum, and use these operators to learn about the quantized nature of angular momentum for a rotating diatomic molecule.

Since the energy of a rotating object is related to its total angular momentum M and moment of inertia I,

$$M^2 = 2IE \qquad (7.4.1)$$

the quantization of energy arising from the quantum-mechanical treatment of rotation, given by Equation 7.4.1, means that the total angular momentum also is quantized.

$$M^2 = J(J+1)\hbar^2 \qquad (7.4.2)$$

Consequently, J is called the rotational angular momentum quantum number. In the equation above, M^2 is a scalar quantity corresponding to the square of the length of the angular momentum vector, M. From this equation, we can learn something about the magnitude of the angular momentum of the rotating molecule, but nothing about the orientation.

> ### Exercise 7.4.1
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> Show that the combination of Equations 7.4.1 and ??? lead to Equation 7.4.2.

Just as there is an operator for the energy, $\hat{H}$, there also is an operator for the square of the angular momentum. We can discover this operator if we make some substitutions and rewrite Equation ???. Start with Equation ???, and use the spherical harmonic function in place of the product function $\Theta(\theta)\psi(\varphi)$ to obtain

$$-\frac{\hbar^2}{2I}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\partial}\sin\theta\frac{\partial}{\partial\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_J^{mJ}(\theta,\varphi) = EY_J^{mJ}(\theta,\varphi) \qquad (7.4.3)$$

Multiplying both sides by 2I and then using Equation 7.4.1 to replace 2IE on the right-hand side with M^2 yields

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\partial}\sin\theta\frac{\partial}{\partial\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = M^2Y(\theta,\varphi) \qquad (7.4.4)$$

Equation 7.4.4 is an eigenvalue equation. The operator on the left operates on the spherical harmonic function to give a value for M^2, the square of the rotational angular momentum, times the spherical harmonic function. This operator thus must be the operator for the square of the angular momentum.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\partial}\sin\theta\frac{\partial}{\partial\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \qquad (7.4.5)$$

The spherical harmonics therefore are eigenfunctions of $\hat{M}^2$ with eigenvalues given by Equation 7.4.2, where J is the angular momentum quantum number. The magnitude of the angular momentum, i.e. the length of the angular momentum vector, $\sqrt{M^2}$, varies with the quantum number J. The classical interpretation of this fact is that the molecule rotates with higher angular velocity in a state with higher J since neither the mass nor the radius of rotation can change.

The m_J quantum number is associated with the φ-equation, Equation ???. Figure 7.4.8 shows that φ describes rotation about the z-axis. Since angular momentum results from rotation about an axis, it seems plausible that the mJ quantum number is related to the z-component of angular momentum. To demonstrate that this association of m with the z-component of angular momentum is indeed correct, we need to write an operator for the z-component of angular momentum. When we operate on the Φ function with this operator, we expect to get an eigenvalue for the z-component of angular momentum.

We create an angular momentum operator by changing the classical expression for angular momentum into the corresponding quantum mechanical operator. The classical expression for the z-component of angular momentum is

$$M_z = xp_y - yp_x \tag{7.4.6}$$

By substituting the equivalents for the coordinates and momenta we obtain

$$\hat{M}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \tag{7.4.7}$$

After changing to spherical coordinates by using the chain rule and trigonometric identities , $\hat{M}_z$ becomes

$$\hat{M}_z = i\hbar \frac{\partial}{\partial \varphi} \tag{7.4.8}$$

Exercise 7.4.2

Start with $\dfrac{\partial}{\partial \varphi}$ and change to Cartesian coordinates by using the chain rule to prove that

$$\frac{\partial}{\partial \varphi} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}. \tag{7.4.9}$$

Exercise 7.4.3

Use the operator $\hat{M}_z$ to operate on the general form of the wavefunction $\phi_m(\varphi)$ given in Equation ???. Based on your result, what are the possible values for the z-component of the angular momentum?

In Exercise 7.4.15 we did indeed produce an eigenvalue equation that tells us that the z-component of angular momentum is

$$M_z = m_J \hbar \tag{7.4.10}$$

The z-component of the angular momentum is very useful because it provides information about the orientation of the total angular momentum vector, M. The magnitude of the total angular momentum vector, M, can be determined from M^2, but it is only through the value of M_z that we know anything about the orientation of M.

Exercise 7.4.4

Determine the lengths of the angular momentum vectors, M, for $J = 0$, 1, and 2 and the lengths of their projections on the z-axis.

One might expect from classical mechanics to be able to obtain the other two components of angular momentum, M_x and M_y, as well. These components are the projections of the angular momentum vector onto the x- and y-axes. In order for the rigid rotor wavefunctions to be eigenfunctions of $\hat{M}_x$ and $\hat{M}_y$ as well as $\hat{M}_z$, these operators must commute with $\hat{M}_z$. They do not **commute**. Since the rigid rotor wavefunctions are not eigenfunctions of $\hat{M}_x$ and $\hat{M}_y$, we cannot obtain their eigenvalues, which is another way of saying that we cannot know anything about the x and y components of angular momentum. Only the z component of the angular momentum can be determined in the quantum mechanical system. This limitation is a manifestation of the Heisenberg Uncertainty Principle. Since we know M_z exactly (there is no uncertainty), we can have no knowledge of M_x or M_y (the uncertainty must be infinite). This conclusion means that the angular momentum vector can be pointing with equal probability anywhere on a circle around the z-axis, giving all possible projections on the x and y axes. See Figure 7.4.1 for an illustration with J = 1 and $m_J = -1$, 0, and +1.
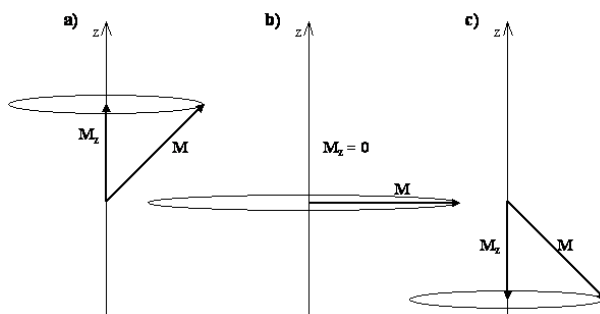
Figure 7.4.1: The three possible orientations of the angular momentum vector M relative to the z axis for the J = 1 states. a) $m_J = 1$, b) $m_J = 0$ and c) $m_J = -1$. The lengths of the vectors are determined by Exercise 7.4.16 and the orientation angle is discussed below. The end of the M vector can lie at any point on the circle perpendicular to the z axis.

As we saw in Exercise 7.4.16, the quantum mechanical results for a rotating diatomic molecule provide us with the magnitudes of the angular momentum vector for each state, along with the projection of the vector for that state along the z-axis. We can get no information about the projection of the vector on the other two axes. Using this collection of results and a little trigonometry, we can construct the quantitative physical picture of the angular momentum vector for each of the rotational states that is shown in Figure 7.4.1. If α is the angle between the angular momentum vector and the z-axis, then in general

$$\cos\alpha = \frac{m_J\hbar}{\sqrt{J(J+1)\hbar^2}} \tag{7.4.11}$$

where α can be obtained using the inverse cosine (arccos)

$$\alpha = arccos\left[\frac{m_J}{\sqrt{J(J+1)}}\right] \tag{7.4.12}$$

Exercise 7.4.5

Calculate the possible angles a $J=1$ angular momentum vector can have with respect to the z-axis.

Exercise 7.4.6

What is the rotational energy and angular momentum of a molecule in the state with $J=0$? Describe the rotation of a molecule in this state.

Classically the plane of rotation is perpendicular to the angular momentum vector. We can locate angular momentum vectors shown in Figure 7.4.1 for any rotational state by calculating the value of α using the appropriate quantum numbers for that state in Equation ???. If we then impose the classical interpretation of the angular momentum vector, we can construct a physical picture of a rotating diatomic molecule associated with the angular momentum vector for each rotational state, as discussed in the next section of this chapter.