

The real functions are constructed by linear superposition of eigenfunctions with $+K$ and $-K$ eigenvalues:

$$\cos K\phi = \frac{1}{2}(e^{iK\phi} + e^{-iK\phi}) \quad (15.17)$$

Hence the angular momentum associated with real functions has an average value of zero. The functions in Eqs. (15.14) and (15.15) contain information on the energy but not on the angular momentum. If the particle has a precise angular momentum (which is the case, for example, for a charged particle in a magnetic field), we must use the eigenfunctions of the angular momentum operator, that is, the complex functions.

We will now consider a more general case for rotational motion. In this model the particle is not restricted to any particular plane. The distance from the center is still fixed. As in the case of the plane rotor, we will set the potential energy V equal to zero.

According to classical mechanics, the total energy of such a system is given by

$$E = \frac{I^2}{2I} \quad (15.18)$$

where I is the moment of inertia and I^2 is the square of the total angular momentum. The relation between the total angular momentum and its components is given by

$$\begin{aligned} I^2 &= I_x^2 + I_y^2 + I_z^2 \\ I^2 &= I^2 + I^2 + I^2 \end{aligned} \quad (15.19)$$

The Schrödinger Equation

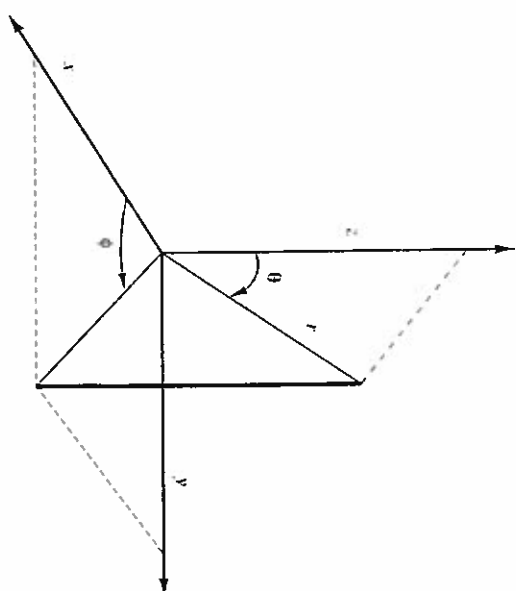
In order to find the wave functions and the energies of a rigid rotor, we must construct the Hamiltonian from Eq. (15.18) and solve the corresponding Schrödinger equation. The results of the theory, however, can be understood without going through the lengthy mathematics involved in solving the Schrödinger equation for a rigid rotor. Hence we will outline the theory and state the results.

The Schrödinger equation for a rigid rotor is solved in a spherical polar coordinate system (Fig. 15.5). In this system r is the distance from the center (θ range 0 to π) is the angle between r and the z axis, and ϕ (range 0 to 2π) is the angle in the xy plane.

Since the distance r is fixed, each wave function Y is a function of only θ and ϕ :

$$Y = Y(\theta, \phi) \quad (15.20)$$

Fig. 15.5. Relation between the spherical and spherical polar coordinate systems. A point is represented by x , y , and z in the Cartesian coordinate system, and by r , θ , and ϕ in the spherical polar coordinate system. $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, and $z = r \cos \theta$. A volume element in spherical polar coordinates is given by $dV = r^2 \sin \theta dr d\theta d\phi$.



(These functions are called *spherical harmonics*, and Y is the standard symbol for them.) The Schrödinger equation for a rigid rotor is

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) \right] = EY \quad (15.21)$$

This is a partial differential equation with two variables. In order to solve Eq. (15.21) we have to separate it into two ordinary differential equations. The separation is accomplished by writing the wave function as a product of two functions:

$$Y = \Theta(\theta)\Phi(\phi) \quad (15.22)$$

Substitution of this equation into Eq. (15.21) followed by a little algebra yields two ordinary differential equations. They are

$$\frac{d^2\Phi}{d\phi^2} = -K^2\Phi \quad (15.23a)$$

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos \theta}{\sin \theta} \frac{d\Theta}{d\theta} - K^2\Theta = \frac{2IE}{\hbar^2} \Theta \quad (15.23b)$$

The first equation is the Schrödinger equation for the plane rotor discussed in the previous section. Energies of a rigid rotor (not confined to a plane) are obtained by solving Eq. (15.23b).

Energies and Wave Functions

Acceptable solutions (periodic, single-valued and continuous functions) for the second equation exist only if

$$J(J+1) = \frac{2IE}{\hbar^2} \quad (15.24)$$

where J is the angular momentum quantum number. It is restricted to the values

$$J = 0, 1, 2, \dots \quad (15.23)$$

As in the case of the plane rotor, K takes the values $0, \pm 1, \pm 2, \dots$. The two differential equations, however, are coupled. Note that K enters into both differential equations. Hence K values are further restricted by J values and are given by the formula

$$K = 0, \pm 1, \pm 2, \dots, \pm J \quad (15.24)$$

The physical reason why $|K|$ cannot exceed J will be clear when we consider the properties of angular momentum in the next section.

From Eq. (15.24) we see that the quantized energies of a rigid rotor are given by

$$E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1) \quad (15.25)$$

where B (J) is called the rotational constant. The energy levels are schematically illustrated in Fig. 15.6. Notice that the energy of the rigid rotor does not depend on K , the quantum number. [Equation (15.12) pertains only to a plane rotor.] In the previous section we noted that K is a measure of angular momentum

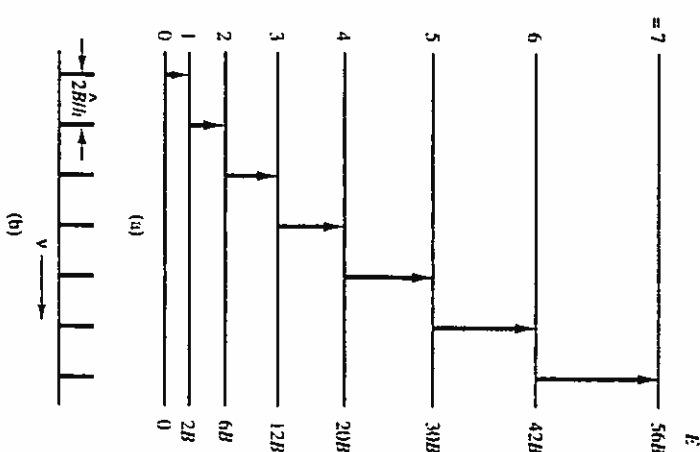


Figure 15.6. (a) Rotational energy levels of diatomic molecules. (b) Expected frequencies in the spectrum. (The relative intensity of the rotational lines, which is not indicated here, depends on the temperature.)

turn along the z axis. Since the choice of the z axis is arbitrary, the energy for a rotor in three dimensions should not depend on K .

There are $(2J+1)$ values of K for each J , as shown by Eq. (15.26). For example, for $J=3$ there are $2 \times 3 + 1 = 7$ values of K . These are $3, 2, 1, 0, -1, -2$, and -3 . Hence each rotational energy level has a $(2J+1)$ -fold degeneracy. This is also indicated in Fig. 15.6.

Table 15.1 lists a few wave functions for a rigid rotor.

TABLE 15.1 SPHERICAL HARMONICS CORRESPONDING TO l, m , AND ϕ FUNCTIONS

$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$
$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$
$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$
$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi}$
$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$

Example 15.2

Show that $Y_{l,0}$ is an eigenfunction of the rigid rotor Hamiltonian. What is the eigenvalue?

The Hamiltonian is given on the left-hand side of Eq. (15.21), and $Y_{l,0}$ in Table 15.1. The first term in the Hamiltonian gives zero since $Y_{l,0}$ is independent of ϕ . The second term gives

$$\begin{aligned} -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y_{l,0}}{\partial \theta} \right) \right] &= -\frac{\hbar^2}{2I} \left[\frac{\partial^2 Y_{l,0}}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial Y_{l,0}}{\partial \theta} \right] \\ &= -\frac{\hbar^2}{2I} \left(\frac{l(l+1)}{4\pi} \right)^{1/2} [-\cos \theta - \cos \theta] = -\frac{\hbar^2}{2I} (l(l+1)) Y_{l,0} \end{aligned}$$

The eigenvalue is $2\hbar^2 l(l+1)/2I$ which is identical to E_l in Eq. (15.27) when $J=l$.

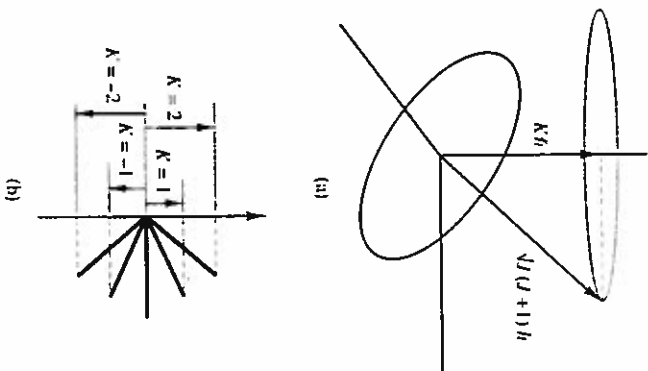


Figure 15.7. Relation between total angular momentum and its z component. According to quantum theory, the total angular momentum vector can take up only certain orientations with respect to an applied field. In (a) the angular momentum vector can be anywhere on the cone around the K axis. For a given value of J a rotor can have $K = J, K = J - 1, \dots, K = -J$ values for the angular momentum along the z axis. Thus the angular momentum vector can take $(2J + 1)$ orientations with respect to the z axis. This is shown for $J = 2$ in (b).

The energy and angular momentum operators play a crucial role in quantum theory. Their importance extends beyond the calculations involving energy and angular momentum. This is because the eigenfunctions of these operators are used in calculating a variety of other properties. We will now describe the angular momentum properties of a rigid rotor. Following that, we will introduce other types of angular momenta encountered in quantum theory.

Rigid Rotor

From Eqs. (15.18) and (15.27) we see that the square of the total angular momentum is quantized and restricted to the following values:

$$I = \sqrt{J(J+1)}\hbar \quad (15.31)$$

Only one of the components—which we have arbitrarily identified as the I_z component—is quantized. The allowed values for the z component of the angular momentum are

$$I_z = K\hbar \quad (15.32)$$

The other two components of the angular momentum do not have precise values, and we can only compute the average values for them. This is a consequence of the commuting properties of angular momentum operators. The total angular momentum operator I^2 commutes with the operators for each of the components I_x , I_y , and I_z , but the latter do not commute among themselves. Hence we can have precise knowledge of the total angular momentum and one of its components. This component is usually taken as the z component.

It may seem odd that the theory identifies a particular component as unique even though the three spatial axes are equivalent. In order to clarify this point about the designation of axes, let us consider a beam of unpolarized light. If a polarizer is inserted into the beam, only half of the intensity of the beam will be transmitted. The polarization of the emergent beam is governed by the orientation of the polarizer. We visualize the unpolarized light as a superposition of two beams polarized along the two directions perpendicular to the axis of propagation. These directions may be designated x and y even though there is no particular reason to distinguish them until we insert the polarizer. In a similar fashion we designate the unique axis when the rotor is in an electric or a magnetic field as the z axis and continue to refer to the designation even in the field-free case.

Space Quantization

If the z component of an angular momentum vector can have only $(2J + 1)$ values, it follows that the angular momentum vector can have only $(2J + 1)$ orientations with respect to the z axis. This is illustrated for the $J = 2$ case in Fig. 15.7. The length of the angular momentum vector is proportional to $\sqrt{J(J+1)}$, and that of the z component, to K . [See Eqs. (15.28) and (15.32)]

Hence the angles between the z axis and the direction of the angular momentum vector are given by the relation

$$\cos \theta = \frac{K}{\sqrt{J(J+1)}} \quad (15.30)$$

Since the phenomenon of restricted orientation is called **space quantization**.

$$K(\max) = J \quad J < \sqrt{J(J+1)} \quad (\text{for } J > 0) \quad (15.31)$$

the total angular momentum vector can never be completely aligned with the z axis. Since I_x and I_y cannot have precise values, the total angular momentum vector cannot be fixed along a particular direction in space. As a consequence, the angular momentum vector precesses around the z axis at an angle given by Eq. (15.30). This behavior is consistent with the uncertainty principle, which would be violated if the angular momentum vector were to have a precise orientation.

At large J values we will have a large number of orientations about the z axis. Besides,

$$K(\max) = J \cong \sqrt{J(J+1)} \quad (15.32)$$

for large J . Hence we can have nearly complete orientation along the z axis. Thus at very high J values quantum results converge to classical results.

Consider a rigid rotor with $J = 2$. Calculate the angles of orientation of its angular momentum vector with respect to the z axis.

Since $J = 2$, the total angular momentum is

$$I = \sqrt{2(2+1)}\hbar = 2.45\hbar$$

The z components of the angular momentum are

$$I_z = 2\hbar, 1\hbar, 0\hbar, -1\hbar, -2\hbar$$

Hence

$$\cos \theta = 2/2.45, 1/2.45, 0, -1/2.45, -2/2.45$$

and

$$\theta = 35.28^\circ, 65.91^\circ, 90^\circ, 114.09^\circ, 144.72^\circ$$

Orbital and Intrinsic Angular Momenta

Even though we are concerned with rotational motion in this chapter, this is a good place to examine related topics. In atomic and molecular theories we come across a variety of angular momenta. They are associated with orbital motion of electrons, rotational motion of molecules, spin of electrons, spin of nuclei, and combinations of two or more of these modes. Table 15.2 lists some of these angular momenta and the standard symbols for them. In each case the total angular momentum and one of its components is quantized as indicated in the table.

There is an important distinction between the orbital or the rotational

Example 15.3

TABLE 15.2 SYMBOLS OFTEN USED FOR ANGULAR MOMENTA

Type of motion	Symbol for angular momentum	Symbol for z component	Allowed values of angular momentum	Allowed values for z component
Orbital motion of electron	l	m_l	$\sqrt{l(l+1)}\hbar, l = 0, 1, \dots$	$0, \pm\hbar, \dots, \pm l\hbar$
Orbital motion of many electrons	L	M_L	$\sqrt{L(L+1)}\hbar$	$0, \pm\hbar, \dots, \pm l\hbar$
Spin of electron	s	m_s	$\sqrt{s(s+1)}\hbar, s = \frac{1}{2}$	$\pm\hbar$
Spin of many electrons	S	M_S	$\sqrt{S(S+1)}\hbar$ S is an integer if the number of electrons is even, it is a half-integer otherwise	$0, \pm\hbar, \dots, \pm S\hbar$ if S is an integer, $\pm\frac{1}{2}\hbar, \pm\frac{3}{2}\hbar, \dots, \pm S\hbar$ if S is a half-integer
Spin of nucleus	I	M_I	$\sqrt{I(I+1)}\hbar$ I is fixed for any given nucleus; it is either an integer or a half-integer	$0, \pm\hbar, \dots, \pm l\hbar$ if I is an integer, $\pm\frac{1}{2}\hbar, \pm\frac{3}{2}\hbar, \dots, \pm I\hbar$ if I is a half-integer
Rotational motion of molecules	J	K, M_J	$\sqrt{J(J+1)}\hbar, J = 0, 1, \dots$	$0, \pm\hbar, \dots, \pm J\hbar$

* K is used to denote the angular momentum along the molecule fixed axis, and M_J the angular momentum along the space fixed axis.

angular momentum and what will be referred to as the spin or the intrinsic angular momentum. The former has a counterpart in classical physics, and it can be visualized as a property of particles moving in orbits. For this type of motion the total angular momentum has integer quantum numbers, as we have seen above. [It should be remembered that if the quantum number is 3, for example, then the actual value of the angular momentum is $\sqrt{3(3+1)}\hbar$.] The z component can have only integer values, as indicated in Eq. (15.29).

In Chap. 17 we will present experimental evidence for the existence of another type of angular momentum called spin or intrinsic angular momentum. There is no classical counterpart to this type of angular momentum even though one customarily associates it with particles rotating around their own axis. (Calling it intrinsic angular momentum, even occasionally, avoids imprinting a firm belief in solid objects whirling around their axes.) According to quantum theory, the intrinsic angular momentum quantum number of a particle can be either an integer or a half-integer. Thus the angular momentum associated with the spin of an electron is $\frac{1}{2}\hbar$. The z component may have the values $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. In general, the quantum numbers for the z component of the intrinsic angular momentum take the values $l, l-1, \dots, -l$, where l is an integer or a half-integer. (See Table 15.2.)

15.8 HETERONUCLEAR DIATOMIC MOLECULES

The theory developed in the previous section can be used, with only a slight modification, to explain the important features of the rotational spectra of diatomic molecules. This is because a diatomic molecule executing rotational motion is mathematically identical to a single-particle rotor. We will prove this statement now.

Rotational Energies of Diatomic Molecules

If a molecule exhibits only rotational motion, its center of mass will remain fixed. The distances of the two atoms, r_1 and r_2 , from the center of mass are related by the equation

$$m_1 r_1 = m_2 r_2 \tag{15.33}$$

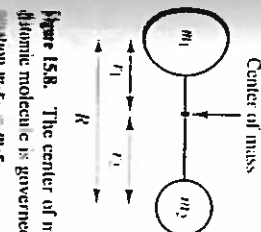


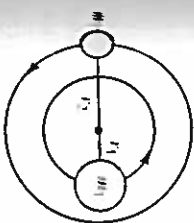
Figure 15.8. The center of mass of a diatomic molecule is governed by the equation $m_1 r_1 = m_2 r_2$.

(See Fig. 15.8.) If we add $m_2 r_1$ to both sides of the above equation and rearrange it, we have

$$r_1 = \frac{m_2 R}{m_1 + m_2} \tag{15.34}$$

where R is the bond length. ($R = r_1 + r_2$.) The same logic also gives

$$r_2 = \frac{m_1 R}{m_1 + m_2} \tag{15.35}$$



The moment of inertia of a diatomic molecule is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \tag{15.36}$$

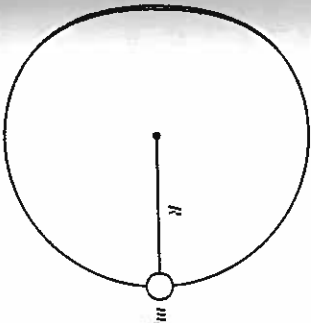
When the expressions for r_1 and r_2 are substituted into this equation, we have

$$I = m_2 R^2 \tag{15.37}$$

where m_2 is called the reduced mass. It is related to the masses of the two atoms by the expression

$$m_2 = \frac{m_1 m_2}{m_1 + m_2} \tag{15.38}$$

Figure 15.9. Two equivalent models. Rotation of a diatomic molecule around its center of mass is equivalent to rotation of a single particle of reduced mass $m_2 = [m_1 m_2 / (m_1 + m_2)]$ at a distance $R = r_1 + r_2$. Note that the reduced mass is smaller than either of the two masses.



Equation (15.37) is the formula for the moment of inertia of a rigid rotor with a mass of m_2 . Hence the rotational energies of a diatomic molecule are given by Eq. (15.27), provided we use the reduced mass instead of the mass of a single particle, and follow the pattern shown in Fig. 15.6.

Figure 15.9 shows the relation between a rotating diatomic molecule and the rigid rotor model.

The bond length of the $^{12}\text{C}^{16}\text{O}$ molecule is determined from the rotational spectrum to be 112.8 pm. Calculate (a) the reduced mass, (b) the moment of inertia, and (c) the first three rotational energies.