7.3: Solving the Rigid Rotor Schrödinger Equation

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a ϕ-function depending only on φ

$$\psi(\theta, \varphi) = \Theta(\theta)\Phi(\varphi) \tag{7.3.1}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 7.3.2:

$$\hat{H}\psi(\theta, \varphi) = E\psi(\theta, \varphi) \tag{7.3.2}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = E\Theta(\theta)\Phi(\varphi) \tag{7.3.3}$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 7.3.3, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = E\Theta(\theta)\Phi(\varphi) \tag{7.3.4}$$

To begin the process of separating the variables in Equation 7.3.4, multiply each side of the equation by $\dfrac{2I}{\hbar^2}$ and $\dfrac{-\sin^\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = \frac{-2IE\sin^2\theta}{\hbar^2} \tag{7.3.5}$$

Simplify the appearance of the right-hand side of Equation 7.3.5 by defining a parameter λ:

$$\lambda = \frac{2IE}{\hbar^2} \tag{7.3.6}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 7.3.6.

Inserting λ, evaluating partial derivatives, and rearranging Equation 7.3.5 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) + \left(\lambda\sin^2\theta\right)\Theta(\theta)\right] = -\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{7.3.7}$$

> ### Exercise 7.3.1
>
> Carry out the steps leading from Equation 7.3.5 to Equation 7.3.7. Keep in mind that, if y is not a function of x,
>
> $$\frac{dy}{dx} = y\frac{d}{dx} \tag{7.3.8}$$

Equation 7.3.7 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta) + \left(\lambda\sin^2\theta - m^2\right)\Theta(\theta) = 0 \tag{7.3.9}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + m^2\Phi(\varphi) = 0 \qquad (7.3.10)$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

> **Exercise 7.3.2**
>
> Show how Equations 7.3.9 and 7.3.10 are obtained from Equation 7.3.7.

The φ-equation is similar to the Schrödinger equation for the free particle. Since we already solved this differential equation in Chapter 5, we immediately write the solutions:

$$\Phi_m(\varphi) = Ne^{\pm im\varphi} \qquad (7.3.11)$$

> **Exercise 7.3.3**
>
> Substitute Equation 7.3.11 into Equation 7.3.10 to show that it is a solution to that differential equation.

The normalization condition, Equation 7.3.12, is used to find a value for N that satisfies Equation 7.3.11.

$$\int_0^{2\pi} \Phi^*(\varphi)\Phi(\varphi)d\varphi = 1 \qquad (7.3.12)$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

> **Exercise 7.3.4**
>
> Use the normalization condition, Equation 7.3.11 to show that
>
> $$N = (2\pi)-\frac{1}{2}. \qquad (7.3.13)$$

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi + 2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi + 2\varphi)$, i.e.

$$e^{im\varphi} = e^{im(\varphi+2\pi)} \qquad (7.3.14)$$

$$= e^{im\varphi}e^{im2\pi} \qquad (7.3.15)$$

For the equality in Equation 7.3.15 to hold, $e^{im2\pi}$ must equal 1, which is true only when

$$m = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \qquad (7.3.16)$$

In other words m can equal any positive or negative integer or zero.

> **Exercise 7.3.5**
>
> Use Euler's Formula to show that $e^{im2\pi}$ equals 1 for m equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_m(\varphi) = (2\pi)^{-1/2}e^{\pm im\varphi} \qquad (7.3.17)$$

$$\text{with } m = 0, \pm 1, \pm 2, \cdots \qquad (7.3.18)$$

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation, Equation 7.3.9, is a more complicated process. Solutions are found to be a set of power series called Associated Legendre Functions, which are power series of trigonometric functions, i.e. products

and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 7.3.1.

Table 7.3.1: Spherical Harmonic Wavefunctions

m	J	$\Theta_J^m(\theta)$	$\Phi(\varphi)$	$Y_J^m(\theta, \varphi)$
0	0	$\dfrac{1}{\sqrt{2}}$	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\dfrac{3}{2}}\cos\theta$	$\dfrac{1}{\sqrt{2\pi}}$	$\sqrt{\dfrac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\dfrac{3}{4}}\sin\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\dfrac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\dfrac{3}{4}}\sin\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\dfrac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\dfrac{5}{8}}(3\cos^2\theta - 1)$	$\dfrac{1}{\sqrt{2\pi}}$	$\sqrt{\dfrac{5}{16\pi}}(3\cos^2\theta - 1)$
1	2	$\sqrt{\dfrac{15}{4}}\sin\theta\cos\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\dfrac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\dfrac{15}{4}}\sin\theta\cos\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\dfrac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\dfrac{15}{16}}\sin^2\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\dfrac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\dfrac{15}{16}}\sin^2\theta$	$\dfrac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\dfrac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 7.3.7 be given by

$$\lambda = J(J+1) \tag{7.3.19}$$

where

$$J \geq |m| \tag{7.3.20}$$

J can be 0 or any positive integer greater than or equal to m. Each pair of values for the quantum numbers, J and m, identifies a rotational state and a wavefunction. For clarity in remembering that J controls the allowed values of m, m is often referred to as m_J, and we will now use that notation.

The combination of Equations 7.3.6 and 7.3.19 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{7.3.21}$$

> **Exercise 7.3.6**
>
> Compute the energy levels for a rotating molecule for J = 0 to J = 5 using units of $\dfrac{\hbar^2}{2I}$.

Using Equation 7.3.21, you can construct a rotational energy level diagram. For simplicity, use energy units of $\dfrac{\hbar^2}{2I}$. The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only one state with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.

The next energy level is $J = l$ with energy $\dfrac{2\hbar^2}{2I}$. There are three states with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. These states are discussed in detail in Sections

7.3 and 7.4. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = l$ energy level is 3 because there are three states with the energy $\dfrac{2\hbar^2}{2I}$.

The next energy level is for $J = 2$. The energy is $\dfrac{6\hbar^2}{2I}$, and there are five states with this energy corresponding to $m_J = +2, +1, 0, -1, -2$. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J + 1$ because m_J ranges from $+J$ to $-J$ in integer steps, including 0.

Exercise 7.3.7

For $J = 0$ to $J = 5$, identify the degeneracy of each energy level and the values of the mJ quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram (see Drawing Energy Level Diagrams) including $J = 0$ through 5. Label each level with the appropriate values for the quantum numbers J and m_J. Describe how the spacing between levels varies with increasing J.

A wavefunction that is a solution to the rigid rotor Schrödinger equation (defined in Equation 7.3.1) can be written as a single function Yθ, φ), which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{7.3.22}$$

The spherical harmonic wavefunction is labeled with mJ and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in Table 7.3.1 plots of some of the θ-functions are shown in Figure 7.3.1.
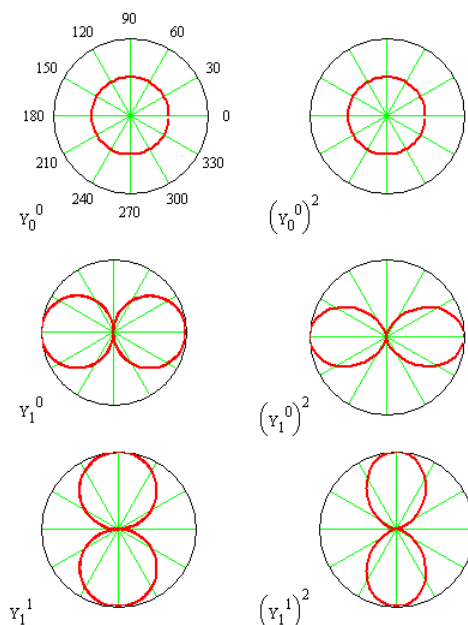

Figure 7.3.1: Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 7.3.2.
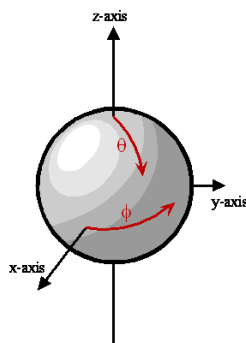
Figure 7.3.2: Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0)Y_J^{m_J}(\theta_0, \varphi_0)ds \tag{7.3.23}$$

where the area element ds is centered at θ_0 and φ_0. The absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi)Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis, and in spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta d\theta d\varphi \tag{7.3.24}$$

Exercise 7.3.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double integral will be needed. Sketch this region as a shaded area on Figure 7.3.1.

Consider the significance of the probability density function by examining the J = 1, mJ = 0 wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta \tag{7.3.25}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 7.3.1. For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when $\theta = 90°$. Therefore, the entire xy-plane is a node. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

Exercise 7.3.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 7.3.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e. the most probable values for θ and θ.

Exercise 7.3.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure $7.3.1$. Compare this information to the classical picture of a rotating object.

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