

14.2: Rotational Quantum Mechanics- Introduction

In chemistry, we are deeply concerned about electrons and how they can bunch up (bond), or not (antibond), between atomic nuclei; this is how molecules form. Unfortunately, atoms are round and their electrons may orbit the nucleus like the Moon rotates about the Earth. This means that electrons have angular momentum and rotational kinetic energy. We must use quantum mechanics to understand how rotation works for light particles such as electrons. Rotational quantum mechanics also applies to rotational spectroscopy of molecules, which is in the microwave region of the electromagnetic spectrum.

The most important thing about rotational energy is to determine the rotational kinetic energy operator. You may be thinking, “how is rotational kinetic energy different than translational kinetic energy?” This indeed sounds like a very difficult question; fortunately, the answer is that *it isn't different*. Meaning, the kinetic energy Hamiltonian we discussed above: $\frac{-\hbar^2}{2 \cdot mass} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$, hasn't changed at all! However, there is one slight problem- Cartesian coordinates are not very useful for round objects like atoms. Rather, we want to use either cylindrical or spherical coordinates. Thus, changing the kinetic energy operator from Cartesian (x, y, z) into cylindrical (r, ϕ , z) or spherical (r, ϕ , θ) coordinates is our first objective.

14.2.1 Cylindrical Coordinate Transformation

If you don't recall how cylindrical and spherical coordinates work see the Example box on the next page. Once you are comfortable with these trigonometric equations, we can start on transforming the coordinate system by describing an object rotating exclusively in the x-y plane using cylindrical variables. This means that x, y \rightarrow r, ϕ , while z remains z. Our first model is for a quantum mechanical particle that rotates in a flat x-y plane with a fixed radius; this is referred to as a 2D rigid rotor. Since the object does not move in the z direction we can leave the z coordinate out of the kinetic energy operator as so:

$$\hat{H}_{2D} = \frac{-\hbar^2}{2 \cdot mass} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

This simplifies our transformation problem. The first step is to use the product rule to relate $x \rightarrow r$ as follows:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r}$$

However, since x is a function of both r and ϕ we must include the ϕ dependency as well:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}$$

Consequently, the transformation requires us to evaluate $\frac{\partial r}{\partial x}$ and $\frac{\partial \phi}{\partial x}$. Based on the relationships on the previous page, we see that $r = \sqrt{x^2 + y^2}$ and thus:

$$\frac{\partial r}{\partial x} = \frac{\partial \sqrt{x^2 + y^2}}{\partial x} = \frac{1}{2} (x^2 + y^2)^{-1/2} \cdot 2x = \frac{x}{\sqrt{x^2 + y^2}} = \frac{x}{r}$$

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$$\frac{\partial \phi}{\partial x} = \frac{\partial \tan^{-1}(y/x)}{\partial x} = \frac{1}{1 + (y/x)^2} \cdot \left(-\frac{y}{x^2} \right) = -\frac{y}{x^2 + y^2} = -\frac{y}{r^2}$$

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$$\frac{\partial \phi}{\partial x} = -\frac{y}{r^2}$$

Recall that we are not here to represent anything with x and y, rather r and ϕ . Thus, we must recognize that $\frac{\partial}{\partial x} = \frac{\partial}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial}{\partial \phi} \frac{\partial \phi}{\partial x}$

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$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r} \frac{x}{r} - \frac{\partial}{\partial \phi} \frac{y}{r^2}$$

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$\cos(\phi)$. Putting this altogether we see:

$$\frac{\partial}{\partial x} \left(\frac{1}{r} \right) = -\frac{x}{r^3}$$

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$$= \frac{1}{r^3} \cdot (-x)$$

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$$\cos(\phi) =$$

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$$\cos(\phi) =$$

Likewise, we evaluate $\frac{\partial \phi}{\partial x}$ as:

$$\frac{\partial \phi}{\partial x} = \frac{\partial}{\partial x} \left(\arctan\left(\frac{y}{x}\right) \right) = -\frac{y}{x^2 + y^2}$$

Tying this all together reveals:

$$\frac{\partial}{\partial x} \left(\frac{1}{r} \right) =$$

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$$\cos(\phi) \frac{\partial}{\partial r} - \frac{\sin(\phi)}{r} \frac{\partial \phi}{\partial x}$$

A similar derivation for the y-coordinate reveals:

$$\frac{\partial}{\partial y} \left(\frac{1}{r} \right) =$$

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$$\sin(\phi) \frac{\partial}{\partial r} + \frac{\cos(\phi)}{r} \frac{\partial \phi}{\partial x}$$

The way to transform the kinetic energy operator is to evaluate $\frac{\partial^2}{\partial x^2}$ and $\frac{\partial^2}{\partial y^2}$ using the relationships above. The algebra involved isn't difficult but there are a very large number of steps; regardless, the end result is:

$$\hat{H} = \frac{-\hbar^2}{2 \cdot mass} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \rightarrow \frac{-\hbar^2}{2 \cdot mass \cdot r^2} \cdot \frac{\partial^2}{\partial \phi^2}$$

14.2.2 2D rigid rotor

For this model problem, called the 2D rigid rotor, we assume that a light particle circulates on a flat potential in the x and y plane with a fixed z coordinate. The radius of the motion is fixed, so the particle travels around and around a completely flat track. We will begin by making an analogy to the particle in a box problem, which will allow us to introduce concepts important to rotation and to calculate the energy. To this end we create a visual representation of what the wavefunctions should look like by drawing the particle in a box states on a piece of paper as shown in Figure 14.4 A. There is one additional $n = 0$ state that has no kinetic energy; please note that the particle in a box doesn't have a $n = 0$ state due to its zero-point energy. Next, we fold the paper over to see how each wavefunction bites its own tail as seen in Figure 14.4 B. Doing so allows us to see whether the wavefunction is smooth and

continuous at the seam, for which we can that is the case for the $n = 0$ and $n = 2$ states. As a result, these are valid 2D rigid rotor wavefunctions. In contrast, the $n = 1$ and $n = 3$ are continuous but they are not smooth, and as such they are not valid 2D rigid rotor wavefunctions. If we analyze the other states we find that odd symmetry ones are ok, while the symmetric ones are not.

We can now calculate the de Broglie wavelength for the allowed states, which provides the momentum and thus the k vectors for the wavefunctions and allows us to calculate the energy. We can see from the figure that the allowed $n=0$ state has an infinite wavelength and that the $n = 2$ has a wavelength $\lambda = C$. We can assume that the other allowed states are $n = 4$ which has $\lambda = \frac{C}{2}$ and $n = 6$ for which $\lambda = \frac{C}{3}$. From here we can generate an empirical relationship: $\lambda = \frac{L}{m}$, where $m = 0, 1, 2, \dots$ and appears to act like a quantum number. As it is not proper to express this wavelength as a function of the circumference of the track (C , same as the length of the particle in a box), rather its radius, for which we substitute $2\pi r = C$. We see that the wavelengths for allowed 2D rigid rotor states are: $\lambda = \frac{2\pi r}{m}$. The de Broglie momenta are then:

$$\frac{h}{\lambda} = \frac{hm}{2\pi r} = \frac{\hbar m}{r}$$

and the energy is momentum squared over mass:

$$E = \frac{\hbar^2 m^2}{2 \cdot mass \cdot r^2}$$

where $\hbar = \frac{h}{2\pi}$. Despite the unconventional approach we have taken the equation for energy above is correct and reveals the existence of a new quantum number “ m ” for 2D rotation. To finish out this section we introduce some terminology. We are describing a component of orbital rotational angular momentum which is typically given the symbol “ l_z ”. It is important to note this here because later we will see that there is another quantity called the spin angular momentum that has to be added to calculate the total. Discussion on these topics are forthcoming; as it applies to the 2D rigid rotor and the energy of rotational motion is:

$$E = \frac{l_z^2}{2I}$$

where $I = mass \cdot r^2$ and is called the moment of inertia. From the analogy to the equation for energy above we can see that $l_z = \hbar m$, and thus rotational momenta are quantized due to the need for the wavefunction to “bite its tail”, i.e. be smooth and continuous.

14.2.2.1 2D Rigid Rotor Wavefunctions

The above is a fine start to demonstrate the principles of rotational quantum mechanics; however here we will employ more rigorous mathematics. We first find the wavefunctions which can be used to calculate the energies and evaluate other properties. This is accomplished by defining the angular momentum operator:

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

which makes potential-free Hamiltonian: $\hat{H} = \frac{\hat{L}_z^2}{2I} = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$. Now the eigenvalue (Schrödinger) equation can be defined as:

$$\frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \Psi(\phi) = E \cdot \Psi(\phi)$$

where, as before, I is the moment of inertia. The wavefunction solution to the above is:

$$e^{i \cdot m \cdot \phi}$$

where “ m ” is a constant that must be determined using boundary conditions. As you recall the same approach allowed us to determine all the details of the particle in a box. Concerning boundary conditions, we can see from Figure 14.4 B that the wavefunctions must be continuous at the “seam”, which is defined where $\phi = 0$ meets $\phi = 2\pi$. Thus, $\Psi(\phi) = \Psi(\phi + 2\pi)$, which when applied to the wavefunction:

$$e^{i \cdot m \cdot (\phi + 0)} = e^{i \cdot m \cdot (\phi + 2\pi)} = e^{i \cdot m \cdot \phi} e^{i \cdot m \cdot 2\pi}$$

This only works if $e^{i \cdot m \cdot 2\pi} = 1$, which means that $m = dots, -2, -1, 0, 1, 2, \dots$ using identities for complex exponentials. As before, we have a new integer quantum number defined in exactly the same way as was found using our earlier approach to explore

the 2D rigid rotor. One difference between the m quantum number and earlier examples is that it can be negative. This actually has a simple meaning; a positive m is for a quantum particle rotating clockwise while a negative value is for a particle rotating counterclockwise. If the 2D rigid rotor decides not to rotate at all, then $m=0$.

The rotational energy is:

$$\frac{\hat{L}_z^2}{2I} \Psi(\phi) = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \Psi(\phi) = \frac{\hbar^2 m^2}{2I} \cdot \Psi(\phi)$$

and is exactly the same result derived previously. As usual we should normalize the state(s) via:

$$\int_0^{2\pi} N^2 \cdot e^{-i \cdot m \cdot \phi} \cdot e^{i \cdot m \cdot \phi} d\phi = N^2 \cdot \phi \Big|_0^{2\pi} = N^2 2\pi = 1$$

which reveals that the proper normalized wavefunction is:

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i \cdot m \cdot \phi}$$

There isn't much more to say about this rather simple introduction to rotation, and as such we now move onto a particle that isn't trapped in the x-y plane as discussed below. Before we do so, you should know that you will see the 2D rigid rotor once more when the wavefunctions for the hydrogen atom are calculated. In fact, this is where we get our notion for p_x , p_y and p_z orbitals; these are revealed in Ch. 15.

14.2.3 The 3D rigid rotor

For exploring rotational motion in three dimensions we will create the most simple model possible by stating that a quantum particle rotates with a fixed radius on a 3D track that has no potential energy. As with the 2D case we first develop the kinetic energy operator. To this end we convert coordinates $x, y, z \rightarrow r, \phi, \theta$ step by step beginning with:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta}$$

and then the same for $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$. With these worked out we can then convert the kinetic energy operator into the same using spherical coordinates. Unfortunately, the algebra to do so is extraordinarily tedious and as a result we will simply provide the end result here:

$$\hat{H} = \frac{-\hbar^2}{2 \cdot mass} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \rightarrow \frac{-\hbar^2}{2I} \cdot \left(\frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right)$$

where the moment of inertial is defined as before: $I = mass \cdot r^2$. The above Hamiltonian is usually simplified as: $\hat{H} = \frac{\hat{L}^2}{2I}$, where \hat{L} is the total (3D) orbital angular momentum operator. Regardless of the notation, the Hamiltonian in spherical coordinates appears pretty fearsome and there isn't much we can do about that other than to begin to solve it using the method of separability. First, we assume that the solution has the form:

$$\psi(\phi, \theta) = \psi(\phi) \psi(\theta)$$

This separated wavefunction is applied to the Hamiltonian: $\hat{H} \psi(\phi) \psi(\theta)$:

$\frac{\partial}{\partial \phi}$

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$\sin(\theta) \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) \psi(\theta) = E \cdot \psi(\theta)$

Moving the constants to right side makes this look a little easier:


$\frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) \psi(\theta) = E \cdot \psi(\theta)$

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$$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{-2I\cdot E}{\hbar^2}\psi\left(\phi\right)\psi\left(\theta\right)$$

And now we divide out the wavefunction on the left side:

$$\frac{1}{\psi\left(\phi\right)\psi\left(\theta\right)}\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)$$

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$$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{1}{\psi\left(\phi\right)\psi\left(\theta\right)}\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{-2I\cdot E}{\hbar^2}$$

If you are slow and methodical you find that the process of solving the above is fairly straightforward. For example, the $\frac{\partial}{\partial\theta}$ derivative captures $\psi(\theta)$ yet allows $\psi(\phi)$ to pass through (and vice versa); after some algebra we see that:

$$\frac{1}{\psi\left(\phi\right)}\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{-2I\cdot E}{\hbar^2}\psi\left(\theta\right)$$

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$$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{-2I\cdot E}{\hbar^2}\psi\left(\theta\right)$$

At this point there is a problem with separation because the first part:

$$\frac{1}{\psi(\phi) \cdot \sin^2(\theta)} \frac{\partial^2}{\partial\phi^2} \psi(\phi)$$

containing mostly ϕ terms but also has a pesky $\frac{1}{\sin^2(\theta)}$ term. To remove the problem we multiply everything by $\sin^2(\theta)$:

$$\frac{1}{\psi(\phi)} \frac{\partial^2}{\partial\phi^2} \psi(\phi) \sin^2(\theta)$$

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$$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)=\frac{-2I\cdot E}{\hbar^2}\sin^2\left(\theta\right)\psi\left(\phi\right)\psi\left(\theta\right)$$

Now we have a clean separation of ϕ and θ terms into mini-Schrödinger equations, although it is interesting to note that the energy is on the θ side:

$$\frac{1}{\psi(\phi)} \frac{\partial^2}{\partial\phi^2} \psi(\phi) = \frac{-2I\cdot E}{\hbar^2 \sin^2(\theta)}$$

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$$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\phi\right)\psi\left(\theta\right)+\frac{2I\cdot E}{\hbar^2}\sin^2\left(\theta\right)\psi\left(\phi\right)\psi\left(\theta\right)=0$$

To solve this, we assume that the solution to the ϕ mini-Schrödinger equation (left side) is the same as the 2D rigid rotor that we worked on previously: $\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i\cdot m\cdot\phi}$. As a result:

$$\frac{1}{\psi(\phi)} \frac{\partial^2}{\partial\phi^2} \psi(\phi) = \sqrt{2\pi} \cdot e^{-i\cdot m\cdot\phi} \frac{\partial^2}{\partial\phi^2} \frac{1}{\sqrt{2\pi}} e^{i\cdot m\cdot\phi} = -m^2$$

which when inserted into the full equation above we find that:

$$\frac{1}{\psi(\phi)} \frac{\partial^2}{\partial\phi^2} \psi(\phi) = -m^2$$

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$\sin\left(\theta\right)\frac{\partial}{\partial\theta}\psi\left(\theta\right)+\frac{2\cdot E}{\hbar^2}\sin^2\left(\theta\right)=m^2$

One of the most interesting aspects of quantum mechanics is that this differential equation was solved in 1782 by Pierre Simon de Laplace, who was called the “Newton of France” and was one of Napoleon Bonaparte’s teachers. The solutions are called the spherical harmonics and are listed in Table 14.1. The wavefunctions are classified by a new quantum number l , which as usual can only have integer values: $l = 0, 1, 2, 3 \dots$. There are $2l + 1$ wavefunctions associated with each l quantum number, which are due to the 2D rigid rotor quantum number that will now be abbreviated as m_l . They can take on integer values $m_l = l, (l - 1), \dots, 0 \dots -l$, and it is important to note that there are $2l + 1$ possibilities. The wavefunctions are thus abbreviated as Y_{l,m_l} to designate the l and sub- m_l quantum states. Now that we know the wavefunctions we can use them to calculate the total orbital angular momentum using the \hat{L}^2 operator, which returns a function based on the l quantum number:

$$\hat{L}^2 Y_{l,m_l} = l(l+1) \hbar^2 \cdot Y_{l,m_l}$$

This allows to calculate the energy of the 3D rigid rotor:

$$E = l(l+1) \frac{\hbar^2}{2mr^2} = l(l+1) \frac{\hbar^2}{2I}$$

which are $2l + 1$ degenerate as discussed above.

The spherical harmonics are important to a very large number of scientific fields and are often abbreviated as $Y_{l,m_l}(\phi, \theta)$. We will now examine them as a function of the l quantum number, which may look surprisingly similar to the wavefunctions you learned about for the hydrogen atom in Freshman chemistry.

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