Chemistry 431

Lecture 6

Rotational motion
Classical Rotation

In a circular trajectory $J_z = pr$ and $E = J_z^2/2I$. $I$ is the moment of inertia.

Mass in a circle $I = mr^2$. Diatomic $I = \mu r^2$

Reduced mass $\mu = \frac{m_1m_2}{m_1 + m_2}$
Rotation in two dimensions

The angular momentum is $J_z = pr$.

Using the deBroglie relation $p = \hbar/\lambda$ we also have a condition for quantization of angular motion $J_z = hr/\lambda$. 
The 2-D rotational hamiltonian

• The wavelength must be a whole number fraction of the circumference for the ends to match after each circuit.

• The condition $2\pi r/m = \lambda$ combined with the deBroglie relation leads to a quantized expression, $J_z = m\hbar$.

• The hamiltonian is:

$$-\frac{\hbar^2}{2l} \frac{\partial^2 \Phi}{\partial \phi^2} = E\Phi$$
The 2-D rotational hamiltonian

- Solutions of the 2-D rotational hamiltonian are sine and cosine functions just like the particle in a box.
- Here the boundary condition is imposed by the circle and the fact that the wavefunction must not interfere with itself.
- The 2-D model is similar to condition in the Bohr model of the atom.
The 2-D rotational hamiltonian

- The wavelength must be a whole number fraction of the circumference for the ends to match after each circuit.
- The condition $2\pi r/m = \lambda$ combined with the deBroglie relation leads to a quantized expression, $J_z = m\hbar$.
- The hamiltonian is:

$$- \frac{\hbar^2}{2I} \frac{\partial^2 \Phi}{\partial \phi^2} = E \Phi$$
Quantization of rotational motion: solution of the $\phi$ equation

The corresponding wavefunctions are:

$$\Phi_m = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}$$

with the constraint that:

$$m = \pm \frac{(2IE)^{1/2}}{\hat{n}}$$

Since the energy is constrained to values $J_z^2/2I$ we find that $m = 0, \pm 1, \pm 2, \ldots$
The wavefunctions of a rigid rotor are called spherical harmonics

The solutions to the $\theta$ and $\phi$ equation (angular part) are the spherical harmonics $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

Separation of variables using the functions $\Theta(\theta)$ and $\Phi(\phi)$ allows solution of the rotational wave equation.

$$ -\frac{\hbar^2}{2l} \left( \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) \right) = EY $$

We can obtain a $\theta$ and $\phi$ equation from the above equation.
The volume element in spherical polar coordinates

To solve the Schrodinger equation we need to integrate over all space. This is the same thing as performing a volume integral. The volume element is:

\[ dV = r^2 dr \sin \theta d\theta \, d\phi \]

This integrates to \(4\pi\), which is the normalization constant. \(4\pi\) stearadians also gives the solid angle of a sphere.
Separation of variables

The spherical harmonics arise from the product of $\Theta \Phi$ after substituting $Y = \Theta \Phi$

$$\frac{\partial^2 \Phi \Theta}{\partial \phi^2} + \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Phi \Theta}{\partial \theta} \right) = \sin^2 \theta E \Phi \Theta$$

For sake of simplicity, we have factored the term

$$- \frac{n^2}{2l}$$

into the energy. At the end of the calculation we will multiply by this term to obtain the energy.
Separation of variables

The operators in variables $\theta$ and $\phi$ operate on functions $\Theta$ and $\Phi$, respectively, so we can write

$$
\Theta \frac{\partial^2 \Phi}{\partial \phi^2} + \Phi \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta}{\partial \theta} \right) = \sin^2 \theta E \Phi \Theta
$$

When we divide by $Y = \Theta \Phi$, we obtain

$$
\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{1}{\Theta} \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta}{\partial \theta} \right) - \sin^2 \theta E = 0
$$

Now, these equations can be separated.
Separation of variables

We use a separation constant equal to $m^2$ to write two equations. The $\theta$ and $\phi$ equations are

$$\sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta}{\partial \theta} \right) - \sin^2\theta E = m^2$$

$$\frac{1}{\Phi} \left( \frac{\partial^2 \Phi}{\partial \phi^2} \right) = -m^2$$

We have already seen the solution to the $\phi$ equation from the example of rotation in two dimensions.
The solution of $\theta$ equation gives Legendre polynomials

Substitute $x = \cos\theta$ and the equation becomes:

$$
\left(1 - x^2\right)\frac{\partial^2 P}{\partial x^2} - 2x\frac{\partial P}{\partial x} + \left(E - \frac{m^2}{1 - x^2}\right)P = 0
$$

The solution requires that $E \leq -(\hbar^2/2I)J(J+1)$ with $J=0,1,2$.
Where $J$ is the rotational quantum number.
The azimuthal quantum number $m$ is also called $J_z$.
The magnitude of $|J_z| < J$.
The solutions are Legendre polynomials

$P_0(x) = 1$
$P_1(x) = x$
$P_2(x) = 1/2 (3x^2 - 1)$
$P_3(x) = 1/2 (5x^3 - 3x)$
The spherical harmonics as solutions to the rotational Hamiltonian

The spherical harmonics are the product of the solutions to the $\theta$ and $\phi$ equations. With normalization these solutions are

$$Y_J^M(\theta, \phi) = N_{JM} P_J^{|M|}(\cos \theta) e^{iM\phi}$$

The $M$ quantum number corresponds to $J_z$, the $z$ component of angular momentum. The normalization constant is

$$N_{JM} = \left(\frac{2J + 1}{2} \frac{(J - |M|)!}{(J + |M|)!}\right)^{1/2}$$
The form of the spherical harmonics

Including normalization the spherical harmonics are

\[ Y^0_0 = \frac{1}{\sqrt{4\pi}} \]
\[ Y^0_1 = \sqrt{\frac{3}{4\pi}} \cos \theta \]
\[ Y^\pm_1 = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \]
\[ Y^0_2 = \sqrt{\frac{5}{16\pi}} \left( 3\cos^2 \theta - 1 \right) \]
\[ Y^{\pm 1}_2 = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} \]
\[ Y^2_2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} \]

The form commonly used to represent p and d orbitals are linear combinations of these functions
Euler relation

Linear combinations are formed using the Euler relation:

\[ e^{\pm i \phi} = \cos \theta \pm i \sin \theta \]

\[ \sin \theta = \frac{e^{i \phi} - e^{-i \phi}}{2i} \]

\[ \cos \theta = \frac{e^{i \phi} + e^{-i \phi}}{2} \]

Projection along the z-axis is usually taken using
\[ z = r \cos \theta \]
Projection in the x,y plane is taken using
\[ x = r \sin \theta \cos \phi \quad \text{and} \quad y = r \sin \theta \sin \phi \]
The 3-D rotational hamiltonian

- There are two quantum numbers
  - J is the total angular momentum quantum number
  - M is the z-component of the angular momentum
- The spherical harmonics called $Y_{JM}$ are functions whose probability $|Y_{JM}|^2$ has the well known shape of the s, p and d orbitals etc.
  - $J = 0$ is s , $M = 0$
  - $J = 1$ is p , $M = -1, 0, 1$
  - $J = 2$ is d , $M = -2, -1, 0, 1, 2$
Space quantization in 3D

- Solutions of the rotational Schrödinger equation have energies $E = \frac{\hbar^2 J(J + 1)}{2I}$
- Specification of the azimuthal quantum number $m_z$ implies that the angular momentum about the z-axis is $J_z = \hbar m_z$.
- This implies a fixed orientation between the total angular momentum and the z component.
- The x and y components cannot be known due to the Uncertainty principle.
Spherical harmonic for $P_0(\cos \theta)$

- Plot in polar coordinates represents $|Y_0^0|^2$ where $Y_0^0 = (1/4\pi)^{1/2}$.
- Solution corresponds to rotational quantum numbers $J = 0$, $M = 0$.
- Polynomial is valid for $n \geq 1$ quantum numbers of hydrogen wavefunctions.
Spherical harmonic for $P_1(\cos \theta)$

- Plot in polar coordinates represents $|Y_1^1|^2$ where $Y_1^1 = (1/2)(3/2\pi)^{1/2} \sin \theta e^{i\phi}$.
- Solution corresponds to rotational quantum numbers $J = 1, J_z = \pm 1$.
- Polynomial is valid for $n \geq 2$ quantum numbers of hydrogen wavefunctions.
Spherical harmonic for $P_{1}(\cos\theta)$

- Plot in polar coordinates represents $|Y_{1}^{0}|^2$ where $Y_{1}^{0}=(1/2)(3/\pi)^{1/2} \cos\theta$ with normalization.
- Solution corresponds to rotational quantum numbers $J = 1, J_z = 0$.
- Polynomial is valid for $n \geq 2$ quantum numbers of hydrogen wavefunctions.
Spherical harmonic for $P_2(\cos \theta)$

- Plot in polar coordinates of $|Y_2|^2$ where $Y_2 = 1/4(15/2\pi)^{1/2}\cos^2 \theta e^{2i\phi}$
- Solution corresponds to rotational quantum numbers $J = 2, J_z = \pm 2$.
- Polynomial is valid for $n \geq 3$ quantum numbers of hydrogen wavefunctions
Spherical harmonic for \( P_2(\cos \theta) \)

- Plot in polar coordinates of \(|Y_2^1|^2\) where
  \[ Y_2^1 = (15/8\pi)^{1/2}\sin \theta \cos \theta e^{i\phi} \]
- Solution corresponds to rotational quantum numbers \( J = 2, J_z = \pm 1 \).
- Polynomial is valid for \( n \geq 3 \) quantum numbers of hydrogen wavefunctions.
Spherical harmonic for $P_2(\cos\theta)$

- Plot in polar coordinates of $|Y_2^0|^2$ where $Y_2^0 = 1/4(5/\pi)^{1/2}(3\cos^2\theta-1)$
- Solution corresponds to rotational quantum numbers $J = 1$, $J_z = 0$.
- Polynomial is valid for $n \geq 3$ quantum numbers of hydrogen wavefunctions
Rotational Wavefunctions

These are the spherical harmonics $Y_{JM}$, which are solutions of the angular Schrodinger equation.
The degeneracy of the solutions

- The solutions form a set of $2J + 1$ functions at each energy (the energies are $E = \hbar^2 J(J + 1)/2I$).
- A set of levels that are equal in energy is called a degenerate set.
Rotational Transitions

- Electromagnetic radiation can interact with a molecule to change the rotational state.
- Typical rotational transitions occur in the microwave region of the electromagnetic spectrum.
- There is a selection rule that states that the quantum number can change only by + or - 1 for an allowed rotational transition ($\Delta J = \pm 1$).
Orthogonality of wavefunctions

- The rotational wavefunctions can be represented as the product of sines and cosines.
- Ignoring normalization we have:
  - s \( \frac{1}{2}(3\cos^2\theta - 1) \), \( \cos^2\theta \cos^2\phi \), \( \cos^2\theta \sin^2\phi \), 
  - \( \cos\theta \sin\theta \cos\phi \), \( \cos\theta \sin\theta \sin\phi \)
- The differential angular element is \( \sin\theta d\theta d\phi/4\pi \) over the limits \( \theta = 0 \) to \( \pi \) and \( \phi = 0 \) to \( 2\pi \).
- The angular wavefunctions are orthogonal.
Orthogonality of wavefunctions

- For the theta integrals we can use the substitution
  - $x = \cos \theta$ and $dx = \sin \theta \, d\theta$
- For example, for s and p-type rotational wave functions we have
  \[
  \langle s | p \rangle \propto \int_0^\pi \cos \theta \sin \theta \, d\theta = \int_1^{-1} x \, dx = \frac{x^2}{2} \bigg|_{-1}^{1} = \frac{1}{2} - \frac{1}{2} = 0
  \]
Which of the following statements is true:
A. The number of z-projection of the quantum numbers is $2J+1$.
B. The spacing between rotational energy levels increases as $2(J+1)$.
C. Rotational energy levels have a degeneracy of $2J+1$.
D. All of the above.
Question

Which of the following statements is true:

A. The number of z-projection of the quantum numbers is 2J+1.
B. The spacing between rotational energy levels increases as 2(J+1).
C. Rotational energy levels have a degeneracy of 2J+1.
D. All of the above.

\[ \Delta E \sim (J+2)(J+1) - J(J+1) = 2(J+1) \]
Question

The fact that rotational wave functions are orthogonal means that

A. They have no overlap
B. They are normalized
C. They are linear functions
D. None of the above
Question

The fact that rotational wave functions are orthogonal means that

A. They have no overlap
B. They are normalized
C. They are linear functions
D. None of the above
The moment of inertia

The kinetic energy of a rotating body is $\frac{1}{2}I\omega^2$. The moment of inertia is given by:

$$I = \sum_{i=1}^{\infty} m_i r_i^2$$

The rigid rotor approximation assumes that molecules do not distort under rotation. The types or rotor are (with moments $I_a$, $I_b$, $I_c$)
- Spherical: Three equal moments ($\text{CH}_4$, $\text{SF}_6$)  
  (Note: No dipole moment)
- Symmetric: Two equal moments ($\text{NH}_3$, $\text{CH}_3\text{CN}$)
- Linear: One moment ($\text{CO}_2$, $\text{HCl}$, $\text{HCN}$)  
  (Note: Dipole moment depends on asymmetry)
- Asymmetric: Three unequal moments ($\text{H}_2\text{O}$)
The rotational partition function

The degeneracy of rotational levels is $J(J+1)$. The energies are given by $\varepsilon = \hbar cBJ(J+1)$ where $J$ is the rotational quantum number and $B$ is the rotational constant.

$$q_r = \sum_{J=0}^{\infty} (2J + 1)e^{-\beta \hbar cBJ(J + 1)}$$

A large number of rotational levels populated since the rotational constant is of the order of 10 cm$^{-1}$ for many molecules and $kT > 10$ cm$^{-1}$ for temperatures higher than about 15 K.
The high temperature form of the rotational partition function

The partition function can be expressed as an integral at high temperature.

\[ q_r = \int_0^\infty (2J + 1)e^{-\beta \hbar c B J (J + 1)} dJ \]

It turns out that the integral can be solved analytically by making the substitution \( u = J(J+1) \).

\[ u = J(J + 1), \quad du = (2J + 1)dJ \]
The rotational partition function is an exponential integral

Making the substitution $u = J(J+1)$ the integral reduces to an easily soluble exponential integral.

$$q_r = \int_0^\infty e^{-\beta \hbar c Bu} du = \frac{1}{\beta \hbar c B}$$

The rotational constant $B$ is:

$$B = \frac{\hbar}{4\pi cI} \text{ where } I \text{ is the moment of inertia}$$