

4 Simple Quantum Mechanical Models and Solutions

Now that we have reviewed postulates of quantum mechanics, it is time for us to apply them to some simple systems. By doing so, we may find some interesting outcomes that arise from quantum mechanics. Before we dive into quantum mechanics, we shall cover few physical concepts that are vital to physical chemists.

4.1 When Is Quantum Mechanics Important?

Quantum mechanics is certainly important for the electronic property of the molecules as Bohr's model incorporate wave nature of electron through de Broglie relation. Since wave-nature of an electron has been demonstrated by double slit experiment, interest readers may look for an online video. For this reason, it is appropriate to apply Schrodinger's formulation which shares the same foundation to wave mechanics. A considerable amount of part 1 of this textbook deal with the quantum state of the electron. However, solving electronic state is just a part of the problem and it is certainly not enough to model any chemical reaction, the ultimate goal for physical chemistry.

Because postulates of quantum mechanics is applied to not only apply to electrons as well as nuclei, Schrödinger Equation is generally difficult to solve, even for simple atomic problems. Meanwhile, we know that the mass of an electron (0.00055AMU) is significantly smaller than that of any nuclei (≥ 1 AMU). Therefore, an electron moves much faster than any of the nuclei in the molecule. In general, it is safe to assume that the motion of atomic nuclei and electrons in a molecule can be separated. This approximation, called the Born-Oppenheimer approximation, greatly simplifies the problem. After separating the motions of the nucleus and the electrons, one generally solves first the part of the electrons associated with the molecule of interest and then proceeds to the motions of the nucleus. After all, chemical reactions are nothing more than rearrangements of atoms, so to consider chemical reactions from a thermodynamic point of view, one must take into account the vibrations, rotations, and translations of the products and reactants.

Consider a molecule consist of $3N$ atoms. Since each atom can move along x,y, & z-direction, the total degrees of freedom is equal to $3N$. If all atoms move in the same direction, center of mass moves. Therefore, three degrees of freedom is used for translation of the center of mass. If the molecule is non-linear, the molecule can be rotated around x, y, or z-axis; three degrees of freedom is used for rotational modes. Rest of the degrees of freedom ($3N-6$) is considered as vibrational modes. If the molecule is linear, the molecule can be rotated around only 2 axes; two degrees of freedom is used for rotational modes. Rest of the degrees of freedom ($3N-5$) is considered as vibrational modes. As Planck pointed out, energy is quantized. However, the energy gap between quantum state is so small for some of the modes; it can be approximated classically to simplify the problem. We shall cover some of these in this chapter.

4.2 Particle in a Box (P.I.B.)

4.2.1 1-D Shrödinger Equation (1-D P.I.B.)

Shrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi + V(x)\psi = E\psi$$

↓

$$\frac{d^2}{dx^2} \psi + q\psi = 0 \quad (0 \leq x \leq a)$$

$$q = \frac{2mE}{\hbar^2}$$

Recall our D.E.

$$y'' + py' + qy = 0$$

↑

∅

Guess $y = e^{sx}$

$$s^2 e^{sx} + q e^{sx} = 0$$

$$s^2 + q = 0$$

$$s = \pm \sqrt{q}i = \pm \frac{(2mE)^{1/2}}{\hbar} i = \pm ki$$

So our solution is

$$\psi = C_1 e^{ikx} + C_2 e^{-ikx}$$

$$= (C_1 + C_2) \cos(kx) + i(C_1 - C_2) \sin kx \because e^{iax} = \cos(ax) + i \sin(ax)$$

$$= A \cos(kx) + B \sin(kx)$$

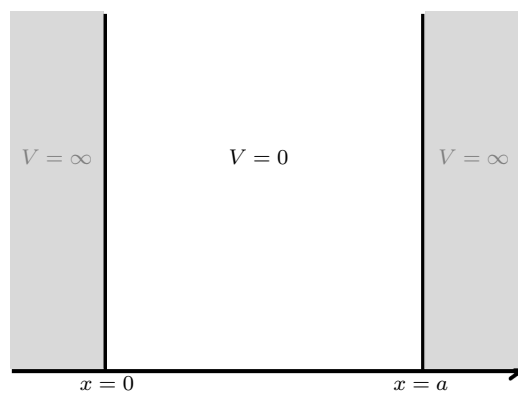


Figure 6: Potential of Particle in a Box

Applying the boundary condition,

$$\psi(0) = \psi(a) = 0 \Rightarrow A = 0$$

$$\psi(a) = B \sin(ka) = 0$$

$$ka = n\pi$$

$$\Downarrow$$

$$\text{So, } \psi(x) = B \sin(kx) \quad \frac{(2mE)^{1/2}}{\hbar} a = n\pi (n = 0, 1, 2, \dots)$$

$$= B \sin\left(\frac{n\pi x}{a}\right)$$

$$E = \frac{\pi^2 n^2 \hbar^2}{2ma^2}$$

$$\downarrow (\hbar = \frac{h}{2\pi})$$

$$= \frac{n^2 h^2}{8ma^2}$$

We still need to find B.

requirement $\int \psi^* \psi dx = 1$

$$1 = |B|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{a|B|^2}{n\pi} \int_0^{n\pi} \sin^2 z dz \quad z = \frac{n\pi x}{a}$$

$$= |B|^2 \frac{a}{n\pi} \left(\frac{n\pi}{2}\right) = |B|^2 \frac{a}{2}$$

$$B = \sqrt{\frac{2}{a}} \quad \text{So, } \psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots$$

Note 0 is missing why? \rightarrow

HW

$$\left(\begin{array}{l} \text{Plot } \psi_n = \sqrt{2/a} \sin\left(\frac{n\pi x}{a}\right) \text{ for up to } n = 20 \\ \text{Plot } E_n \text{ versus } n \end{array} \right.$$

HW

Consider Helium atom trapped in a 10 cm^3 box and it is moving only in x-direction. From statistical mechanics (Part II of this book), average motion along x axis is $k_B T$. At room temperature, solve the average value of n. Then, solve the energy gap between n state and n+1 state. Is the energy gap look important for chemistry problem?

Laboratory 1

see appendix

4.2.2 3-D Shrödinger Equation (3-D P.I.B.)

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

How do we solve this?

Assume $\psi(x, y, z) = X(x)Y(y)Z(z)$

$$E = E_x + E_y + E_z$$

then,

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} X(x) = E_x X(x)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} Y(y) = E_y Y(y)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} Z(z) = E_z Z(z)$$

Solution

$$X(x) = A_x \sin \left(\frac{n_x \pi x}{a} \right)$$

$$Y(y) = A_y \sin \left(\frac{n_y \pi y}{b} \right)$$

$$Z(z) = A_z \sin \left(\frac{n_z \pi z}{c} \right)$$

$\psi = XYZ$ &

$$A_x, A_y, A_z = \left(\frac{8}{abc} \right), E_n = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

HW Verify this.

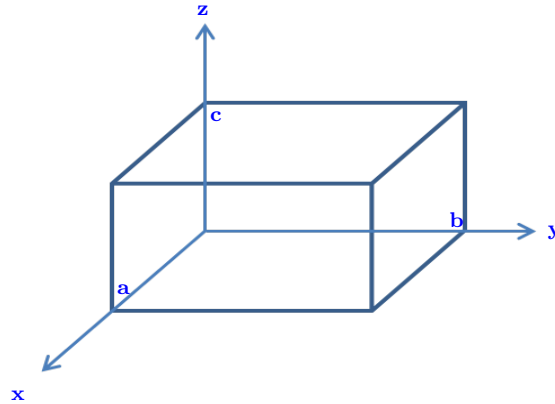


Figure 7: 3-D Particle In a Box

4.3 Harmonic Oscillator

4.3.1 Classical

In harmonic oscillator, restoring force is given by

$$f = -k(l - l_0) = -kx.$$

By Newton force balance,

$$f = ma$$

$$m \frac{d^2x}{dt^2} + kx = 0$$

By same ODE technique,

$$x = c_1 \sin(\omega t) + c_2 \cos(\omega t) = A \sin(\omega t + \phi)$$

$$\text{where } \omega = \left(\frac{k}{m}\right)^{1/2}$$

From Physics I

\hookrightarrow

$$f(x) = -\frac{\partial V}{\partial x} \Rightarrow V = \frac{1}{2}kx^2$$

$$H = \frac{p^2}{2m} + V = \frac{m}{2} \left(\frac{dx}{dt}\right)^2 + \frac{1}{2}kx^2 = E$$

If we choose $x(t) = A \cos(\omega t)$, then,

$$E = \frac{1}{2}m\omega^2 A^2 \cos^2(\omega t) + \frac{1}{2}kA^2 \sin^2(\omega t)$$

$$\begin{aligned} \omega = \left(\frac{k}{m}\right)^{1/2} \Rightarrow E &= \frac{kA^2}{2} (\sin^2(\omega t) + \cos^2(\omega t)) \\ &= \frac{kA^2}{2} \leftarrow \text{Energy is constant w.r.t. time.} \end{aligned}$$

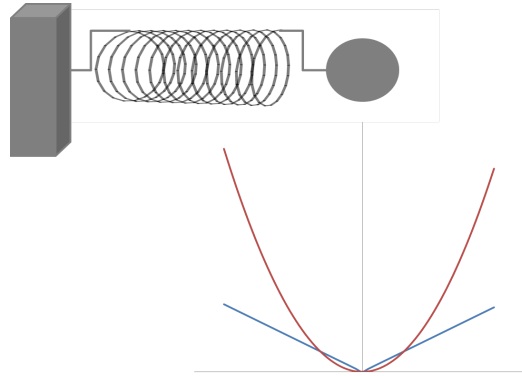


Figure 8: Harmonic Oscillator

4.3.2 Center of Mass & Reduced Mass (2-body problem to 1-body)

Center of mass for 2-body is defined as

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = \frac{m_1 x_1 + m_2 x_2}{M}$$

By force(ma) balance(sum of change in momentum of each fragment),

$$\frac{d^2}{dt^2}(MX) = \frac{d^2}{dt^2}(m_1 x_1 + m_2 x_2) = 0$$

So, X is stationary.

Newton's force balance

$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - l_0)$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - l_0)$$

Letting $x = x_2 - x_1 - l_0$,

$$\frac{d^2 x}{dt^2} = \frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)x = -kx\left(\frac{m_1 + m_2}{m_1 m_2}\right)$$

alg \downarrow

$$\mu \frac{d^2 x}{dt^2} + kx = 0 \text{ where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

\downarrow

μ is the reduced mass.

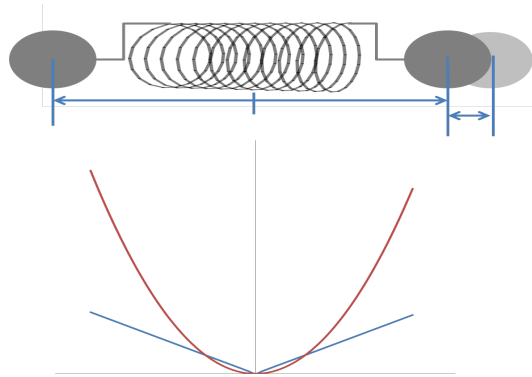


Figure 9: Simple Harmonic Oscillator

4.3.3 Quantum Mechanics Version of Harmonic Oscillator

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0$$

The solution is already found by mathematician.

$$\psi_v(x) = N_v \underbrace{H_v(\alpha^{1/2}x)}_{\text{called Hermite polynomial}} e^{-\alpha x^2/2}$$

called Hermite polynomial

$$\alpha = \left(\frac{k\mu}{\hbar^2} \right)^{1/2}$$

$$N_v = \frac{1}{(2^v v! \pi)^{1/2}} \left(\frac{\alpha}{\pi} \right)^{1/4}$$

Laboratory 2

see appendix

Using the laboratory results, the energy of harmonic oscillator is given by:

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, 3, \dots$$

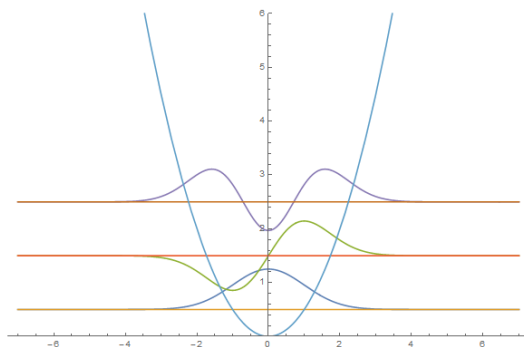


Figure 10: Solutions of a Harmonic Oscillator

HW

Consider a H_2 molecule. The energy gap of the vibration is measured as 4401 cm^{-1} by the experiment. What is the zero point energy of this system? What is the force constant for this molecule? Does energy gap look important to chemistry problem? What is the obvious weakness of the Harmonic Oscillator approximation?

4.4 More Realistic Potential

We have learned that Harmonic Oscillator has infinite potential at large bond distance, and the molecule will not break apart no matter how strong they oscillate. This is a very poor approximation for the chemistry and more accurate model should be introduced.

4.4.1 Morse Potential

Potential energy of Morse potential is given as

$$E_v = D \left(1 - e^{-\alpha(l-l_o)} \right)^2$$

where $\alpha = \sqrt{\frac{k_e}{2D_e}}$

D_e represent the classical well depth. Note that harmonic oscillator is similar to the Morse potential near the bottom of the well.

HW Show that Harmonic potential is identical to the Morse potential near the bottom of the potential well. Hint: Expand the exponential

It can be shown that allowed vibrational energy of the morse potential (up to some point) is given as

$$E_v = \hbar v_o \left(v + \frac{1}{2} \right) - \frac{(\hbar v_o (v + \frac{1}{2}))^2}{4D_e}$$

where $v_o = \alpha \sqrt{\frac{2D_e}{m}} = \sqrt{\frac{k_e}{m}}$

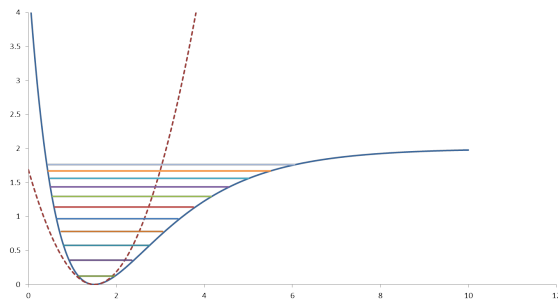


Figure 11: Energy level of Morse Potential

Note that energy gap becomes narrower as v becomes large. This is and harmonic oscillator fails to predict this correct behavior .

4.4.2 Lennard Jones Potential

This potential (also known as 6-12 potential) is a popular choice for modeling chemistry problems because of its simplicity.

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

HW Take a derivative w.r.t. internuclear distance r and solve for zero to find the bottom of the well. What is the well depth there?

4.5 Rigid Rotor

4.5.1 A Mass Orbiting in Circular Path

Circular path \perp to x at $\vec{r} = \vec{x}$

$$\begin{aligned}
 L_z &= \vec{r} \times \vec{P} = xP_y - yP_x \\
 &= xP_y \\
 &\downarrow |v| \text{ constant magnitude} \\
 &= xmv \\
 &= rmv \\
 &= mr^2 \frac{v}{r} \\
 &\downarrow \text{momentum of inertia } I = mr^2 \\
 &= I \frac{v}{r} = I\omega
 \end{aligned}$$

Let ν_{rot} = frequency of rotation

$$v = 2\pi r \nu_{rot} \Rightarrow \frac{v}{r} = 2\pi \nu_{rot} = \omega \leftarrow \text{angular velocity}$$

The equation should look similar to linear momentum.

$$\begin{array}{ccc}
 p = m \vec{v} & L_z = I\omega \\
 \uparrow \quad \nwarrow & \uparrow \quad \nwarrow \\
 \text{mass} \quad \text{velocity} & \text{inertia} \quad \text{angular velocity}
 \end{array}$$

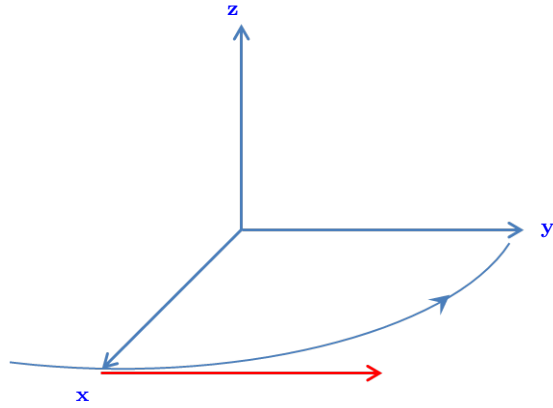


Figure 12: Circular Path

4.5.2 K.E. Associated with Circular Motion

Classical Version

$$T_{\text{linear}} = \frac{p^2}{2m} = \frac{1}{2}mv^2$$

$$T_{\text{ang}} = \frac{L_z^2}{2I} = \frac{1}{2}I\omega^2$$

Quantum Mechanics Version

Short Cut

Because $L_z = \pm pr = \pm \frac{hr}{\lambda}$ (By de Broglie $p = \frac{h}{\lambda}$)
From boundary condition,

$$2\pi r = m_l \lambda \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$L_z = \frac{m_l h}{2\pi} = m_l \hbar$$

So, K.E. of circular motion is

$$E = \frac{L_z^2}{2I} = \frac{(m_l \hbar)^2}{2I}$$

Long Version

Assume particle follow circular orbit
on xy - plane (no potential $V(x) = 0$)

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

$$= -\frac{\hbar^2}{2m} \left(\cancel{\frac{\partial^2}{\partial r^2}} + \cancel{\frac{1}{r}} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)$$

$$\text{So, } \hat{H} = -\frac{\hbar^2}{2mr^2} \frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2}$$

$$\rightarrow I = mr^2$$

Schrödinger Equation is

$$-\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \psi = E\psi$$

↓ This is identical to 1-D Schrödinger Equation

$$\frac{d^2}{d\phi^2} \psi + \frac{2IE}{\hbar^2} \psi = 0$$

$$\downarrow m_e = \frac{2IE}{\hbar^2}$$

$$\frac{d^2}{d\phi^2} \psi + m_e \psi = 0$$

↓ From previous page. You don't need this but it simplify algebra.

$$\psi(\phi) = Ae^{im_e \phi}$$

note $\psi(\phi) = \psi(\phi + 2\pi)$ force m_l to be integer.

Now, $\psi(\phi)$ must be normalized

$$\begin{aligned}\int_0^{2\pi} \psi^*(\phi)\psi(\phi)d\phi &= |A|^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi \\ &= |A|^2 \int_0^{2\pi} d\phi \\ &= |A|^2 2\pi \\ \Rightarrow \psi &= \sqrt{\frac{2}{2\pi}} e^{im_l\phi}\end{aligned}$$

HW (Particle on a Ring) Using normalized ψ , obtain rotational energy expression. Then, consider electron moving on circular orbit on benzen ring with radius of 1.44 Å. What is the excitation energy from ground state to first excited state?

4.5.3 Rigid Rotor(2-body problem to 1-body)

Kinetic Energy

$$\begin{aligned} T &= \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \\ &= \frac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2 \\ &= \frac{1}{2}I\omega^2 \end{aligned}$$

$$\begin{aligned} I &= m_1r_1^2 + m_2r_2^2 \\ &= \mu r^2 \end{aligned}$$

where $\mu = \frac{m_1m_2}{m_1+m_2}$ and $r = r_1 + r_2$.

HW

Check $I = \mu r^2$.

(Hint: $m_1r_1 = m_2r_2 \leftarrow$ center of mass. Just plug in & do alg.)

$T = \frac{L^2}{2I}$ where $L = I\omega$.

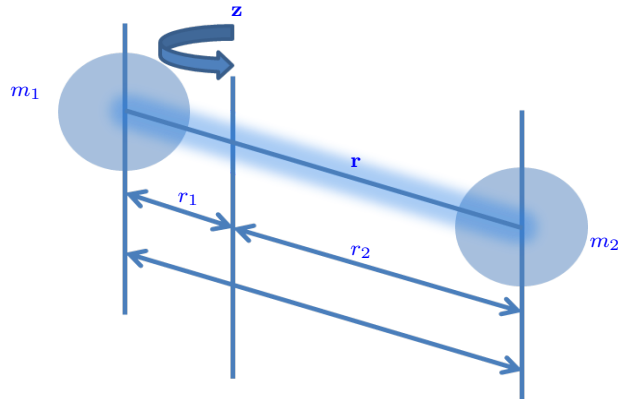


Figure 13: Rigid Rotor

4.5.4 Rigid Rotor (3-D Quantum Mechanics)

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}$$

Because r is constant in Rigid Rotor, we should use spherical coordinate system.

↑ from previous page

From Calc II and III,

$$\begin{aligned} \nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \\ &\downarrow r \text{ const} \\ &= \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \end{aligned}$$

Eq 1

$$\hat{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right]$$

$$\hat{H}\psi = E\psi$$

Assume $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

then,

$$\hat{H}Y(\theta, \phi) = EY(\theta, \phi).$$

The solution (Spherical Harmonics Y_l^m) is already tabulated by mathematicians (See tables).

HW

Plug in solution to this Eq to verify $E = \frac{\hbar^2}{2I} l(l+1)$.

Note that above Schrödinger Equation can be slightly simplified by setting $\beta = \frac{2IE}{\hbar^2}$.

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} + (\beta \sin^2 \theta) Y = 0.$$

HW

Consider rotation of HCl molecule rotating around z axis. Using 1.27 \AA as a bond length, what is the energy spacing of ground state to 1st excited state (kJ/mol)? Does the quantization of rotational energy look important to you? (Answer is "Yes")

★ Note that spherical harmonics allows $2l+1$ solutions for each value of l . This means that there are $2l+1$ degenerate states available for each l rotational level. This increase in degeneracies with respect to l can be observed by simply taking $\frac{dE}{dl}$.