Lecture 16: Rigid Rotor I

So far we have seen several exactly soluble quantum mechanical problems.

1. Particle in an infinite-wall box.

    * useful insights into "valence states" of diatomic and conjugated polyatomic molecules. The system size is related to the energy of the HOMO→LUMO electronic transition.

    * in 5.62, direct relationship between the energy levels of a particle in a 3D box and the ideal gas law.

2. Harmonic Oscillator

    * *all* molecular vibrations for diatomic molecules and "normal modes" in polyatomic molecules

    * almost all particle-in-a-well situations are harmonic near equilibrium

    * perturbation theory used to account for diagonal and inter-mode effects (anharmonicity in the energy level spacing and Intramolecular Vibrational Redistribution) of anharmonicity in the potential energy function

We are about to deal with the rigid rotor.

* All molecules have rotational energy levels that are rigid-rotor like.

* All central force systems (electronic structure of atoms, rotational structure of molecules, nuclear spins) may be separated into a *universal* spherical problem, described by angular momenta, and a *system-specific* radial problem.

* The properties of angular momenta are universally described by spherical harmonics and by a set of commutation rules by which an angular momentum may be defined, even when the angular momentum cannot be defined by the usual vector equation

$$\hat{\vec{\ell}} = \hat{\vec{r}} \times \hat{\vec{p}}.$$

  The electron spin is an example of an angular momentum that must be defined by commutation rules because there is no spatial coordinate associated with spin.

Once we have dealt with the rigid rotor, there are two more frontiers to cross.

* **The Hydrogen atom**. This provides a different (from particle-in-a-box) and more useful template for understanding "electronic structure" and is directly relevant to the "Rydberg" electronic states of all molecules.

* **Many-electron systems**. We will use LCAO-MO to provide a qualitative picture of molecular "valence states", the evil $1/r_{ij}$ inter-electron repulsion (that spoils all of the individual electron angular mementum quantum numbers), and the necessity to "anti-symmetrize" many-electron wavefunctions (the Pauli Exclusion principle) because electrons are "fermions".

There are two quite different approaches to angular momentum. Both are used.

* Express $\widehat{H}$ in terms of spherical polar coordinates (r, θ, ϕ):
1) find the differential operators, $\widehat{L^2}, \hat{L}_i$, that correspond to the total angular momentum and the Cartesian components of the total angular momentum;
2) find the eigenfunctions of both $\widehat{L^2}$ and $\hat{L}_z$, which are known as "spherical harmonics".

* Define each angular momentum abstractly in terms of commutation rules, e.g.

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar \sum_k \varepsilon_{ijk} \hat{L}_k$$

and derive the values of *all* angular momentum integrals using raising and lowering operators (reminiscent of vibrational $\mathbf{a}, \mathbf{a}^{\dagger}$ operators)

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y .$$

You will see these two approaches in this and the next lecture.

Today's Lecture:

1. Relationship between linear and angular momenta

$$\vec{p} = m\vec{v}$$
$$\vec{\ell} = I\vec{\omega}.$$

2. Relationship between two masses connected by a rigid bar and one mass on a string of length r_0 anchored at $r = 0$.

$$I = \mu r_0^2 \qquad \text{(moment of inertia)}$$
$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{(reduced mass)}$$

3. Mass μ confined to surface of a sphere of radius r_0.

- $\hat{T}$ expressed in spherical polar coordinates
- $\hat{V} = 0, r = r_0$; $\hat{V} = \infty, r \neq r_0$
- transformation from Cartesian to spherical polar coordinates (NON-LECTURE)
- volume element

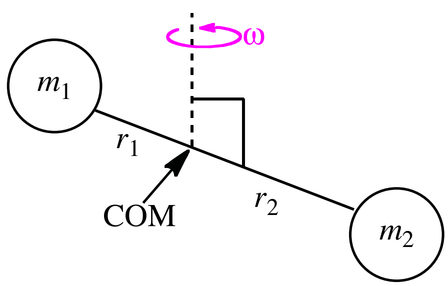
4. Separation of θ,ϕ variables.

5. Solution of rigid-rotor Schrödinger Equation.

6. Spherical Harmonics, Legendre Equation (NON-LECTURE).

THE RIGID ROTOR

<u>Diatomic Molecule</u>



$r_1 + r_2 \equiv r_0$

$m_1 + m_2 = \mathrm{M}$

$\mu = \dfrac{m_1 m_2}{M}$ (reduced mass)

$m_1 r_1 = m_2 r_2$ (defines coordinates of atoms 1 and 2 relative to the center of mass)

$r_2 = \dfrac{\mu}{m_2} r_0$, $r_1 = \dfrac{\mu}{m_1} r_0$

$\vec{\omega} \perp$ internuclear axis

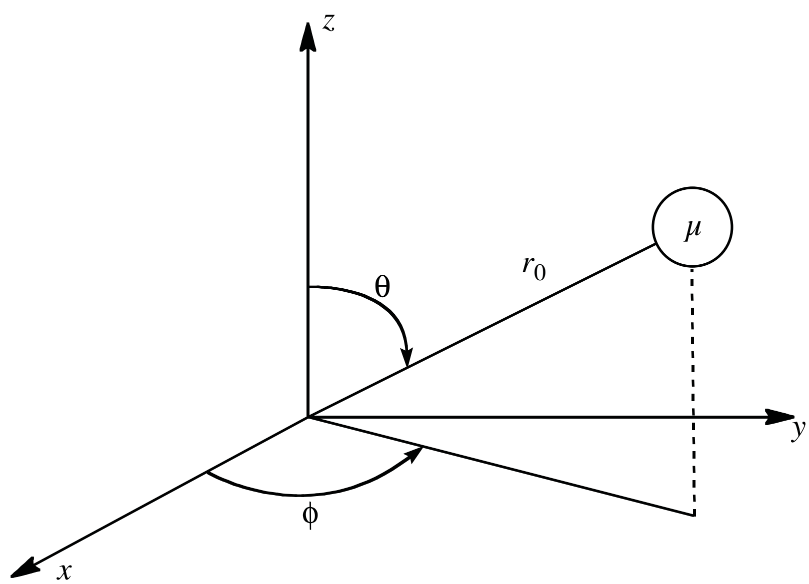
K.E. $$T = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2 = \frac{1}{2} \underbrace{\left(m_1 r_1^2 + m_2 r_2^2\right)}_{I \,\equiv\, \text{moment of inertia}} \omega^2$$

$$\therefore \qquad T = \frac{1}{2} I \omega^2 \quad (\text{recall } T = p^2/2\mu)$$

$$I = m_1 r_1^2 + m_2 r_2^2 = m_1 \left(\frac{\mu}{m_1} r_0 \right)^2 + m_2 \left(\frac{\mu}{m_2} r_0^2 \right) = \mu r_0^2$$

$$T = \frac{1}{2} \mu r_0^2 \omega^2$$

2-body problem reduced to a one-body problem (free motion of a particle confined to the surface of a sphere) with mass μ.



Angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

For rotation, $r_i \perp p_i$ thus $|r_i \times p_i| = r_i p_i$

$$L = |\mathbf{L}| = r_1 p_1 + r_2 p_2 = m_1 r_1 \mathrm{v}_1 + m_2 r_2 \mathrm{v}_2 = m_1 r_1^2 \omega + m_2 r_2^2 \omega = I\omega$$

$$\therefore \boxed{T = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}}$$

Relationship between angular momentum and kinetic energy for rotation.
Analogous to linear momentum, p, and kinetic energy for translation, $p^2/2\mu$.

Now need to describe free motion on the surface of a sphere quantum mechanically.

$$\widehat{H} = \widehat{T} + \widehat{V}(x,y,z) = -\frac{\hbar^2}{2\mu} \widehat{\nabla}^2_{xyz} + V(x,y,z)$$

$$\widehat{\nabla}^2_{xyz} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

Change to spherical polar coordinates

Cartesian $\leftrightarrow$ spherical polar

$$(x,y,z) \quad \leftrightarrow \quad (r,\theta,\phi)$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$\nabla^2_{r\theta\phi} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

Thus, in spherical polar coordinates, the Schrödinger equation,

$\hat{H}(r,\theta,\phi)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$, is (skipping the algebra)

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r,\theta,\phi)\right\}\psi(r,\theta,\phi)$$
$$= E\psi(r,\theta,\phi)$$

In our rigid rotor example

$$V(r,\theta,\phi) = 0 \qquad (r = r_0)$$
$$V(r,\theta,\phi) = \infty \qquad (r \neq r_0)$$

i.e. r is held constant at r_0.

$$\psi(r,\theta,\phi) \quad \rightarrow \quad \psi(r_0,\theta,\phi) \quad (\psi = 0 \text{ for } r \neq r_0)$$
$$\frac{\partial}{\partial r}\psi(r_0,\theta,\phi) = 0$$

thus all of the $\frac{\partial}{\partial r}$ terms go to zero.

Rewrite Schrödinger Eq. without the variable r:

$$-\frac{\hbar^2}{\underbrace{2\mu r_0^2}_{I}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r_0,\theta,\phi) = E\psi(r_0,\theta,\phi)$$

Set $\psi(r_0,\theta,\phi) = BY(\theta,\phi)$ (B is a constant and Y is a function of θ,ϕ that we want to find)

Need to solve this differential equation:

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

SOLUTIONS TO THE RIGID ROTOR

For the rigid rotor problem, we must now solve the differential equation:

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

This is $\hat{H}Y(\theta,\phi)=EY(\theta,\phi)$ with $\hat{H}=\hat{T}$ since the potential $\hat{V}=0$

Rearranging the differential equation separating the θ-dependent terms from the ϕ-dependent terms:

$$\underbrace{\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta\right]}_{\text{only }\theta}Y(\theta,\phi)=-\underbrace{\frac{\partial^2}{\partial\phi^2}}_{\text{only }\phi}Y(\theta,\phi)$$

We've separated the variables in spherical polar coordinates, just as for Cartesian coordinates in the 3D particle in a box problem.

∴ Try $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$ as a solution

Define $\beta\equiv\frac{2IE}{\hbar^2}$ $\quad(\text{note }\beta\propto E)$

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\beta\sin^2\theta\right]\Theta(\theta)\Phi(\phi)=-\frac{\partial^2}{\partial\phi^2}\Theta(\theta)\Phi(\phi)$$

Dividing (on the left) by $\Theta(\theta)\Phi(\phi)$, recognizing that LHS operator does not operate on $\Phi(\phi)$ and RHS operator does not operate on $\Theta(\theta)$, and simplifying, we obtain

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta}_{\text{only }\theta}=\underbrace{-\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)}_{\text{only }\phi}.$$

Since θ and ϕ are independent variables, each side of the equation must be equal to a constant $\equiv m^2$.

$$\Rightarrow \qquad \boxed{\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)=-m^2} \qquad \text{(I)}$$

$$\text{and} \quad \Rightarrow \qquad \boxed{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta=m^2} \qquad \text{(II)}$$

First solve for $\Phi(\phi)$ using (I)

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

Solutions are $\Phi(\phi)=A_m e^{im\phi}$ and $A_{-m}e^{-im\phi}$

Periodic boundary conditions lead to quantization

$$\Phi(\phi+2\pi)=\Phi(\phi)$$

$$\Rightarrow \qquad A_m e^{im(\phi+2\pi)}=A_m e^{im\phi} \quad \text{and} \quad A_{-m}e^{-im(\phi+2\pi)}=A_{-m}e^{-im\phi}$$

This is satisfied if

$$e^{im(2\pi)}=1 \quad \text{and} \quad e^{-im(2\pi)}=1$$

This can only be true if $\boxed{m=0,\ \pm1,\ \pm2,\ \pm3,....}$.

m is the "magnetic" quantum number

$$\therefore \qquad \Phi(\phi)=A_m e^{im\phi} \qquad m=0,\ \pm1,\ \pm2,\ \pm3,....$$

Normalization: $\int_0^{2\pi} \Phi^*(\phi)\Phi(\phi)\, d\phi = 1$

$$\Rightarrow \quad \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3, \ldots$$

Now let's look at $\Theta(\theta)$. Need to solve (II.) Much more difficult.

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right)\Theta(\theta) + \beta \sin^2\theta = m^2 .$$

Change variables: $x = \cos\theta \qquad \Theta(\theta) = P(x) \qquad \frac{dx}{-\sin\theta} = d\theta .$

Since $0 \le \theta \le \pi \quad \Rightarrow \quad -1 \le x \le +1 .$

Also $\sin^2\theta = 1 - \cos^2\theta = 1 - x^2 .$

After some rearrangement we obtain the ***Legendre*** equation ……

$$\boxed{\left(1 - x^2\right)\frac{d^2}{dx^2}P(x) - 2x\frac{d}{dx}P(x) + \left[\beta - \frac{m^2}{1 - x^2}\right]P(x) = 0} .$$

The constraint that $\Theta(\theta)$ is continuous leads to quantization of β. Stated without derivation:

$$\beta = l(l+1) \qquad \text{where} \qquad l = 0,\ 1,\ 2, \ldots$$
$$\text{and} \qquad m = 0,\ \pm 1,\ \pm 2, \ldots, \pm l .$$

This directly leads to quantization of the energy!

$$\beta = \frac{2IE}{\hbar^2} \quad \Rightarrow \quad E = \frac{\hbar^2}{2I}\beta$$

$$E = \frac{\hbar^2}{2I} l(l+1) \qquad l = 0,\ 1,\ 2, \ldots \quad \text{(for rigid rotor, use } J \text{ instead of } l\text{)}$$

$$\boxed{E_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0,\ 1,\ 2, \ldots} .$$

The solutions of the Legendre Eq. are the *associated Legendre polynomials* $P_l^{|m|}$

$$P_l^{|m|}(x) = P_l^{|m|}(\cos\theta)$$

$$P_0^0(\cos\theta) = 1 \qquad P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_1^0(\cos\theta) = \cos\theta \qquad P_2^1(\cos\theta) = 3\cos\theta\sin\theta$$

$$P_1^1(\cos\theta) = \sin\theta \qquad P_2^2(\cos\theta) = 3\sin^2\theta$$

etc.

We find that $\Theta(\theta) = A_{lm}P_l^{|m|}(\cos\theta) \qquad A_{lm} = \left[\left(\frac{2l+1}{2}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}$,

where A_{lm} is the normalization constant

$$\Rightarrow \qquad A_{lm}^2 \int_0^\pi \left[P_l^{|m|}(\cos\theta)\right]^2 \sin\theta d\theta = 1.$$

Putting it all together:

$$\psi_{lm}(r_0,\theta,\phi) = Y_l^m(\theta,\phi) = \Theta_l^{|m|}(\theta)\Phi_m(\phi)$$

where, because the θ and ϕ dependent parts appear as separate factors, $Y_l^m(\theta,\phi)$ is a more convenient and commonly used form of $P_\ell^{|m|}$(cos θ),

$$Y_l^m(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)e^{im\phi}$$

These Y_l^m functions are called <u>spherical harmonics</u>.

They are the eigenfunctions of $\hat{H}Y = EY$ for the rigid rotor.

What does $Y_\ell^m(\theta,\phi)$ look like and what does it tell us about the probability distribution of $\vec{J}$ (vector) and the rotor axis?

1. $\vec{J} = \vec{r} \times \vec{p}$. $\vec{J}$ is a vector that is perpendicular to the plane of rotation.

2. θ,φ are the coordinates of the fictitious particle on the surface of a sphere. For a rigid rotor, the rotor axis (not $\vec{J}$) is along the axis from $r = 0$ to $\vec{r} = (r_0, \theta, \phi)$. This is the internuclear axis. When $\theta = 0$, the rotor axis is along z and $\vec{J}$ is ⊥ to z. When $\theta = \pi/2$, the rotor axis is in the xy plane and $\vec{J}$ is parallel or anti-parallel to z.

3. M_J tells you the orientation of $\vec{J}$ relative to the z axis. The angle, α, between $\vec{J}$ and z is given by $\cos\alpha = \dfrac{M_J}{[J(J+1)]^{1/2}}$. When $|M_J| = J$, $\alpha = 0$ or π. This requires the rotor axis to be in the xy plane, $\theta = \pi/2$.

Non-Lecture

Legendre's Equation

Legendre's equation, expressed in terms of the function $\Theta(\theta)$, is

$$\sin\theta \frac{d}{d\theta}\left[\sin\theta \frac{d\Theta}{d\theta}\right] + \left(\beta \sin^2\theta - m^2\right)\Theta(\theta) = 0$$

or

$$\sin^2\theta \frac{d^2\Theta}{d\theta^2} + \sin\theta\cos\theta \frac{d\Theta}{d\theta} + \left(\beta\sin^2\theta - m^2\right)\Theta(\theta) = 0 .$$

Now change variables.

Let $x = \cos\theta$ and $\Theta(\theta) = P(x)$ and $\sin\theta = [1 - \cos^2\theta]^{1/2}$.

$$\frac{d\Theta}{d\theta} = \frac{dP}{dx}\frac{dx}{d\theta} = -\sin\theta \frac{dP}{dx} = -\left(1-x^2\right)^{1/2}\frac{dP}{dx}$$

$$\frac{d^2\Theta}{d\theta^2} = \frac{d}{d\theta}\left[\frac{d\Theta}{d\theta}\right] = \left[\frac{dx}{d\theta}\right]\frac{d}{dx}\left[-\left(1-x^2\right)^{1/2}\frac{dP}{dx}\right]$$

$$= -\sin\theta\left[\frac{x}{\left(1-x^2\right)^{1/2}}\frac{dP}{dx} - \left(1-x^2\right)^{1/2}\frac{d^2P}{dx^2}\right]$$

$$= -x\frac{dP}{dx} + \left(1-x^2\right)\frac{d^2P}{dx^2}$$

Substituting these results into Legendre's equation gives

$$\left(1-x^2\right)^2\frac{d^2P}{dx^2} - 2x\left(1-x^2\right)\frac{dP}{dx} + \left(\beta\left(1-x^2\right) - m^2\right)P(x) = 0$$

Divide by $\left(1-x^2\right)$ to obtain

$$\left(1-x^2\right)\frac{d^2P}{dx^2}-2x\frac{dP}{dx}+\left[\beta-\frac{m^2}{1-x^2}\right]P(x)=0$$

which is the Legendre equation, expressed in terms of $x = \cos\theta$ as the independent variable.

Next Lecture:

1. Rotational Spectrum.

2. Pictures of $Y_\ell^m(\theta,\phi)$: like s, p, d, f orbitals
   Polar plots of $(r,\theta,\phi) = \left(\psi_{L,M_L}(\theta,\phi),\theta,\phi\right)$
   Real vs. complex forms
   $\hookrightarrow \psi_{L,M_L} \pm \psi_{L-M_L} \hookrightarrow$ angular momentum eigenstates of $\widehat{L^2}$ and $\hat{L}_z$

3. Commutation Rule definition of angular momentum
   Mostly Non-Lecture (McQuarrie, pages 296-300)
   Derivation of

$$L^2\left|LM_L\right\rangle = \hbar^2 L(L+1)\left|LM_L\right\rangle$$

$$L_z\left|LM_L\right\rangle = \hbar M_L\left|LM_L\right\rangle$$

$$L_\pm\left|LM_L\right\rangle = \hbar\left[L(L+1)-M_L\left(M_L\pm 1\right)\right]^{1/2}\left|LM_L\pm 1\right\rangle$$

   from $\left[L_i,L_j\right] = i\hbar\sum_k \varepsilon_{ijk}L_k$

   Levi-Civita symbol, ε, is “anti-symmetric tensor”

Friday: we will begin Hydrogen Atom.