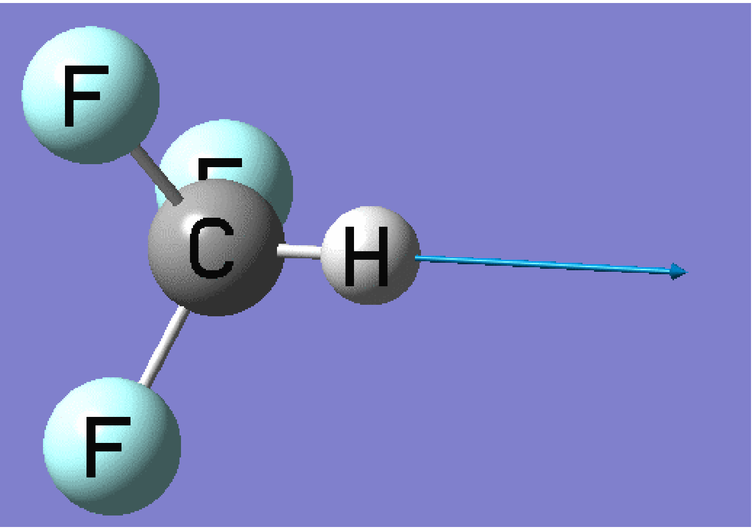
CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-07, 24-01-2018

Summary: Lecture - 06



$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Simple harmonic oscillation

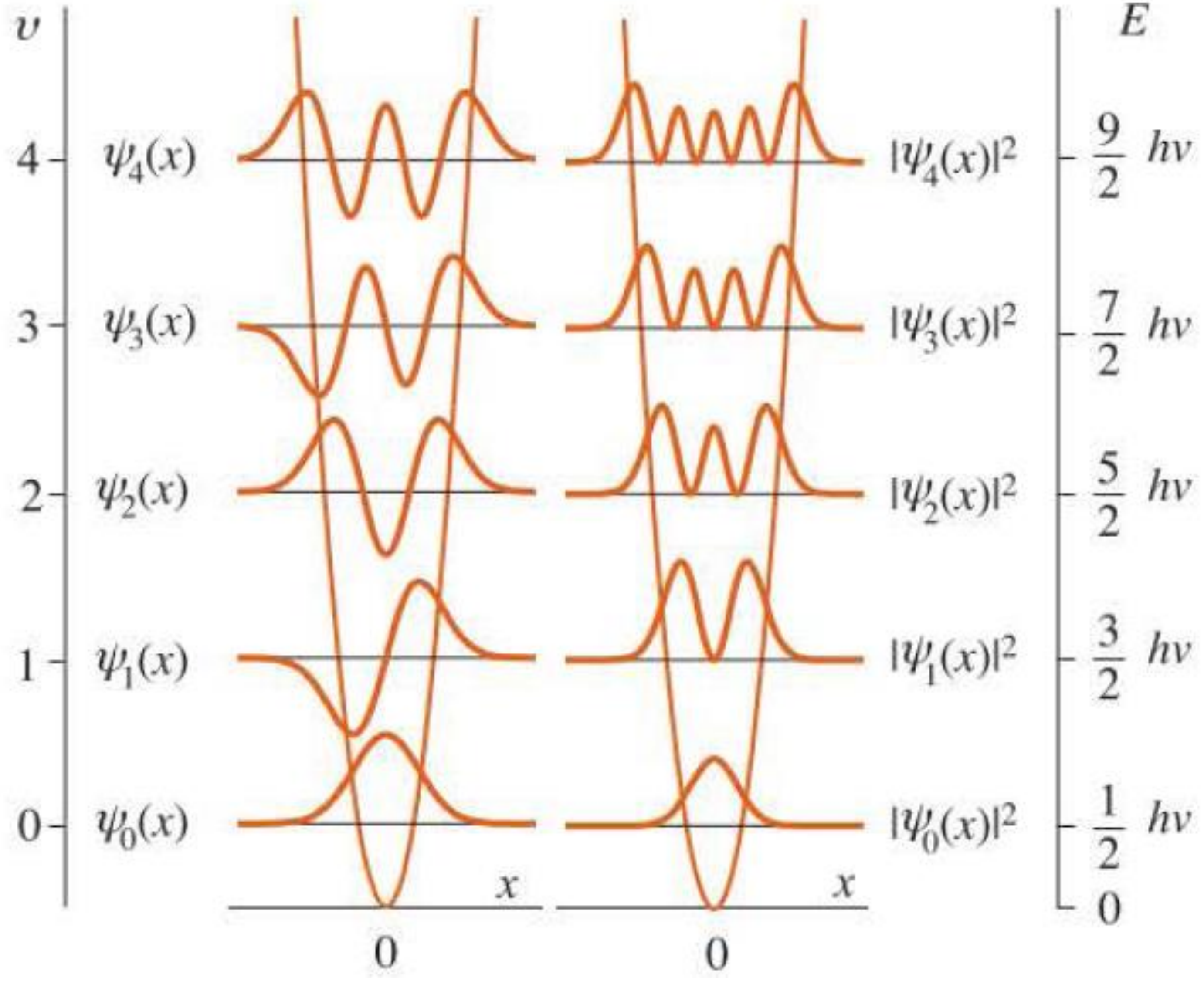
$$E_v = \left(v + \frac{1}{2}\right) h\nu, v = 0, 1, 2, \dots (\textit{vibrational quantum number})$$

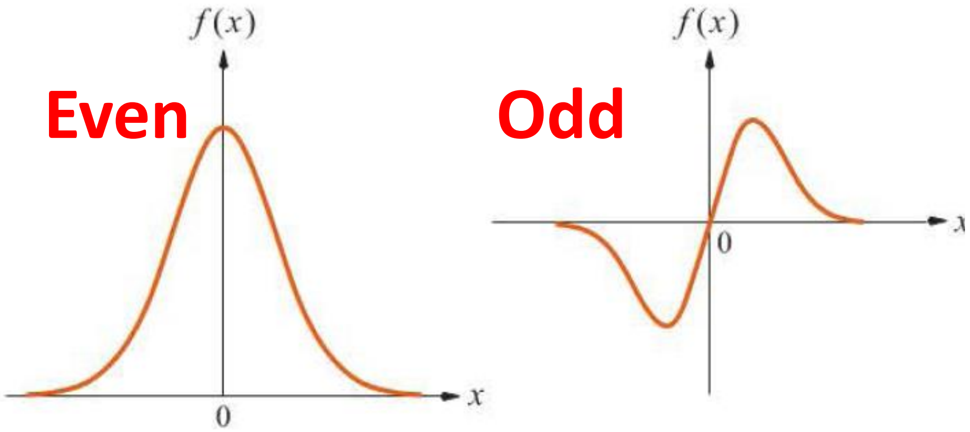
Ground state: v = 0, $E_0 = \frac{1}{2}h\nu = \frac{1}{2}\hbar\omega$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

Zero point energy

Summary: Lecture - 06





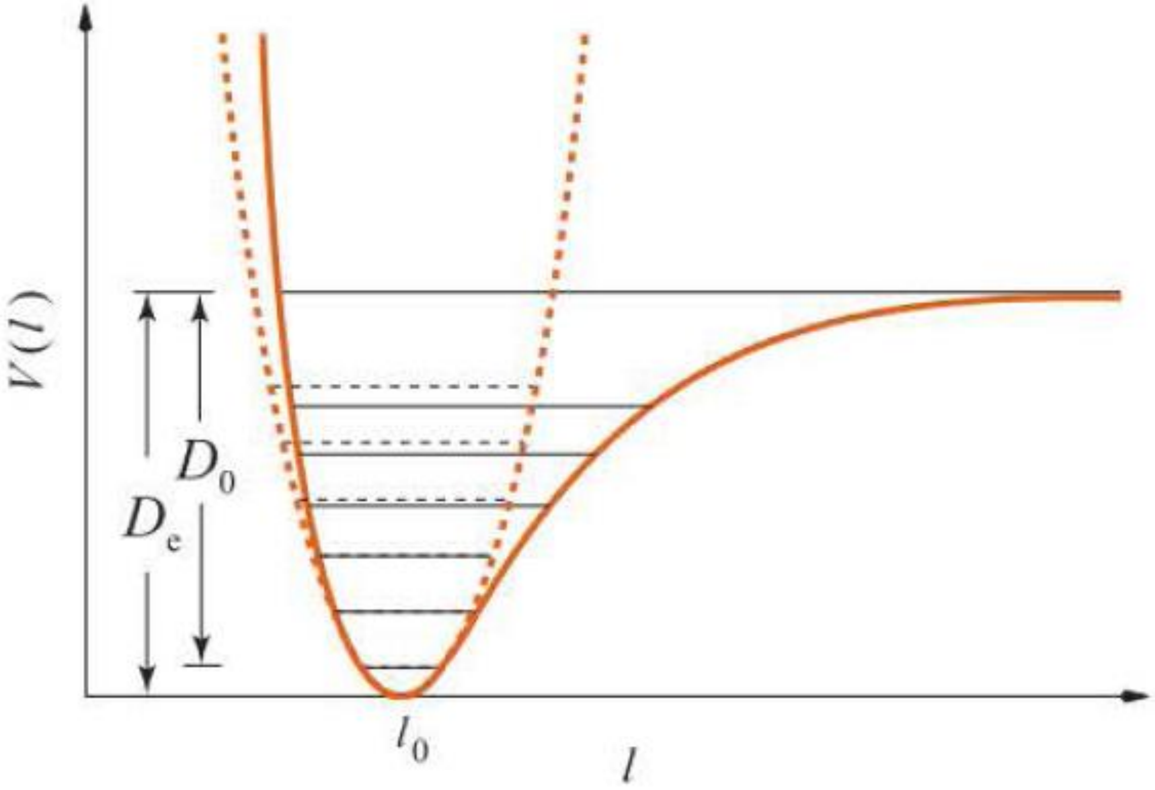
- Number of nodes is v
- Wavefunctions are alternately symmetric or antisymmetric about x = 0.

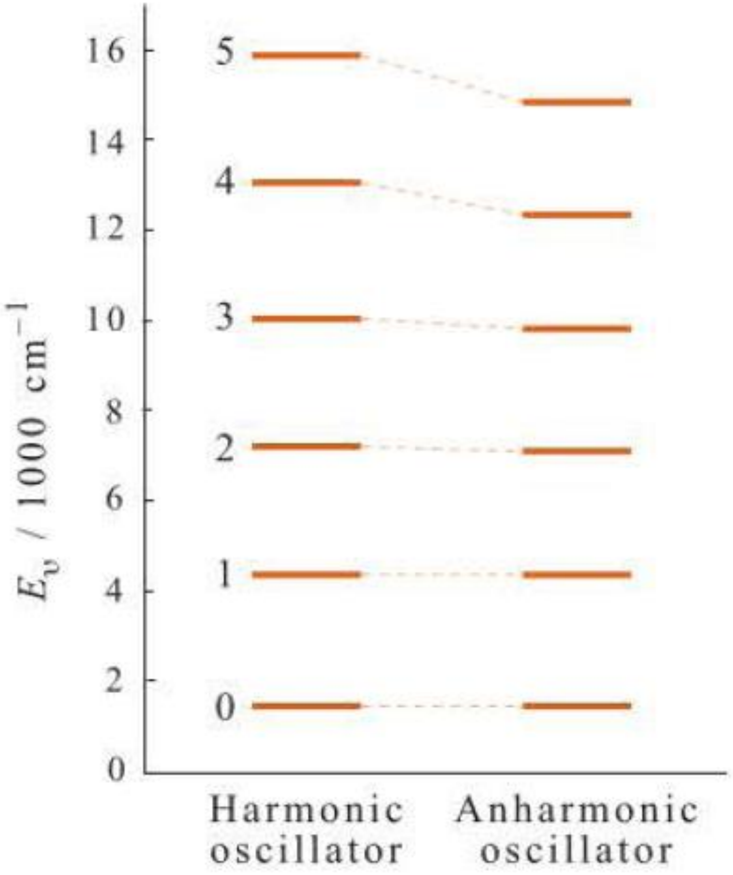
Summary: Lecture - 06

Anharmonicity

Molecular vibrations are really harmonic?

Chemical reactions??





Interested in equilibrium geometry

Hamiltonian in 3-D

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

$$= -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$$

∇^2 is known as Laplacian operator

Aim:

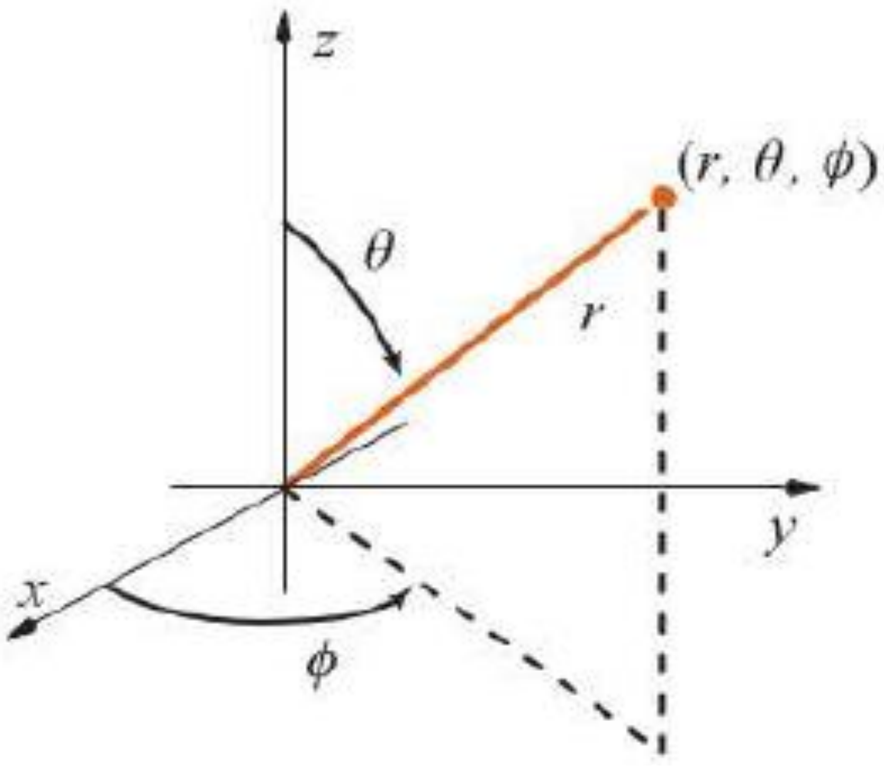
- Rotation in three dimension – very close to H-atom problem.
- Simple system would be a rigid rotor

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

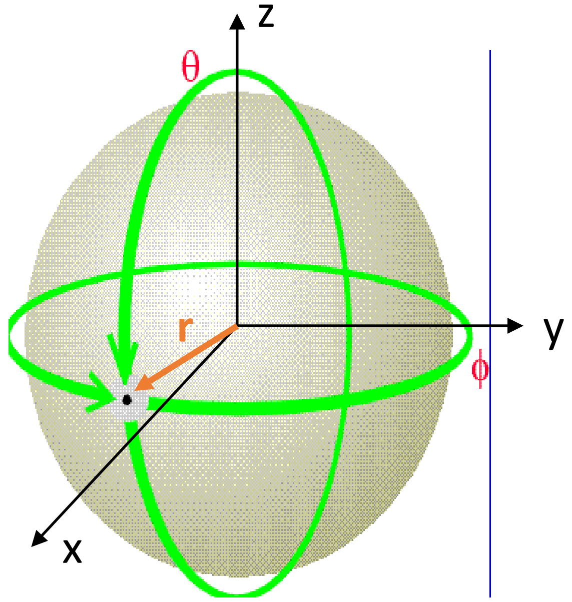
Read: *The separation of variable procedure {Further information 12.1 of Text Book};

Rigid rotor – rotation on a sphere

It is convenient to describe the solutions to the Schrodinger equation in spherical polar coordinates (r, θ, ϕ) rather than cartesian (x,y,z)



Center of symmetry



$$X = r \sin\theta \cos\Phi$$
$$y = r \sin\theta \sin\Phi$$
$$z = r \cos\theta$$

r is constant, Thus, $\Psi(\theta,\varphi)$

Rigid rotor – rotation on a sphere

Laplacian in spherical polar coordinate:

$$\nabla^2 = \frac{\delta^2}{\delta r^2} + \frac{1}{r}\frac{\delta}{\delta r} + \frac{1}{r^2}\Lambda^2 \longrightarrow \text{Legendrian}$$

Legendrian, $\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\delta^2}{\delta\varphi^2} + \frac{1}{\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\,\frac{\delta}{\delta\theta}\right)$

Rigid rotor: r is constant; V (θ, ϕ) = c and c can be considered to be zero

Schrödinger equation: $-\frac{\hbar^2}{2m}\nabla^2\Psi(\theta,\phi) = E\,\Psi(\theta,\phi)$

Separation of variable: $\boxed{\Psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)}$

Rigid rotor – rotation on a sphere

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{1}{r^2}[\Lambda^2\Psi(\theta,\phi)] = E\,\Psi(\theta,\phi),$$ since r is constant

Once, we separate the variables:

$$\Rightarrow \underbrace{\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}}}_{-m_l^2} + \underbrace{\boxed{\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(sin\theta\,\frac{d\Theta}{d\theta}\right) + \epsilon\, sin^2\theta}}_{+m_l^2} = 0$$

$$\epsilon = \frac{2IE}{\hbar^2}$$

where, $\boxed{\Psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)}$

Rigid rotor – rotation on a sphere

Variables, θ &ϕ are separated; we have two equations:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -\boldsymbol{m_l^2} \qquad \text{...Equn. 1}$$

$$\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(sin\theta\,\frac{d\Theta}{d\theta}\right) + \boldsymbol{\epsilon}\, sin^2\theta = +\,\boldsymbol{m_l^2} \qquad \text{...Equn. 2}$$

Equation 1 involves azimuthal angle ϕ

- The solution of Equn. 1 with the application of boundary condition is already solved $\{\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\, exp^{im\phi}\}$
- Wave function is specified by $m_l = 0, \pm1, \pm2, \pm3,\ldots.$

Rigid rotor – rotation on a sphere

- The solution of the second equation (Eq. 2) involves the polar angle θ and the azimuthal angle ϕ as variables. The solution is complicated.

- Solution of the Equn 2 can be obtained by power series method.

- The cyclic boundary conditions on θ ($0 \le \theta \le \pi$): introduction of a second quantum number, *l*, which gives acceptable solutions.

- The presence of m_l in the Eq.2 implies that the range of acceptable values of m_l is restricted by the value of *l*.

- The solution of Schrödinger equation shows that the acceptable wave functions are specified by two quantum numbers, l and m_l.

Rigid rotor – rotation on a sphere

$$\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+\boldsymbol{\epsilon}\,sin^2\theta=+\boldsymbol{m_l^2} \quad \text{...Equn. 2}$$

Solution of above equation provides the condition:

$$\boldsymbol{\epsilon}=l(l+1)\Rightarrow E_l=\frac{\hbar^2}{2I}l(l+1), with\ l=0,1,2,\dots\dots\dots$$

- $l\ is\ the\ orbital\ angular\ momentum\ quantum\ number, 0,1,2,\dots\dots$
- For a given value of l there are $(2l+1)$ permitted values of m_l
- m_l quantum number is called magnetic quantum number,

$$\mathbf{m}_{l}=\boldsymbol{l},\boldsymbol{l}-\mathbf{1},\dots\dots\dots\dots,-\boldsymbol{l}$$

Rigid rotor – rotation on a sphere

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On solving, and imposing the appropriate boundary conditions, obtain the normalized wavefunctions,

$Y_{l,m_l}(\theta, \phi)$, characterized by two quantum numbers *l* and m_l and are called 'spherical harmonics'.

Rigid rotor – rotation on a sphere

Spherical harmonics, $Y_{l,m_l}(\theta,\phi)$.

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	± 1	$\boxed{\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	± 1	$\boxed{\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta e^{\pm i\phi}}$
	± 2	$\boxed{\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}}$

Rigid rotor – Energy states

$$\epsilon = l(l+1) \Rrightarrow E_l = \frac{\hbar^2}{2I} l(l+1), with\ l = 0, 1, 2, \dots$$

Energy is quantized and independent of m_l

- A state with quantum number l is ($2l$+1) fold degenerate.
- Degeneracy is ($2l$+1)

Classical energy, E = $\frac{J^2}{2I}$ Equn. 3

Energy obtained for quantum rotor: $E_l = l(l+1)\frac{\hbar^2}{2I}$ Equn. 4

Rigid rotor – Angular momentum

Comparing Equn. 3 & Equn. 4

$$\boldsymbol{J^2} = \boldsymbol{l(l+1)\hbar^2}$$

Therefore, $J = \sqrt{l(l+1)}\,\hbar$, l = 0, 1, 2, 3, …….

Magnitude of angular momentum

Angular momentum is Quantized

Rigid rotor – Angular momentum

Rotation in a plane:

- Z-component of angular momentum: $L_z = m_l\hbar$,

$m_l = l, l-1, \ldots\ldots, -l$ *(including zero)*

- The component of angular momentum about the z-axis takes only $2l+1$ values.
- Two aspects of the quantization of angular momentum vector, the magnitude and its orientation.
- The orientation of a rotating body is quantized. Space quantization.

Rigid rotor – Space quantization

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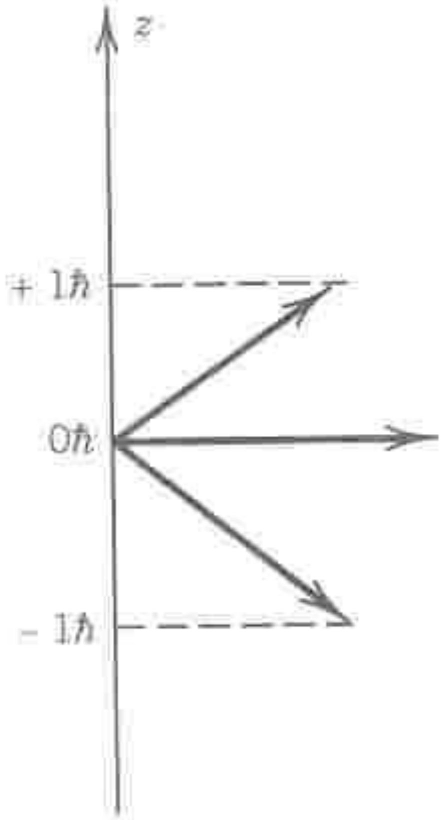
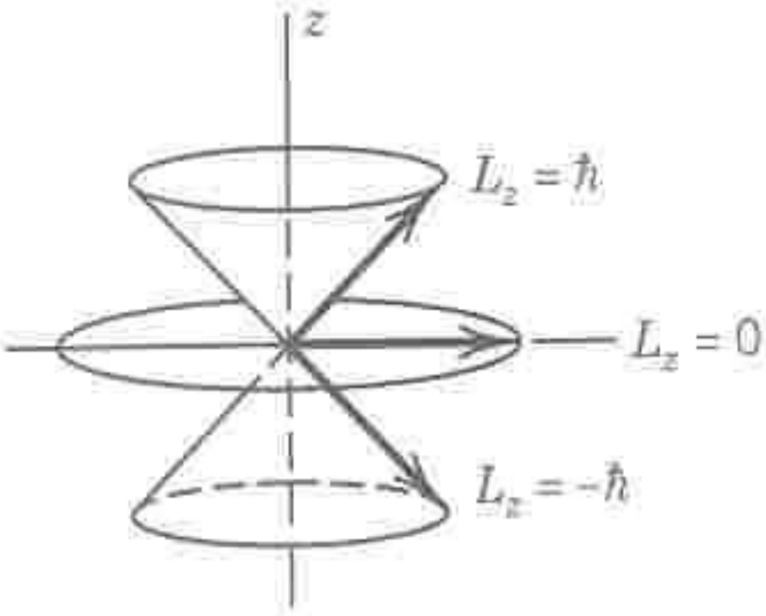
- $\mathbf{m}_l$ is confined to the values $\boldsymbol{l}, \boldsymbol{l}-\mathbf{1}, \ldots \ldots \ldots \mathbf{0}, \ldots \ldots \ldots, -\boldsymbol{l},$
- Component of angular momentum about the Z-axis may take on only $(2\boldsymbol{l}+\mathbf{1})$ values.
- Angular momentum is represented by a vector of length proportional to its magnitude, $\sqrt{l(l+1)}\,\hbar$.
- $\mathbf{m}_l$: projection of angular momentum on the Z-axis
- A rotating body may not take up an arbitrary orientation w.r.t. some **specified axis** (an axis defined by the direction of an externally applied electric or magnetic field)– called space quantization.

Rigid rotor – Space quantization

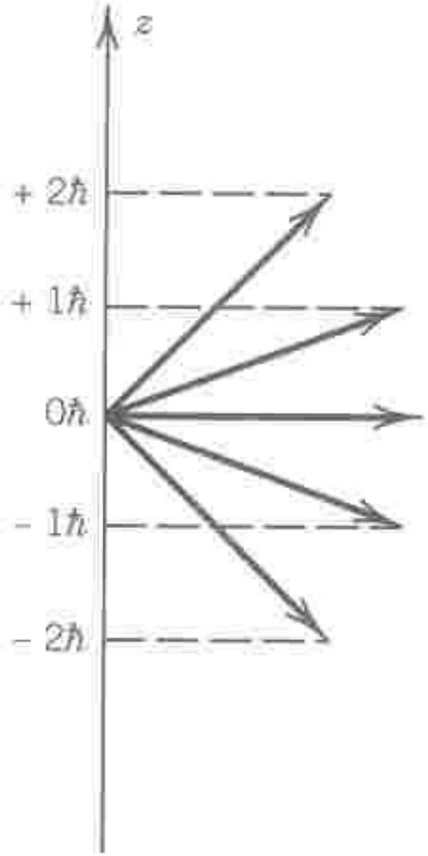
Case-I: $l = 1$, $m_l = 1, 0, -1$

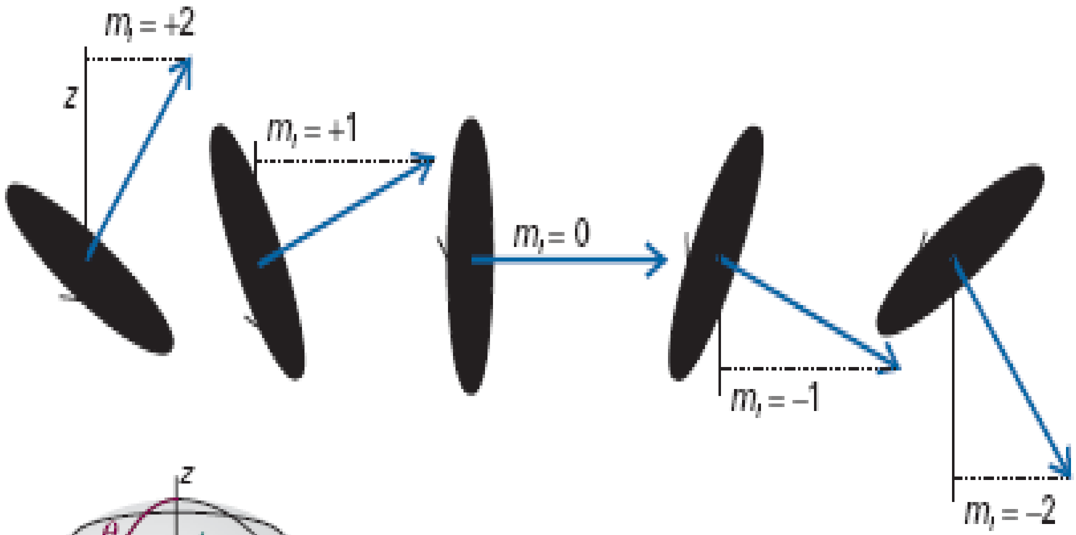


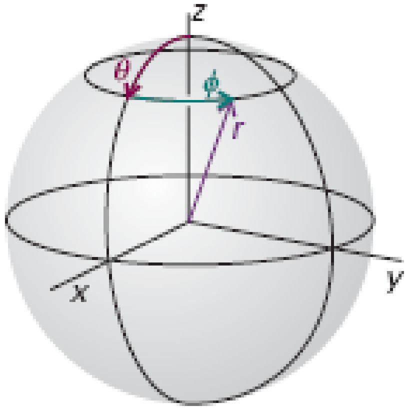


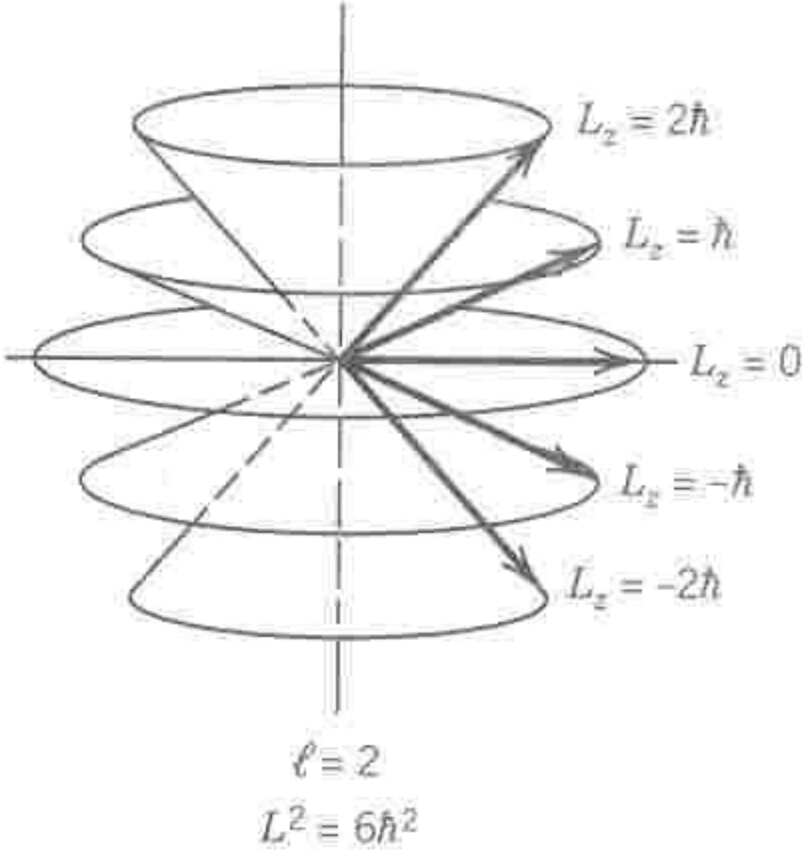
Rigid rotor – Space quantization

Case-II: $l = 2$, $m_l = 2, 1, 0, -1, -2$









$^{1}H^{127}I$ molecule – A Rigid rotor

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Under certain circumstances the particle on a sphere is a reasonable model for the description of the rotation of diatomic molecule. Consider, the rotation of a $^{1}H\ ^{127}I$ molecule: because of the large differences in atomic masses, it is appropriate to picture the ^{1}H atom as orbiting w.r.t. a stationary ^{127}I atom at a distance r = 160 pm, the equilibrium bond distance.

The moment of inertia of $^{1}H\ ^{127}I$ is, $I = m_H r^2 = 4.288 \times 10^{-47}$ kg m^2

It follows that, $\frac{\hbar^2}{2I} = 1.297 \times 10^{-22}$ J = 0.1297 Z J

This energy corresponds to 78.09 J mol^{-1}

$$\boxed{E_l = \frac{\hbar^2}{2I} l(l+1)}$$

$^{1}H^{127}I$ molecule – A Rigid rotor

l	E_l	J	Degeneracy
0	0	0	1
1	0.2594 Z J	$\sqrt{2}\,\hbar$	3
2	0.7782 Z J	$\sqrt{6}\,\hbar$	5
3	1.556 Z J	$\sqrt{12}\,\hbar$	7

$$E_1 - E_0 = 0.2594\ \text{Z J} = h\nu \Rightarrow \nu = 391.5\ \text{GHz}$$

In Microwave region

Hydrogen atom – simplest of all atoms

- Energy eigen value problem can be solved exactly – a two body problem. Composed of nucleus (n) and electron (e).
- Potential, V(q) is Columbic interaction.
- Solution of Schrödinger equation are eigen-/wave- functions – referred to as orbitals.
- H-atoms wave functions are staring point for the description of all atoms and/or molecules.
- 3-D H-atom problem in spherical polar coordinates (r, θ, ϕ) is separable into three 1-D equations w.r.t. ϕ, θ, and r.
- Spherical Harmonics: Solution of θ & ϕ – solution of orbital angular momentum problem – determine the shape of wave functions.

Hydrogen atom – simplest of all atoms

- Solution to the r equation determines the size of the wave function.
- H-atom problem is centrally symmetric – only the equation in r contains the Coulomb potential term.
- Form of Coulomb potential makes one atom different from another.
- The angular part of the wave functions are to a first approximation, independent of the form of the potential.
- Thus, shapes of the orbital are approximately same for all atoms.
- H-atom energy eigen value problem can be solved exactly – means the approximate shapes of the orbitals of all atoms are known.
- H-atom problem is important – because molecules can be described in terms of superposition of AOs with shapes that are known (approx.).

Hydrogen atom – simplest of all atoms

- Spherical harmonics are the general solution to the orbital angular momentum problem.
- Can be used to describe the angular momentum states of any atom and similar problem in molecular rotation.

Rigid rotor – Supporting information

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{1}{r^2}[\Lambda^2\Psi(\theta,\phi)] = E\,\Psi(\theta,\phi),$$ since r is constant

We can rearrange the above equation:

$$\Rightarrow \Lambda^2\,\Psi(\theta,\phi) = -\frac{2mr^2E}{\hbar^2}\Psi(\theta,\phi) = -\frac{2IE}{\hbar^2}\Psi(\theta,\phi)$$

$$\Rightarrow \Lambda^2\,\Psi(\theta,\phi) = -\,\boldsymbol{\epsilon}\,\Psi(\theta,\phi),$$ where $\boldsymbol{\epsilon} = \frac{2IE}{\hbar^2}$

$\psi(\theta,\phi)$ is separated into θ part and ϕ part, i.e.

$$\boxed{\Psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)}$$

Rigid rotor – Supporting information

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$$\Lambda^2\Psi\,(\theta,\phi) = -\,\boldsymbol{\epsilon}\,\Psi(\theta,\phi)$$

Substitute, $\Psi\,(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

$$\frac{1}{sin^2\theta}\,\frac{\delta^2(\Theta\,\Phi)}{\delta\varphi^2} + \frac{1}{sin\theta}\,\frac{\delta}{\delta\theta}\left(sin\theta\,\frac{\delta(\Theta\,\Phi)}{\delta\theta}\right) = -\,\boldsymbol{\epsilon}\,\Theta\Phi$$

$$\Rightarrow\;\frac{\Theta}{sin^2\theta}\,\frac{d^2\Phi}{d\varphi^2} + \frac{\Phi}{sin\theta}\,\frac{d}{d\theta}\left(sin\theta\,\frac{d\Theta}{d\theta}\right) = -\,\boldsymbol{\epsilon}\,\Theta\Phi$$

Multiplication of both sides by $\sin^2\theta/\Theta\Phi$, and rearrangement gives,

Rigid rotor – Supporting information

$$\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\varphi^2} + \frac{\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) = -\,\epsilon\,\Theta\Phi$$

Multiplication by $\sin^2\theta/\Theta\Phi$,

$$\Rightarrow \underbrace{\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}}}_{-m_l^2} + \underbrace{\boxed{\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) + \epsilon\sin^2\theta}}_{+m_l^2} = 0$$