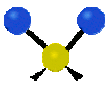
Quantum Mechanical Models of Vibration and Rotation of Molecules Chapter 18

Molecular Energy
- Translational
- Vibrational
- Rotational
- Electronic
- …

Translational, Vibrational, Rotational → Molecular Motions

Vibrations of Molecules:

Model approximates molecules to atoms joined by springs. A vibration (one type of – *a normal mode* of vibration) of a CH_2 moiety would look like;



http://en.wikipedia.org/wiki/Molecular_vibration

The motions are considered as harmonic oscillators.

For a molecule of N atoms there are 3N-6 normal modes (nonlinear) or 3N-5 (linear).

Frequency of vibration – classical approach

Water (3) http://www.youtube.com/watch?v=1uE2lvVkKW0

CO_2 (4) http://www.youtube.com/watch?v=W5gimZlFY6I

O_2 (1) http://www.youtube.com/watch?v=5QC4OVadKHs

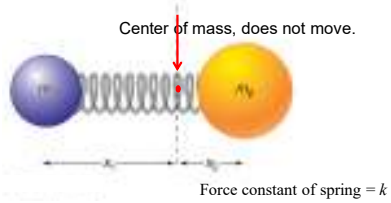
During a molecular vibration the motion of the atoms are with respect to the center of mass, and the center of mass is stationary as far as the vibration is concerned.

This concept is true for all normal modes of vibrations of molecules.

Working with center of mass coordinates simplifies the solution.

Vibrational motion - harmonic oscillator, KE and PE – classical approach

Diatomics:



Whether pulled apart or pushed together from the equilibrium position, the spring resists the motion by an opposing force.

$$F = -k\,x$$

$$x = [x_{m_1}(t) + x_{m_2}(t)] - [x_{m_1} + x_{m_2}]_{equilibrium}$$

Center of mass coordinates $x_{cm} = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$

reduced mass, μ; $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$\sim$

$$F = \mu a = \mu \frac{d^2x}{dt^2}$$

$$F = -k\,x$$

Spring extension of a mass μ from it's equilibrium position.

The physical picture changes from masses (m_1 and m_2) connected by a spring (force constant k) to a reduced mass, μ, connected by a spring (same k) to an immovable wall.

Second Law $F = \mu a = \mu \dfrac{d^2x}{dt^2}$ and $F = -k\,x$ $\Rightarrow$ $\mu \dfrac{d^2x}{dt^2} + kx = 0$

Solutions (general) of the DE will be of the form;

$$x(t) = c_1 e^{+i\sqrt{(k/\mu)}t} + c_2 e^{-i\sqrt{(k/\mu)}t}$$ Use Euler's Formula

$$x(t) = c_1\left(\cos\sqrt{\frac{k}{\mu}}t + i\sin\sqrt{\frac{k}{\mu}}t\right) + c_2\left(\cos\sqrt{\frac{k}{\mu}}t - i\sin\sqrt{\frac{k}{\mu}}t\right)$$

$$x(t) = b_1\cos\sqrt{\frac{k}{\mu}}t + b_2\sin\sqrt{\frac{k}{\mu}}t$$

where $b_1 = c_1 + c_2$ and $b_2 = i(c_1 - c_2)$

Amplitudes are real numbers, b_1 and b_2 are real or = 0.

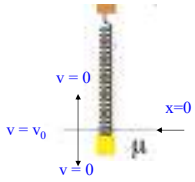
Applying the BC, at t = 0; x(0) = 0, v(0) = v_0.

$$x(0) = b_1 \cos\left(\sqrt{\frac{k}{\mu}} \times 0\right) = b_1 = 0 \quad (\cos(0) = 1)$$

$$v(0) = \left(\frac{dx(t)}{dt}\right)_{t=0} = b_2\sqrt{\frac{k}{\mu}} \cos\left(\sqrt{\frac{k}{\mu}} \times 0\right) = b_2\sqrt{\frac{k}{\mu}} \quad \text{and}$$

$$b_2 = \sqrt{\frac{\mu}{k}} v_0$$

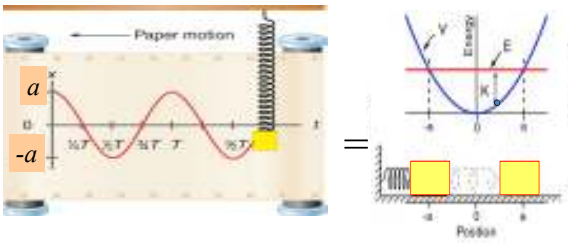
Therefore: $x(t) = \sqrt{\frac{\mu}{k}} v_0 \sin\sqrt{\frac{k}{\mu}} t$



and to find T period: $\sqrt{\frac{k}{\mu}}(t + T) - \sqrt{\frac{k}{\mu}} t = 2\pi$

$$\Rightarrow \quad T = 2\pi\sqrt{\frac{\mu}{k}}$$

Frequency; $\nu = \frac{1}{T}$ $\qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$



angular velocity $= \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$

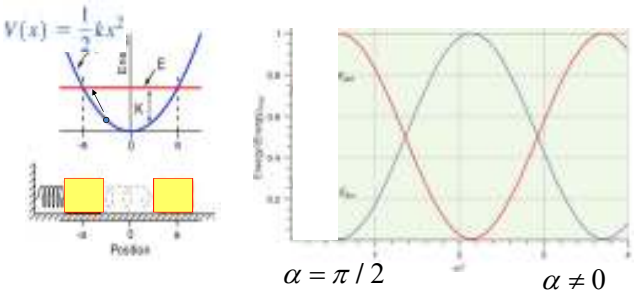
where ν = frequency $\qquad \alpha$ = phase angle

General equation; $x(t) = A\sin(\omega t + \alpha)$

Energy terms (KE, PE) are;

$$KE = \frac{1}{2}\mu v^2 \qquad PE = \frac{1}{2}kx^2$$

where v and x are velocity and position (displacement from equilibrium).



$E_{potential} = \frac{1}{2}kx^2$ and $E_{kinetic} = \frac{1}{2}\mu v^2$ No restriction on E values, classically.

Study Example Problem 18.1

EXAMPLE PROBLEM 18.1

For a harmonic oscillator described by $x(t) = A\sin(\omega t + \alpha)$, $\omega = (k/\mu)^{1/2}$, answer the following questions.

a. What are the units of A? What role does α have in this equation?

b. Graph the kinetic and potential energies given by the following equations as a function of time:

$$E_{kinetic} = \frac{1}{2}mv^2 \quad \text{and} \quad E_{potential} = \frac{1}{2}kx^2$$

c. Show that the sum of the kinetic and potential energies is independent of time.

Solution

a. Because $x(t)$ has the units of length and the sine function is dimensionless, A must have the units of length. The quantity α sets the value of x at $t = 0$, because $x(0) = A\sin(\alpha)$.

b. We begin by expressing the kinetic and potential energies in terms of $x(t)$:

$$E_{kinetic} = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2$$

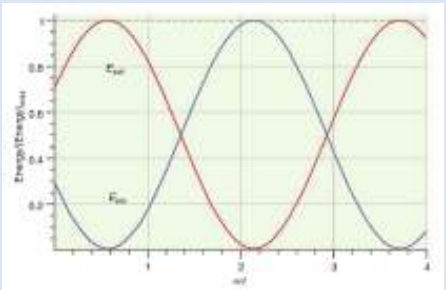
$$= \frac{\mu}{2}\left(A\omega\cos(\omega t + \alpha)\right)^2$$

$$= \frac{1}{2}\mu\omega^2 A^2\cos^2(\omega t + \alpha)$$

$$E_{potential} = \frac{1}{2}kx^2 = \frac{1}{2}kA^2\sin^2(\omega t + \alpha)$$

$$= \frac{1}{2}\mu\omega^2 A^2\sin^2(\omega t + \alpha) \text{ because } \omega = \sqrt{\frac{k}{\mu}} \text{ and } k = \mu\omega^2$$

In the following figure, the energy is expressed in increments of $(1/2)\mu\omega^2A^2$ and we have arbitrarily chosen $\alpha = \pi/6$. Note that the kinetic and potential energies are out of phase. Why is this the case?



c. The dashed line in the preceding figure is the sum of the kinetic and potential energies, which is a constant. This can be verified algebraically by adding the expressions for $E_{kinetic}$ and $E_{potential}$:

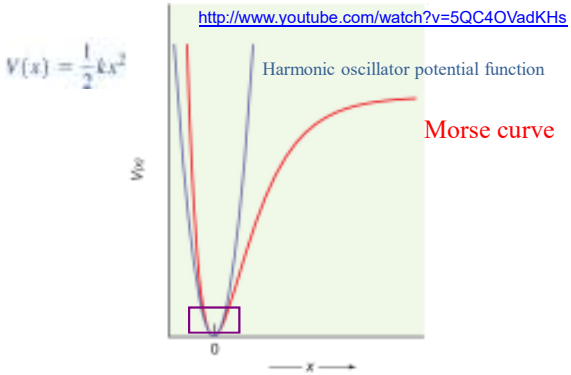
$$E_{total} = \frac{1}{2}\mu\omega^2 A^2\cos^2(\omega t + \alpha) + \frac{1}{2}\mu\omega^2 A^2\sin^2(\omega t + \alpha)$$

$$= \frac{1}{2}\mu\omega^2 A^2\left[\cos^2(\omega t + \alpha) + \sin^2(\omega t + \alpha)\right]$$

$$= \frac{1}{2}\mu\omega^2 A^2$$

Note that the sum of the kinetic and potential energies is independent of time, as must be the case, because no energy is added to the system after the initial stretching of the spring and there is no mechanism such as frictional forces for losing energy.

Harmonic oscillator potential function



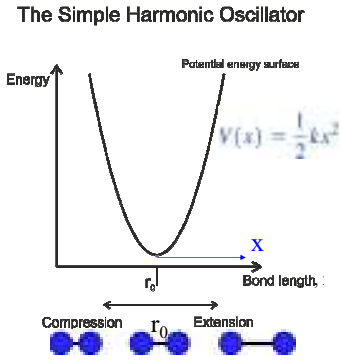
Similar for low energy situations ~ ground state

https://www.youtube.com/watch?v=3RqEIr8NtMI

At room temperature the potential function very closely follow the quadratic function.

Vibrational motion is equivalent to a particle of mass μ, vibrating about its equilibrium distance, r_0.

How can a particle like that be described by a set of wave functions.



Our interest is to model the oscillatory motion of the diatomic molecule (relative motions of atoms).

Also – of interest kinetic and potential energy of the diatomic molecule during the oscillatory motion. Not necessarily the energies of individual atoms of the molecule.

The ultimate goal is to find the (eigen) energies and the eigen functions (wavefunction) of the vibrational states of the diatomic by solving the Schrödinger equation;

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

Recipe to Construct the Schrodinger equation

1. Expression for total energy (classical)
2. Construct the total energy Operator, the Hamiltonian, by expressing KE in terms of momentum operator and mass, PE in terms of position operator.
3. Setup the Schrodinger equation, eigenequation

1. Expression for total vibrational energy,

$$E_{tot,vib} = KE + PE = \frac{1}{2}\mu v^2 + \frac{1}{2}kx^2$$

$$= \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$

2. Construct the total energy Operator, the Hamiltonian

$$\hat{H} = \frac{1}{2\mu}\hat{p}^2 + \frac{1}{2}k\hat{x}^2 = \frac{1}{2\mu}\left(i\hbar\frac{d}{dx}\right)^2 + \frac{1}{2}kx^2$$

3. Set the Schrodinger equation, eigenequation

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

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_n(x)}{dx^2} + \frac{kx^2}{2}\psi_n(x) = E_n\psi_n(x)$$

Solutions (i.e. normalized wavefunctions, eigenfunctions) of which are;

$$\psi_n(x) = A_n H_n\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2}, \quad \text{for } n = 0, 1, 2, \ldots$$

With the normalization constant $A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$

$$\psi_n(x) = A_n H_n\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2}, \quad \text{for } n = 0, 1, 2, \ldots$$

$H_n(\alpha^{1/2}x)$ = Hermite polynomials

$$A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

n = vibrational quantum number

Hermite polynomials :

$$H_n(z) = (-1)^n e^{z^2}\frac{d^n}{dz^n}e^{-z^2}$$

The first six Hermite polynomials

v	$H_v(z)$
0	1
1	$2z$
2	$4z^2 - 2$
3	$8z^3 - 12z$
4	$16z^4 - 48z^2 + 12$
5	$32z^5 - 160z^3 + 120z$

The first few wavefunctions (n = 0,..3)

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-(1/2)\alpha x^2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-(1/2)\alpha x^2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-(1/2)\alpha x^2}$$

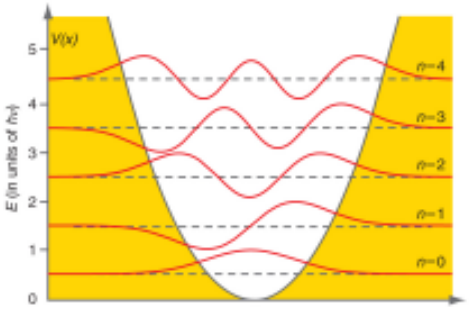
$$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x) e^{-(1/2)\alpha x^2}$$

The respective eigen energies are;

$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right) = h\nu\left(n + \frac{1}{2}\right) \quad \text{with } n = 0, 1, 2, 3, \ldots$$

zpe

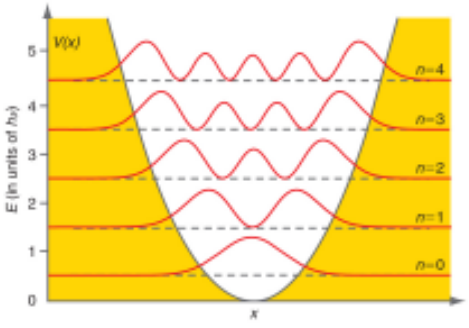
The first few wavefunctions, ψ_n (n = 0,..4)



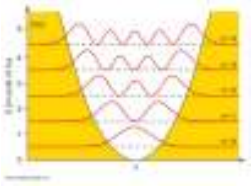
Note:
the resemblance to 1D box non-infinite potential well results.

Equal energy gaps are equal in contrast to 1D box case.

The first few wavefunctions, ψ_n^2 (n = 0,..4)



Note the resemblance to 1D box.

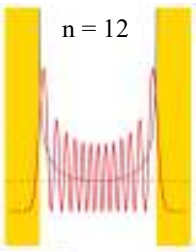


The *constraint imposed* on the particle by a spring results in zero point energy.

The energy values of vibrational states are precisely known, but the position of the particles (as described by the amplitude) is imprecise, only a probability density $\psi^2(x)$ of x can be stated, $[\hat{x}, \hat{H}] \neq 0$.

Note: the overflow of the wave function (forbidden) of the wavefunction beyond the potential barrier wall.

At high quantum numbers *n* (high energy limit) the system gets closer to a classical system (red - probability of x in q.m. oscillator, blue - probability of x classical oscillator).



high low high

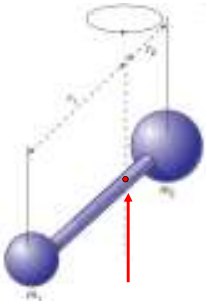
n >>0

high low high

Blue to black, a particle in a barrel classical model.

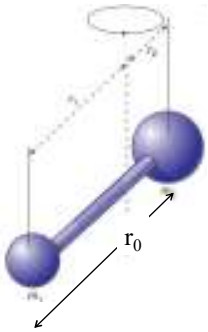
Rotational energies of a classical ***rigid rotor*** (diatomic).

In vibrational motion, velocity, acceleration and momentum are parallel to the direction of motion.



No opposing force to rotation – no PE (stored of energy) term. All energy = KE.

In the center of mass coordinate system, rigid rotor motion equivalent to a mass of μ moving in a circle of radius r_0 (= bond length, *constant*) with an angular velocity ω and a tangential velocity v. Rotation in 2D (on a plane)



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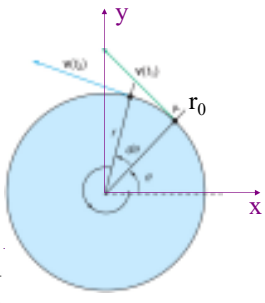
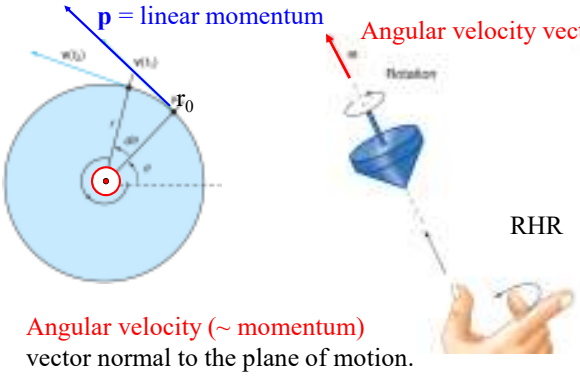


$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



Angular velocity (~ momentum) vector normal to the plane of motion. (coming out of the plane)

Acceleration in the radial direction $= \dfrac{|\mathbf{v}(t)|^2}{r}$

Angular velocity ω and angular acceleration α,

$$|\boldsymbol{\omega}| = \frac{d\theta}{dt} \quad \text{and} \quad \alpha = \frac{d|\boldsymbol{\omega}|}{dt} = \frac{d^2\theta}{dt^2}$$

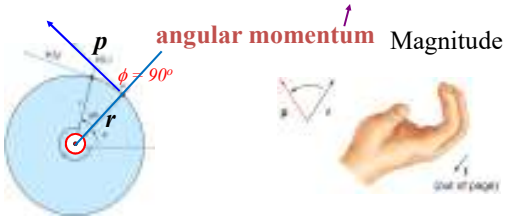
Mass with constant ω makes $\alpha = 0$.

Tangential linear velocity, $\mathbf{v} = \dfrac{\mathbf{r}d\theta}{dt} = r\omega$

$$E_{kinetic} = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}I\omega^2$$

$\omega = \sqrt{\dfrac{2E}{I}}$ $= I$, moment of inertia

QM Angular momentum (2D): $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$



Magnitude of $\boldsymbol{l} = l$

$$l = pr\sin\phi = \mu v r \sin\phi \quad \Rightarrow p = \frac{l}{r}$$

Energy Rotational: $E = \dfrac{p^2}{2\mu} = \dfrac{l^2}{2\mu r^2} = \dfrac{l^2}{2I}$

Classical rotor - no restriction on l (or E.

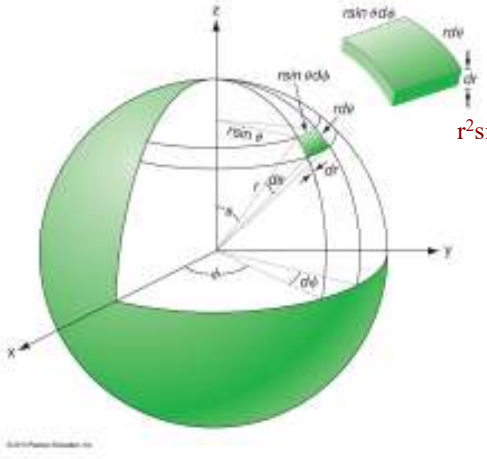
The rotation on the x,y plane (2D) *occurs freely*. Equivalently the particle of mass μ= moves on the circle (constant radius $r = r_0$) *freely;* $E_{pot} = V(x,y) = 0$

$$E_{tot,rot} = KE + PE = KE = \frac{p^2}{2\mu}$$

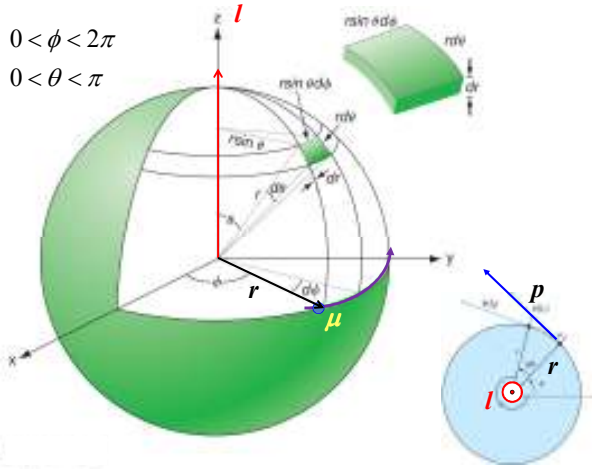
$$\hat{H} = \frac{\hat{p}^2}{2\mu} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

SE:

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right)_{r=r_0} = E\psi(x,y)$$



$r^2 \sin\theta \, d\theta \, d\phi \, dr$



$0 < \phi < 2\pi$

$0 < \theta < \pi$

In *polar* coordinates (variable is ϕ):

$$-\frac{\hbar^2}{2\mu r_0^2}\frac{d^2\Phi(\phi)}{d\phi^2} = E\Phi(\phi)$$

Rotational eigenfunction.

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

General solution for DE), wavefunctions:

$$\Phi_+(\phi) = A_{+\phi} e^{i|m_l|\phi} \quad \text{and} \quad \Phi_-(\phi) = A_{-\phi} e^{-i|m_l|\phi}$$

m_l = integer

clockwise rotation

counter-clockwise rotation

m_l = rotational quantum number, quantization, next page

$$\Phi_+(\phi) = A_{+\phi} e^{i|m_l|\phi} \quad \text{and} \quad \Phi_-(\phi) = A_{-\phi} e^{-i|m_l|\phi}$$

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

$e^{im_l\phi} = e^{im_l(\phi+2\pi)}$

$e^{im_l\phi} = e^{im_l(\phi+2\pi)} = e^{im_l\phi} e^{im_l 2\pi}$

i.e. $e^{im_l 2\pi} = 1$

Using the Euler's Formula

Now; $\cos(2\pi m_l) + i\sin(2\pi m_l) = 1$

$\cos(2\pi m_l) = 1$ real number

Therefore $m_l = 0, \pm 1, \pm 2, \ldots$

Note: One boundary condition leads to one q.n., m_l.

$\Phi_+(\phi) = A_+ e^{i|m_l|\phi}$ and $\Phi_-(\phi) = A_- e^{-i|m_l|\phi}$

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

$e^{-im_l\phi} = e^{-im_l(\phi+2\pi)}$

$e^{-im_l\phi} = e^{-im_l(\phi+2\pi)} = e^{-im_l\phi} e^{-im_l 2\pi}$

i.e. $e^{-im_l 2\pi} = 1$

Now; $\cos(-2\pi m_l) + i\sin(-2\pi m_l) = 1$

thus $\cos(2\pi m_l) = 1$ real number

Therefore $m_l = 0, \pm1, \pm2, \ldots$

Normalization constant $A_{+\phi}$;

$$\int_0^{2\pi} \Phi^*_{m_l}(\phi)\Phi_{m_l}(\phi)d\phi = 1$$

Normalization condition

$$A^2_{+\phi} \int_0^{2\pi} e^{-im_l\phi} e^{+im_l\phi} d\phi = 1$$

$$A^2_{+\phi} \int_0^{2\pi} d\phi = 1 \qquad A^2_{+\phi}(2\pi) = 1$$

$$A_{+\phi} = \frac{1}{\sqrt{2\pi}}$$

Normalization constant $A_{\pm\phi}$;

Normalization condition

$$\int_0^{2\pi} \Phi^*_{m_l}(\phi)\Phi_{m_l}(\phi)d\phi = 1$$

$$A^2_{\pm\phi} \int_0^{2\pi} e^{\mp im_l\phi} e^{\pm im_l\phi} d\phi = 1$$

$$A^2_{\pm\phi} \int_0^{2\pi} d\phi = 1 \qquad A^2_{\pm\phi}(2\pi) = 1$$

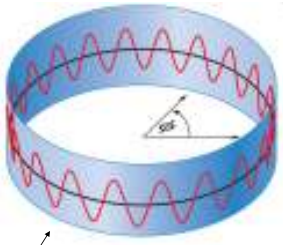
$$A_{\pm\phi} = \frac{1}{\sqrt{2\pi}}$$

Same regardless of m_l value.

$$\Phi_\pm(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im_l\phi}$$

Rotational wave function

m_l is an integer.



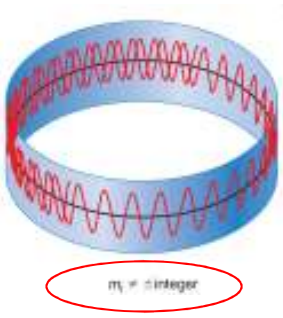
real part

m_l = ±integer

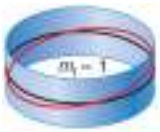
$$\Phi_+(\phi) = \frac{1}{\sqrt{2\pi}} e^{+im_l\phi} = \frac{1}{\sqrt{2\pi}}(\cos m_l\phi + i \sin m_l\phi)$$

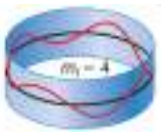
Stationary state - exist

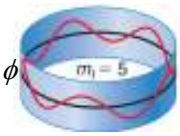
$$\Phi_{\pm}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_l \phi}$$



Non-stationary state
- Unacceptable wavefunction, annihilates

$\frac{1}{\sqrt{2\pi}}\cos\phi$   $\frac{1}{\sqrt{2\pi}}\cos 2\phi$

$\frac{1}{\sqrt{2\pi}}\cos 3\phi$   $\frac{1}{\sqrt{2\pi}}\cos 4\phi$

$\frac{1}{\sqrt{2\pi}}\cos 5\phi$   $\frac{1}{\sqrt{2\pi}}\cos 6\phi$

Energy of rotational states:

$$\Phi_{\pm}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_l \phi}$$

$$-\frac{\hbar^2}{2\mu r_0^2}\frac{d^2\Phi(\phi)}{d\phi^2} = E\Phi(\phi)$$

$$E_{m_l} = \frac{\hbar^2 m_l^2}{2\mu r_0^2} = \frac{\hbar^2 m_l^2}{2I} \quad \text{for } m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Note; No non-zero ZPE.
ZPE appears if the potential energy confinement exists, not here ($V(\phi)$=0)

Degenerate states
- *two fold degenerate* (*of equal energy*)

$$E = \frac{|\boldsymbol{l}|^2}{2\mu r_0^2} = \frac{|\boldsymbol{l}|^2}{2I} = \frac{1}{2} I\omega^2$$

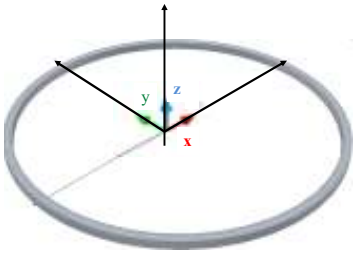
$\omega = \sqrt{\frac{2E}{I}}$ and angular momentum $|\boldsymbol{l}| = I\omega$

$$\omega = \sqrt{\frac{2E_{m_l}}{I}} = \sqrt{\frac{2}{I}E_{m_l}} = \sqrt{\frac{2}{I}\frac{\hbar^2 m_l^2}{2I}} = \frac{\hbar m_l}{I}$$

m_l being an integer, rotational frequency ω will take finite values. – *discrete set of rotational frequencies* !!

For 2D rotor, $\boldsymbol{l} = \boldsymbol{l}_z$.

The wavefunctions, …. of a rigid rotor are similar to the wavefunctions of a free particle restricted to a circle (particle in a ring)!



$$E_{kinetic} = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}I\omega^2$$

For a rigid rotor, angular momentum lies in the z direction.

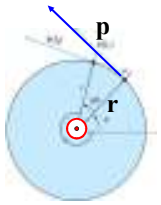
Angular momentum z component operator;

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

Angular Momentum – 2D rigid rotor.

Operator: $\hat{l}_z = -i\hbar\frac{\partial}{\partial\phi}$ angular analogue of momentum

$\Phi_{\pm}(\phi) = \frac{1}{\sqrt{2\pi}}e^{\pm im_l\phi}$ wave functions



$$\hat{l}_z\Phi_{\pm}(\phi) = \frac{-i\hbar}{\sqrt{2\pi}}\frac{d\,e^{\pm im_l\phi}}{d\phi}$$

$$= \frac{\pm\, m_l\hbar}{\sqrt{2\pi}}e^{\pm im_l\phi} = \pm m_l\hbar\,\Phi_{\pm}(\phi)$$

Angular momentum (in z direction) is quantized!!

Note: *for 2D rigid rotor both* $\hat{H}$, $\hat{l}_z$ *have same* Φ, $[\hat{H},\hat{l}_z] = 0$

Note: *for 2D rigid rotor* $[\hat{H},\hat{l}_z] = 0$

Both operators has the same eigenfunctions.

Hence angular momentum (z component) for this case can be precisely measured.

But the position, here represented by ϕ, cannot be measured precisely; the *probability* for *any interval of* $d\phi$ is the same,

$[\hat{\phi},\hat{l}_z] \neq 0$

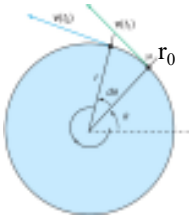
$$P(\phi)\,d\phi = \Phi^*(\phi)\Phi(\phi)\,d\phi$$

$$= \left(\frac{1}{\sqrt{2\pi}}\right)^2 e^{\pm im_l\phi}e^{\mp im_l\phi}\,d\phi$$

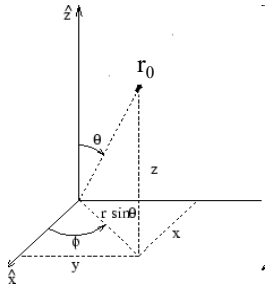
$$= \frac{d\phi}{2\pi}$$

QM Angular momentum (3D):

Particle on a circle (2D).

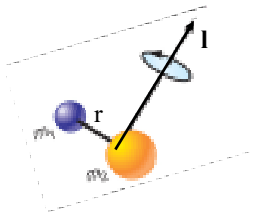


2D



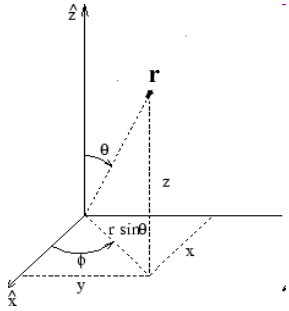
3D

Particle on the surface of a sphere (3D).



Classical 3D rotor

≡



Particle of mass μ on the surface of a sphere of radius r.

PE confinement – none; $V(\theta,\phi) = 0$
Set PE operator set to zero. E = KE + PE = KE

KE (energy) operator for rotor in polar coordinates:

$$\hat{H}_{rot} = -\frac{\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

SE: Note the form of $\hat{H}_{rot}$

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right] = EY(\theta,\phi)$$

Wavefunction; $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

Just the steps in solving the SE for rigid rotor

a. collect the constants: $\beta = \frac{2\mu r_0^2 E}{\hbar^2}$ note

b. multiply by $\sin^2\theta$, rearrange to get

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

Differentiation only w.r.t.; θ ϕ

Therefore $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$;separation of variables possible.

spherical harmonic functions

c. substitute for Y(θ,ϕ) divide by Θ(θ)Φ(ϕ), we get

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

Because each side of the equation depends only one of the variables and the equality exists for all values of the variables, both sides must be equal to a constant.

$$\Rightarrow\quad \frac{1}{\Theta(\theta)}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=m_l^2$$

$$\Rightarrow\quad \frac{1}{\Phi(\phi)}\frac{d^2\Phi(\phi)}{d\phi^2}=-m_l^2$$

$$\frac{1}{\Phi(\phi)}\frac{d^2\Phi(\phi)}{d\phi^2}=-m_l^2$$

solutions ⇓

$$\Phi_+(\phi)=A_{+\phi}e^{i|m_l|\phi}\quad\text{and}\quad\Phi_-(\phi)=A_{-\phi}e^{-i|m_l|\phi}$$

BC leads to q.n.; $m_l = 0, 1, 2, 3, \ldots$

$m_l = 0, \pm1, \pm2, \pm3, \ldots$

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=m_l^2$$

solutions ⇓

BC leads to more q.n.;

$\beta = l(l+1)$, for $l = 0, 1, 2, 3, \ldots$ and

$m_l = -l, -(l-1), -(l-2), \ldots, 0, \ldots, (l-2), (l-1), l$

For a *given* q.n. l there are $(2l+1)$, m_l values. That is the state described by a l quantum number is comprised of $(2l+1)$ sub-states *of equal energy*.

Degeneracy of state with q. n. l, **is** $2l+1$**.**

spherical harmonic functions written in more detail would take the form:

$$Y(\theta,\phi)=Y_l^{m_l}(\theta,\phi)=\Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$$

Energy of degenerate states of q. n. l :

$$\Rightarrow\quad \beta=\frac{2\mu r_0^2E}{\hbar^2}=\frac{2I}{\hbar^2}E=l(l+1)$$

$$E_l=\frac{\hbar^2}{2I}l(l+1)$$ quantization of rotational energy

Eigen-energy: $E_l = \frac{\hbar^2}{2I} l(l+1)$

Verifiable in SE:

$\hat{H}_{total}\, Y_l^{m_l}(\theta,\phi) = \frac{\hbar^2}{2I} l(l+1) Y_l^{m_l}(\theta,\phi)$, for $l = 0, 1, 2, 3, \ldots$

$\hat{H}_{rot}$ Spherical harmonics are eigen functions of the total rotational energy operator. ➡

All m_l states of a 3D rotor has the same energy, E_l ! (degenerate)

the quantum number m_l determines the z-component of the angular momentum vector $\boldsymbol{l}$.

Quantization of Angular Momentum

As will be seen later, the shapes, directional properties and degeneracy of atomic orbitals are dependent on the q.n. l and m_l vales associated with these orbitals.

For 3D rotor; $E_{tot} = \frac{l^2}{2I} \Rightarrow \hat{H} = \frac{\hat{l}^2}{2I}$

Constant for rotor.

Therefore both operators have a common set of eigenfunctions. The operators *should* commute!

$$[\hat{H}, \hat{l}^2] = 0$$

Now; $\hat{H}_{total}\, Y_l^{m_l}(\theta,\phi) = \frac{\hbar^2}{2I} l(l+1) Y_l^{m_l}(\theta,\phi)$

and therefore

$$\hat{l}^2 Y_l^{m_l}(\theta,\phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta,\phi)$$

Note that the above operators differ only by the multiplication constant ($1/2I$), thus the eigen values differ by ($1/2I$). $\hat{H} = \frac{\hat{l}^2}{2I}$

Also note the calculated (and measurable) angular momentum quantity (of *precise* (eigen) value) is that of $|\boldsymbol{l}^2|$ (therefore $|\boldsymbol{l}|$).

$$|\boldsymbol{l}| = \hbar\sqrt{l(l+1)}$$

Components of the angular momentum in x, y and z.

The respective operators are (*Cartesian coordinates*):

$$\hat{l}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{l}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{l}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

The respective operators are in *spherical coordinates* would be:

$$\left.\begin{aligned}\hat{l}_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\\ \hat{l}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\end{aligned}\right\} = f(\theta,\phi)$$

$$\hat{l}_z = -i\hbar\left(\frac{\partial}{\partial\phi}\right) \quad = f(\phi)$$

The following commutator relationships exist.

$$\left.\begin{aligned}[\hat{l}_x, \hat{l}_y] &= i\hbar\hat{l}_z\\ [\hat{l}_y, \hat{l}_z] &= i\hbar\hat{l}_x\\ [\hat{l}_z, \hat{l}_x] &= i\hbar\hat{l}_y\end{aligned}\right\} \neq 0$$

The component operators *do not commute* with one another

As a result the direction of vector ***l*** *cannot be specified (known) 'precisely'* for rotations in 3D in QM systems as opposed to classical 2D rigid rotors. Need to know all vectors at the same time to specify direction of vector ***l***.

However, angular momentum wavefunction is an eigenfunction of the Hamiltonian too and therefore, $\hat{H} = \frac{\hat{l}^2}{2I}$

$$\hat{l}^2 Y_l^{m_l}(\theta,\phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta,\phi)$$

$$Y(\theta,\phi) = Y_l^{m_l}(\theta,\phi) = \Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$$

Examining l_z;

$$\hat{l}_z(Y_l^{m_l}(\theta,\phi)) = \Theta(\theta)\left[-i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}e^{im_l\phi}\right)\right]$$

$$= m_l\hbar\Theta(\theta)\Phi(\phi) \quad !!!$$

$$l_z = m_l\hbar$$

for $m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l$

Conclusion –

Spherical harmonics are eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$.

Magnitudes of both $|\boldsymbol{l}|$ and l_z can be known simultaneously and precisely, but not the x and the z component values of the angular momentum vector, ***l*** .

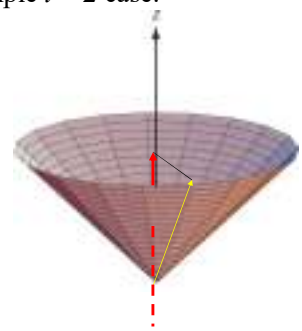
Note/
show explicitly: $[\hat{l}^2, \hat{l}_z] = 0$

The Picture: Vector model of angular momentum

$\widehat{H}$, $\widehat{l}^2$ and $\widehat{l}_z$ commute and $\widehat{l}_x$, $\widehat{l}_y$ and $\widehat{l}_z$ do not commute. with one another. Example $l = 2$ case.

$m_l = 0, \pm 1, \pm 2$

$m_l = +2$

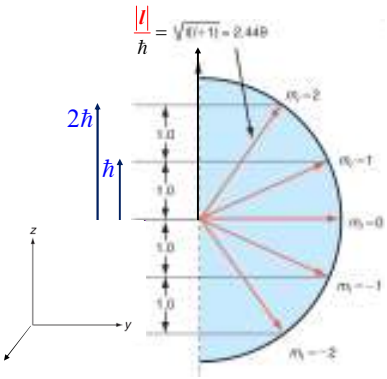


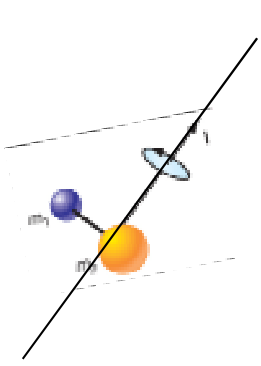
Example $l = 2$ case.

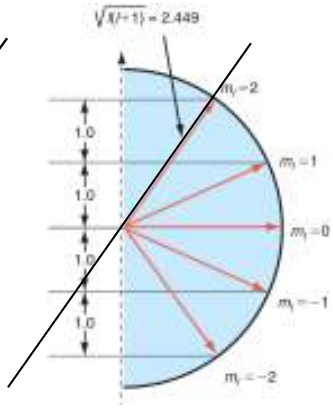
$m_l = 0, \pm 1, \pm 2$

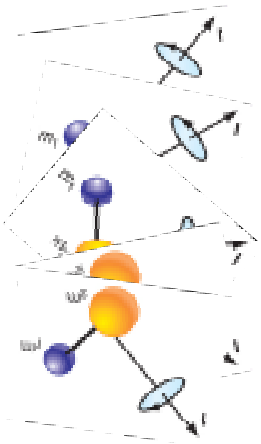
$|\boldsymbol{l}| = \sqrt{l(l+1)}\hbar$

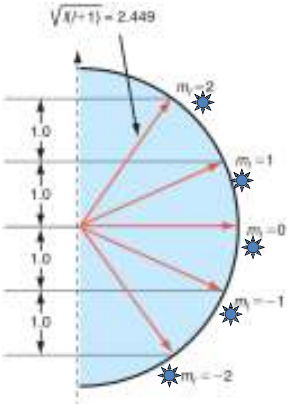
$l_z = m_l\hbar$

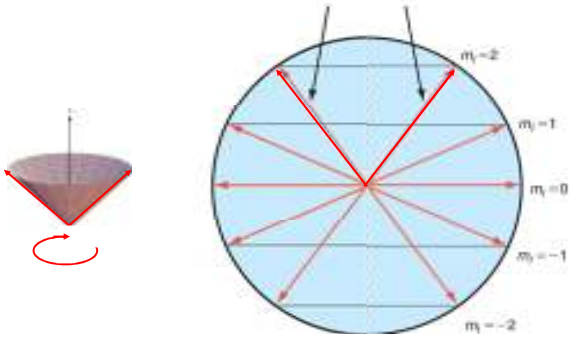




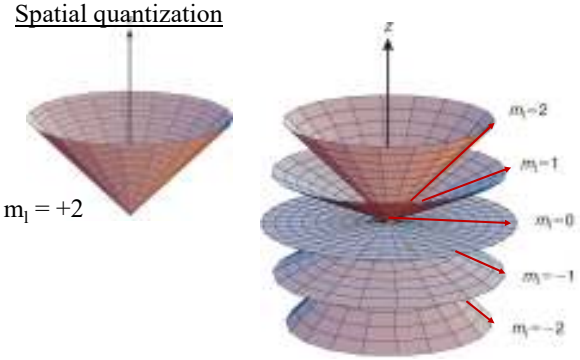








Spatial quantization



Vector model of angular momentum

Spherical harmonic wavefunctions and their shapes: $Y_l^{m_l}(\theta, \phi) = \Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$

$$l = 0 \qquad Y_0^0(\theta, \phi) = \frac{1}{(4\pi)^{1/2}}$$

$$l = 1 \begin{cases} Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\ Y_1^{\pm 1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi} \end{cases}$$

$$l = 2 \begin{cases} Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\ Y_2^{\pm 1}(\theta, \phi) = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{\pm i\phi} \\ Y_2^{\pm 2}(\theta, \phi) = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm 2i\phi} \end{cases}$$

Complex functions - visualization – not possible.