Lecture 4

Angular Momentum and Rigid-Rotor Models and

Outline

1. Review of basics tool (Vectors and Commutation)

2. Basic Definition

3-Quantum Mechanics treatment of Angular Momentum

3.1.Operator Commutation and Simultaneous Eigenfunctions

3.2 Spherical Polar Coordinates for Angular Momentum

3.3 Model system. *The 2D Quantum Mechanical Rigid Rotor*

3.4. The Solution of S.E Wavefumction and Energy

3.5. Application of the 2D Rigid Rotor

3.6. The 3D Quantum Mechanical Rigid Rotor

3.7 Angular Momentum and the Rigid Rotor

3.8 Application of Angular momentum

3.9 The ladder operators

3.10 Spin angular Momentum

I- review of basic tools: Commutation

$$[A,B]=AB-BA$$

$$[A,B]=-[B,A]$$

$$[kA,B]=[A,kB]=k[A,B]$$

$$[A,B+C]=[A,B]+[A,C]$$

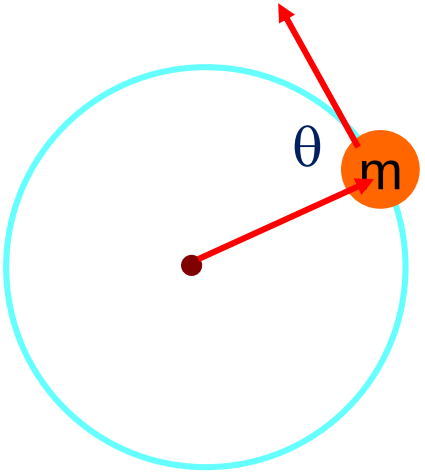
$$[A+B,C]=[A,C]+[B,C]$$

$$[A,BC]=[A,B]C+B[A,C]$$

$$[AB,C]=[A,C]B+A[B,C]$$

II- Basic definition

Angular Momentum (L)



$$L = \vec{r} x \vec{p}$$

Magnitude: $L = rp\sin(\theta)$

Circular Motion: $L = rp\sin(90^0) = rp$

or: $L = rp = rmv = \left(mr^2\right)\left(\frac{v}{r}\right) = (mr^2)\omega$

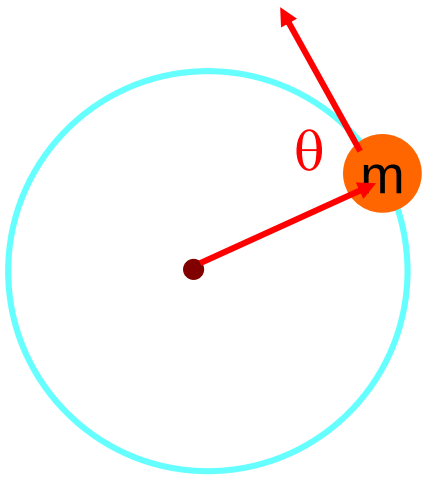
$L = I\omega$ where $I = mr^2$ $\omega = \frac{v}{r}$

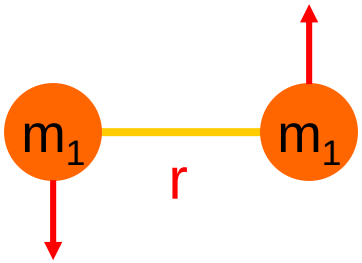
Moment of Inertia **Angular Frequency**

Energy

$$E = \frac{p^2}{2m} = \frac{mv^2}{2} = \frac{m(r\omega)^2}{2} = \frac{mr^2\omega^2}{2} = \frac{I\omega^2}{2}$$ or: $$E = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

Modification: Rotation of two masses about Center of Mass





$$I = m r^2$$

$$I = \mu r^2$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

Comparison of Equations for Linear and Circular Motion

	Linear Motion	Circular Motion	
Mass	m	$I = mr^2$	Moment of inertia
Velocity	v	$\omega = \frac{v}{r}$	Angular velocity
Momentum	p=mv	$L = I\omega$	Angular momentum
Energy	$E = \frac{p^2}{2m}$	$E = \frac{L^2}{2I}$	Energy
or	$E = \frac{mv^2}{2}$	$E = \frac{I\omega^2}{2}$	Energy

3-Quantum Mechanics treatment of Angular Momentum

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k} \qquad \vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$$

$$\vec{L} = \vec{r}x\vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\vec{L} = (yp_z - zp_y)\vec{i} + (zp_x - xp_z)\vec{j} + (xp_y - yp_x)\vec{k}$$

$$L_y = zp_x - xp_z \qquad L_x = yp_z - zp_y \qquad L_z = xp_y - yp_x$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}$$

$$\hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y} = -i\hbar\frac{\partial}{\partial y}$$

$$\hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} = -i\hbar\frac{\partial}{\partial z}$$

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

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

$$L^2 = \hat{L}_x \bullet \hat{L}_x + \hat{L}_y \bullet \hat{L}_y + \hat{L}_z \bullet \hat{L}_z$$

3.1Operator Commutation and Simultaneous Eigenfunctions

It can be shown that:

$$\left[\hat{L}_x, \hat{L}_y\right] \neq 0 \quad \left[\hat{L}_y, \hat{L}_z\right] \neq 0 \quad \left[\hat{L}_x, \hat{L}_z\right] \neq 0$$

Do not commute

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar L_z \quad \left[\hat{L}_y, \hat{L}_x\right] = -i\hbar L_z \quad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar L_x \quad \left[\hat{L}_z, \hat{L}_y\right] = -i\hbar L_x$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar L_y \quad \left[\hat{L}_x, \hat{L}_z\right] = -i\hbar L_y$$

Because the operators for the individual components do not commute, one ***cannot*** determine two separate components simultaneously.

i.e. they cannot have simultaneous eigenfunctions.

$$\left[\hat{L}_x, L^2\right] = \left[\hat{L}_y, L^2\right] = \left[\hat{L}_z, L^2\right] = 0$$

Do commute

Because these operators commute, one ***can*** determine L_z and L^2 simultaneously; i.e. they can have simultaneous eigenfunctions.

3.2 Spherical Polar Coordinates for Angular momentum

In Cartesian Coordinates, the 3D Schrödinger Equation is:

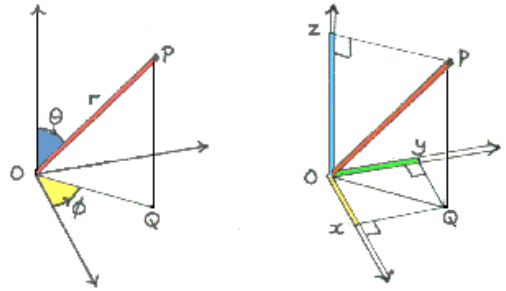
$$\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}}_{\mathbf{T(x)}}\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial y^2}}_{\mathbf{T(y)}}\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial z^2}}_{\mathbf{T(z)}}+\underbrace{V(x,y,z)}_{\mathbf{V(x,y,z)}}\psi = E\psi \qquad \psi = \psi(x,y,z)$$

The Laplacian in Cartesian Coordinates is: $\nabla^2 \equiv \frac{\partial}{\partial x^2}+\frac{\partial}{\partial y^2}+\frac{\partial}{\partial z^2}$

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

The “Rigid Rotor” and the Hydrogen Atom can be solved exactly in Spherical Polar Coordinates.

3.2 Spherical Polar Coordinates for Angular Momentum

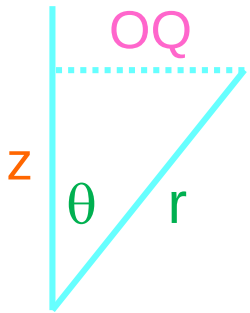


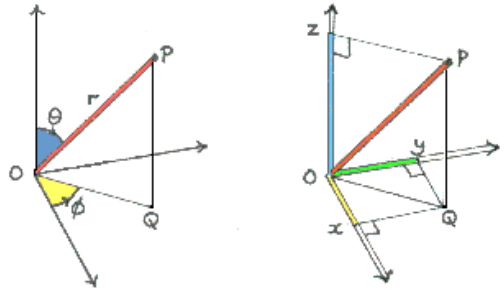
$OQ = r\sin\theta$ so $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$

To specify a point in space requires three coordinates.
In the spherical polar coordinate system, they are:

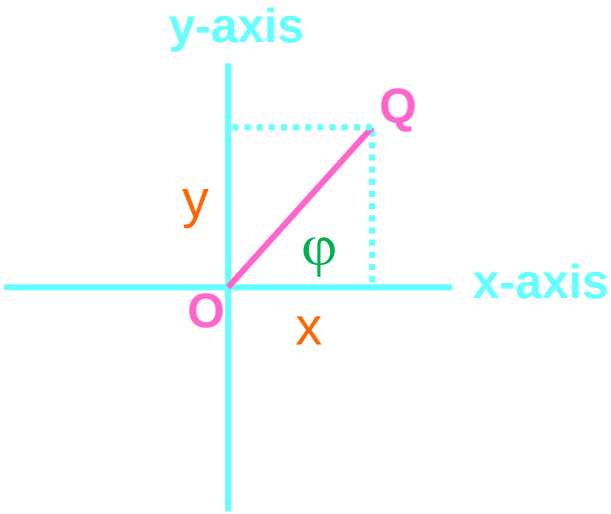
r	$0 \le r < \infty$	Distance of point from origin (OP)
θ	$0 \le \theta < \pi$	Angle of vector (OP) from z-axis
ϕ	$0 \le \phi < 2\pi$	Angle of x-y projection (OQ) from x-axis

Relation of Cartesian to Spherical Polar Coordinates





$OQ = r\sin\theta$ so $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$



$$\cos(\theta) = \frac{z}{r}$$

$$\boxed{z = r\cos(\theta)}$$

OQ=rsin(θ)

$$\cos(\varphi) = \frac{x}{OQ}$$

$$x = OQ\cos(\varphi)$$

$$\boxed{x = r\sin(\theta)\cos(\varphi)}$$

$$\sin(\varphi) = \frac{y}{OQ}$$

$$y = OQ\sin(\varphi)$$

$$\boxed{y = r\sin(\theta)\sin(\varphi)}$$

The Laplacian in Spherical Polar Coordinates

Cartesian Coordinates: $\nabla^2 \equiv \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$

the Laplacian in spherical polar coordinates is given by:

$$\boxed{\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin(\theta)}\frac{\partial}{\partial \theta}\left(\sin(\theta)\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2(\theta)}\frac{\partial^2}{\partial \varphi^2}}$$

$$dV = dx\,dy\,dz$$

$$dV = dr \bullet r\,d\theta \bullet OQ\,d\varphi \qquad dV = dr \bullet r\,d\theta \bullet r\sin(\theta)\,d\varphi \qquad \boxed{dV = r^2 \sin(\theta)\,dr\,d\theta\,d\varphi}$$

Angular Momentum Operators in Spherical Polar Coordinates

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

It may be shown that

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

$$L^2 = \hat{L}_x \bullet \hat{L}_x + \hat{L}_y \bullet \hat{L}_y + \hat{L}_z \bullet \hat{L}_z$$

It may be shown that

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

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

$$L_x = i\hbar\left\{\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right\}$$

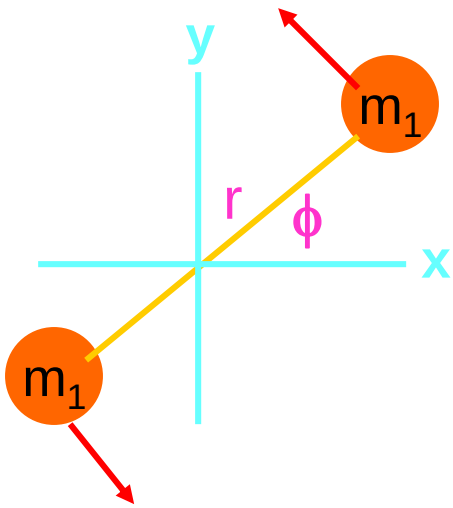
$$L_y = -i\hbar\left\{\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right\}$$

3.3 Model system. *The 2D Quantum Mechanical Rigid Rotor*

Assume that two masses are attached by a rigid rod (i.e. ignore vibrations) at a fixed distance, r,and are free to rotate about the Center of Mass in their x-y plane.

The angle ϕ represents the angle of rotation relative to the x-axis.

The 2D Schrödinger equation for the relative motion of two masses is:



$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi$$

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

Two Dimensional Laplacian in Cartesian Coordinates

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

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi$$

If one (a) converts the Laplacian to polar coordinates

(b) assumes that the potential energy is constant (arbitrarily 0)

(c) holds r fixed (i.e. neglects derivatives with respect to r)

It can be shown that the Schrödinger Equation for a 2D Rigid Rotor becomes:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2\psi}{\partial\varphi^2} = E\psi$$

or $$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\varphi^2} = E\psi$$

where $I = \mu r^2$ is the moment of inertia

3.4. The Solution of S.E Wavefumction and Energy

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\varphi^2} = E\psi$$

Assume

$$\psi = Ae^{im\varphi}$$

$$\frac{d\psi}{d\varphi} = (im)Ae^{im\varphi}$$

$$\frac{d^2\psi}{d\varphi^2} = (im)^2 Ae^{im\varphi}$$

$$\frac{d^2\psi}{d\varphi^2} = -m^2\psi$$

$$\frac{\partial^2\psi}{\partial\varphi^2} = -\frac{2IE}{\hbar^2}\psi = -\mathrm{Constant}\cdot\psi$$

$$-m^2\psi = -\frac{2\mathrm{IE}}{\hbar^2}\psi$$

$$m^2 = \frac{2IE}{\hbar^2} \quad \text{or} \quad E = \frac{\hbar^2 m^2}{2I}$$

Note: So far, m can have any value;

i.e. there is no energy quantization

Application of the Boundary Conditions: Quantization of Energy

Wavefuncion:

$$\psi = A e^{im\varphi}$$

To be a physically realistic solution, one must have:

$$\psi(\varphi + 2\pi) = \psi(\varphi)$$

Therefore: $A e^{im\varphi} e^{2\pi m i} = A e^{im\varphi}$ or $e^{2\pi m i} = 1$

$$\cos(2\pi m) + i \sin(2\pi m) = 1$$

This is valid only for: $m = 0, \pm 1, \pm 2, \pm 3, \ldots$

Therefore, only certain values for the energy are allowed; i.e. the energy is quantized:

$$\boxed{E = \frac{\hbar^2 m^2}{2I} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots}$$

Zero Point Energy $E_0 = 0$

One encounters a ZPE only when the particle is bound (e.g. PIB, HO, H-Atom), but not in freely moving systems (e.g. 2D and 3D Rigid Rotor, free particle)

Example

For the wavefunction of the rigid rotor:

$$\psi = Ae^{im\varphi}$$

1- Find the normalization constant A

2. $<\phi>$

3.5. Application of the 2D Rigid Rotor

Solving the 2D Rigid Rotor is not just a learning exercise. However, the model has a real world application, it can be used to characterize the rotation of molecules adsorbed on surfaces.

However,

Example

When an H_2 molecule is chemisorbed on a crystalline surface, its rotation can be approximated as that of a 2D rigid rotor.

The H_2 bond length is 0.74 Å Calculate the frequency (in cm^{-1}) of the lowest energy rotational transition of chemisorbed H_2.

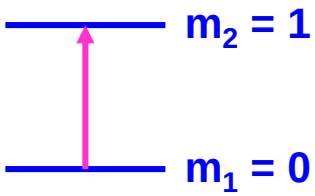
$$E = \frac{\hbar^2 m^2}{2I} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

r = 0.74 Å = 0.74x10^{-10} m
1 amu = 1.66x10^{-27} kg
ħ = 1.05x10^{-34} J•s
h = 6.63x10^{-34} J•s
c = 3.00x10^{10} cm/s

$$\mu = \frac{m_H^2}{m_H + m_H} = \frac{(1amu)^2}{1amu + 1amu} = 0.50\,amu \cdot \frac{1.66x10^{-27}\,kg}{amu} = 8.30x10^{-28}\,kg$$

$$I = \mu r^2 = \left(8.30x10^{-28}\,kg\right)\left(0.74x10^{-10}\,m\right)^2 = 4.55x10^{-48}\,kg \cdot m^2$$

$$\Delta E = \frac{\hbar^2 m_2^2}{2I} - \frac{\hbar^2 m_1^2}{2I} = \frac{\hbar^2}{2I} = \frac{\left(1.05x10^{-34}\,J \cdot s\right)^2}{2\left(4.55x10^{-48}\,kg \cdot m^2\right)} = 1.21x10^{-21}\,J$$



$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{1.21x10^{-21}\,J}{\left(6.63x10^{-34}\,J \cdot s\right)\left(3.00x10^{10}\,cm/s\right)} = 60.9\,cm^{-1}$$

3.6. The 3D Quantum Mechanical Rigid Rotor

3D Schrödinger Equation for a particle (Sph. Pol. Coords.)

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r,\theta,\varphi)\psi = E\psi \qquad \psi = \psi(r,\theta,\varphi)$$

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

Modification: Two masses moving relative to their CM

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

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

The Schrödinger Equation in terms of the $\hat{L}^2$ operator

The $\hat{L}^2$ operator is: $$L^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right\}$$

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

$$\downarrow$$

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

$$\downarrow$$

$$\underbrace{-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \right]}_{\text{Radial KE}} + \underbrace{\frac{1}{2I} L^2 \psi}_{\text{Rotational KE}} + \underbrace{V\psi}_{\text{PE}} = E\psi \quad \text{where} \quad I = \mu r^2$$

The Quantum Mechanical Rigid Rotor

$$\cancel{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right]} + \frac{1}{2I}L^2\psi + \cancel{V\psi} = E\psi$$

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

The Rigid Rotor model is used to characterize the rotation of diatomic molecules (and is easily extended to linear polyatomic molecules)

It is assumed that: (1) The distance between atoms (r) does not change.

(2) The potential energy is independent of angle [i.e. $V(\theta,\phi)$ = Const. = 0]

Therefore: $\frac{1}{2I}\hat{L}^2\psi = E\psi$

$$\boxed{-\frac{\hbar^2}{2I}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2\psi}{\partial\varphi^2}\right] = E\psi}$$

Solution of the Rigid Rotor Schrödinger Equation

We will only outline the method of solution.

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2\psi}{\partial\varphi^2}\right]=E\psi \qquad \psi=\psi(\theta,\varphi)$$

This equation can be separated into two equations, one containing only θ and the second containing only ϕ.

Assume: $\Psi(\theta,\varphi)=\Theta(\theta)\bullet\Phi(\varphi)$

Algebra + Separation of Variables

$$\left[-\frac{\hbar^2}{2I}\frac{1}{\Theta}\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\Theta}{\partial\theta}\right)-E\sin^2(\theta)\right]=C$$

and $$-\frac{\hbar^2}{2I}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-C$$

$$\left[-\frac{\hbar^2}{2I}\frac{1}{\Theta}\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\Theta}{\partial\theta}\right) - E\sin^2(\theta)\right] = C$$

and $$-\frac{\hbar^2}{2I}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -C$$

Solution of the Φ equation is rather simple.

However, solution of the Θ equation most definitely is NOT.

Therefore, we will just present the results for the quantum numbers, energies and wavefunctions that result when the two equations are solved and boundary conditions are applied.

The Rigid Rotor Quantum Numbers and Energies

The Quantum Numbers: $\ell = 0, 1, 2, 3, \ldots$

$$m = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

Note that because this is a two dimensional problem, there are two quantum numbers.

The Energy: $E_\ell = \dfrac{\hbar^2}{2I}\ell(\ell+1)$ $\qquad g_\ell = 2\ell + 1$

Note that the energy is a function of ℓ only. However, there are $2\ell + 1$ values of m for each value of ℓ. Therefore, the degeneracy of the energy level is $2\ell + 1$

Remember that for a classical Rigid Rotor: $E = \dfrac{L^2}{2I}$

Comparing the expressions, one finds for the angular momentum, that: $L = \sqrt{\ell(\ell+1)} \cdot \hbar$

An Alternate Notation

When using the Rigid Rotor molecule to describe the rotational spectra of linear molecules, it is common to denote the two quantum numbers as J and M, rather than ℓ and m.

With this notation, one has:

The Quantum Numbers: $J = 0, 1, 2, 3, \ldots$

$$M = 0, \pm 1, \pm 2, \ldots, \pm J$$

The Energy: $E_J = \frac{\hbar^2}{2I} J(J+1) \qquad g_J = 2J + 1$

The Wavefunctions

When both the Θ and Φ differential equations have been solved, the resulting wavefunctions are of the form:

$$\psi(\theta,\varphi) = \Theta(\theta) \bullet \Phi(\varphi) = N_{\ell,m} e^{im\varphi} P_\ell^{|m|}(\theta)$$

The $P_\ell^{|m|}(\theta)$ are known as the associated Legendre polynomials.

The first few of these functions are given by:

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

$$P_1^0 = \cos(\theta) \qquad P_2^1 = \frac{1}{2}\sin(\theta)\cos(\theta)$$

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

We will defer any visualization of these wavefunctions until we get to The Hydrogen Atom

Spherical Harmonics

The product functions of θ and ϕ are called "Spherical Harmonics", $Y_{lm}(\theta, \phi)$:

$$Y_{lm}(\theta,\varphi) = \Theta(\theta) \bullet \Phi(\varphi) = N_{\ell m} e^{im\varphi} P_{\ell}^{|m|}(\theta)$$

They are the angular solutions to the Schrödinger Equation for any spherically symmetric potential; i.e. one in which V(r) is independent of the angles θ and ϕ.

Some examples are:

$$Y_{11}(\theta,\varphi) = N_{11} e^{i\varphi} P_1^1(\theta) = N_{11} e^{i\varphi} \sin(\theta)$$

$$Y_{10}(\theta,\varphi) = N_{10} e^{0i\varphi} P_1^0(\theta) = N_{10} \cos(\theta)$$

$$Y_{1-1}(\theta,\varphi) = N_{1-1} e^{-i\varphi} P_1^1(\theta) = N_{1-1} e^{-i\varphi} \sin(\theta)$$

$$Y_{22}(\theta,\varphi) = N_{22} e^{2i\varphi} P_2^2(\theta) = N_{22} e^{2i\varphi} \sin^2(\theta)$$

$$Y_{21}(\theta,\varphi) = N_{21} e^{i\varphi} P_2^1(\theta) = N_{21} e^{i\varphi} \sin(\theta)\cos(\theta)$$

$$Y_{20}(\theta,\varphi) = N_{20} e^{0i\varphi} P_2^0(0) = N_{20}\left(3\cos^2(\theta) - 1\right)$$

$$Y_{2-1}(\theta,\varphi) = N_{2-1} e^{-i\varphi} P_2^1(\theta) = N_{2-1} e^{-i\varphi} \sin(\theta)\cos(\theta)$$

$$Y_{2-2}(\theta,\varphi) = N_{2-2} e^{-2i\varphi} P_2^2(\theta) = N_{2-2} e^{-2i\varphi} \sin^2(\theta)$$

Example One of the Spherical Harmonics is: $Y(\theta,\varphi) = Ne^{-i\varphi}\sin(\theta)$

Show that this function is an eigenfunction of the Rigid Rotor Hamiltonian and determine the eigenvalue (i.e. the energy).

$$HY = \frac{1}{2I}L^2Y = EY \qquad \text{or} \qquad -\frac{\hbar^2}{2I}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\varphi^2}\right] = EY$$

$$\frac{\partial Y}{\partial\theta} = Ne^{-i\varphi}\cos(\theta)$$

$$\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) = \frac{\partial}{\partial\theta}\left(Ne^{-i\varphi}\sin(\theta)\cos(\theta)\right) = Ne^{-i\varphi}\left[-\sin^2(\theta) + \cos^2(\theta)\right]$$

$$= Ne^{-i\varphi}\left[1 - 2\sin^2(\theta)\right]$$

$$\boxed{\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) = \frac{Ne^{-i\varphi}}{\sin(\theta)} - 2Ne^{-i\varphi}\sin(\theta)}$$

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

$$Y(\theta,\varphi)=Ne^{-i\varphi}\sin(\theta)$$

$$\frac{\partial Y}{\partial\varphi}=-iNe^{-i\varphi}\sin(\theta)$$

$$\frac{\partial^2 Y}{\partial\varphi^2}=-Ne^{-i\varphi}\sin(\theta)$$

$$\longrightarrow \quad \boxed{\frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\varphi^2}=\frac{-Ne^{-i\varphi}}{\sin(\theta)}}$$

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

$$=-\frac{\hbar^2}{2I}\left[\cancel{\frac{Ne^{-i\varphi}}{\sin(\theta)}}-2Ne^{-i\varphi}\sin(\theta)-\cancel{\frac{Ne^{-i\varphi}}{\sin(\theta)}}\right]$$

$$=+\frac{\hbar^2}{2I}2\left[Ne^{-i\varphi}\sin(\theta)\right]=+\frac{\hbar^2}{2I}\cdot 2Y$$

$$HY = +\frac{\hbar^2}{2I}\cdot 2Y$$

Therefore: $$E = 2\frac{\hbar^2}{2I}$$

Note: Comparing to: $$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)$$

we see that: $$\ell = 1$$

3.7 Angular Momentum and the Rigid Rotor

The Spherical Harmonics, $Y_{lm}(\theta, \phi)$, are eigenfunctions of the angular momentum operators:

$$L^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right\}$$

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$$

The eigenvalues are given by the equations:

$$\hat{L}^2 Y_{lm}(\theta, \varphi) = \ell(\ell + 1)\hbar^2 Y_{lm}(\theta, \varphi)$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi)$$

Note: It is straightforward to show that $\hat{L}^2$ and $\hat{L}_z$ commute; i.e. $[\hat{L}^2, \hat{L}_z] = 0$.

Because of this, it is possible to find simultaneous eigenfunctions of the two operators which are, as shown above, the Spherical Harmonics.

As discussed earlier, the restrictions on the quantum numbers are given by:

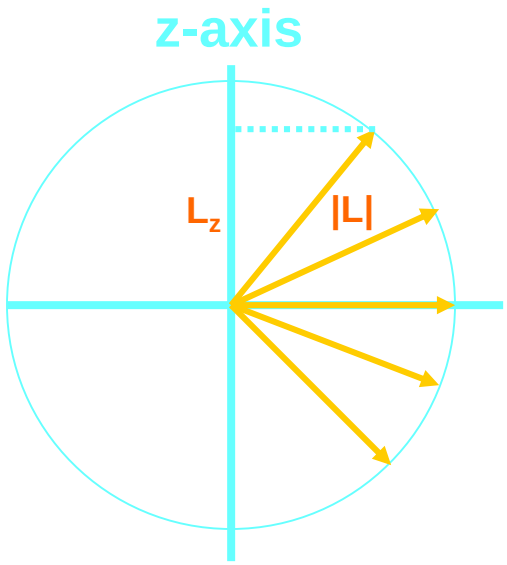
$$\ell = 0, 1, 2, 3, \ldots$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

Therefore, both the magnitude, |L|, and the z-component, L_z, of the angular momentum are quantized to the values:

$$|L| = \sqrt{\ell(\ell+1)}\hbar \qquad \ell = 0, 1, 2, 3, \ldots$$

$$L_z = m\hbar \qquad m = 0, \pm 1, \pm 2, \ldots, \pm \ell$$



If a magnetic field is applied, its direction defines the z-axis.

If there is no magnetic field, the z-direction is arbitrary.

One of the Spherical Harmonics is: $Y(\theta,\varphi) = N e^{-i\varphi} \sin(\theta)$

Show that this function is an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ and determine the eigenvalues.

$$L^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2} \right\} \qquad \hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

We've actually done basically the first part a short while ago.

Remember: $HY = \frac{1}{2I} L^2 Y = EY = 2\frac{\hbar^2}{2I} Y$

Therefore: $L^2 Y = 2\hbar^2 Y = \ell(\ell+1)\hbar^2 Y \longrightarrow \ell = 1$

$$\hat{L}_z Y = \frac{\hbar}{i}\frac{\partial Y}{\partial\varphi} = \frac{\hbar}{i}(-i) N e^{-i\varphi}\sin(\theta) = -\hbar Y = m\hbar Y$$

$$\downarrow$$

$$m = -1$$

Just keep in mind: The Hydrogen Atom Schrödinger Equation

3D Schrödinger Equation in Spherical Polar Coordinates

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

The Hydrogen atom is an example of a "centrosymmetric" system, which is one in which the potential energy is a function of only r, V(r).

In this case, the Schrödinger equation can be rearranged to:

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

Radial Part **Angular Part**

Note that the Angular part of the Hydrogen atom Schrödinger equation is the same as Rigid Rotor equation, for which the radial part vanishes.

Therefore, the angular parts of the Hydrogen atom wavefunctions are the same as those of the Rigid Rotor

3.8 Application of Angular momentum

Rotational Spectroscopy of Linear Molecules

Rotational Spectroscopy of Linear Molecules

Energy Levels

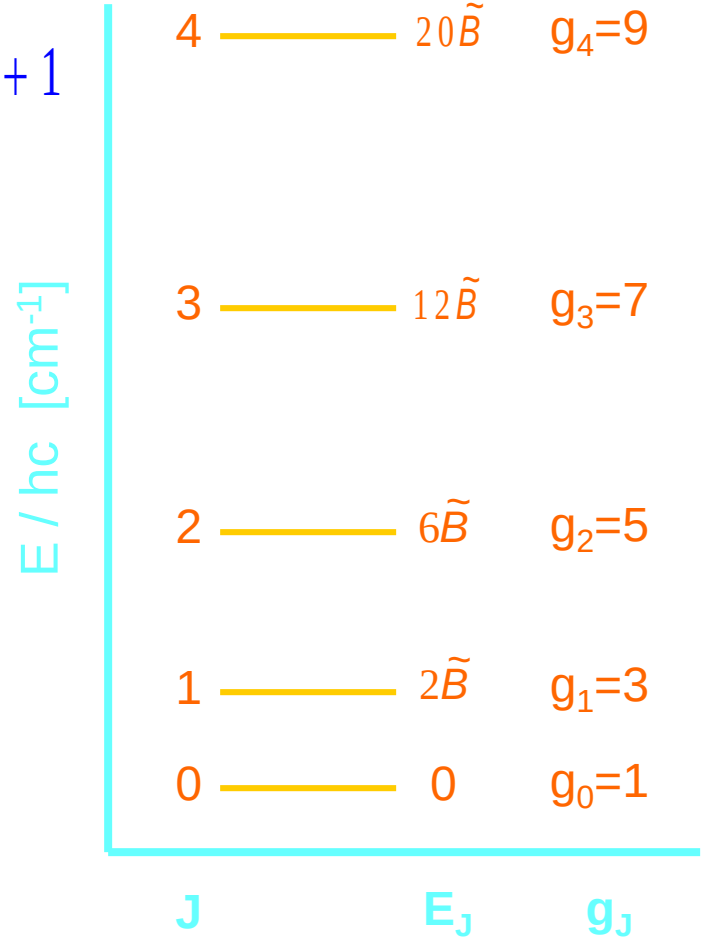
$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad g_J = 2J+1$$

Equivalent Form: $$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$E_J = hc \frac{h}{8\pi^2 Ic} J(J+1)$$

$$E_J = hc\tilde{B} J(J+1)$$

Rotational Constant (cm^{-1}): $$\tilde{B} = \frac{h}{8\pi^2 Ic}$$



Note: You must use c in cm/s, even when using MKS units.

Diatomic versus Linear Polyatomic Molecules

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

In general, for linear molecules, the moment of inertia is given by:

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

N is the number of atoms
m_i is the mass of the atom i
r_i is the distance of atom i from the Center of Mass.

If N=2 (diatomic molecule) the moment of inertia reduces to:

$$I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$ where r is the interatomic distance

Selection Rules

Absorption (Microwave) Spectroscopy

For a rotating molecule to absorb light, it must have a permanent dipole moment, which changes direction with respect to the electric vector of the light as the molecule rotates.

$\Delta J = \pm 1$ ($\Delta J = +1$ for absorption)

e.g. HCl, OH (radical) and O=C=S will absorb microwave radiation.

O=C=O and H-C≡C-H will ***not*** absorb microwave radiation.

Rotational Raman Spectroscopy

For a rotating molecule to have a Rotation Raman spectrum, the polarizability with respect to the electric field direction must change as the molecule rotates. All linear molecules have Rotational Raman spectra.

$\Delta J = \pm 2$

$\Delta J = +2$: Excitation (Stokes line)

$\Delta J = -2$: Deexcitation (Anti-Stokes line)

Intensity of Rotational Transitions

The intensity of a transition in the absorption (microwave) or Rotational Raman spectrum is proportional to the number of molecules in the initial state (J”); i.e. Int. $\propto N_{J''}$

Boltzmann Distribution: $$N_{J''} \propto g_{J''} e^{-\frac{E_{J''}}{kT}}$$

$$N_{J''} \propto (2J''+1) e^{-\frac{hc\tilde{B}J''(J''+1)}{kT}}$$

Rotational Spectra

Absorption (Microwave) Spectra

J'' → J'

$$\Delta E = E_{J'} - E_{J''}$$

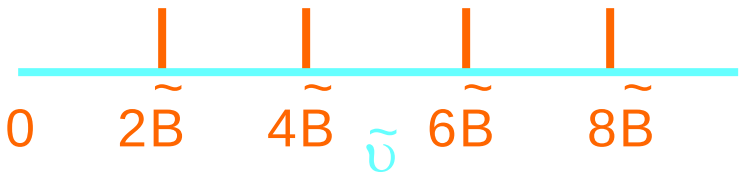
$$\Delta E = hc\tilde{B}J'(J'+1) - hc\tilde{B}J''(J''+1)$$

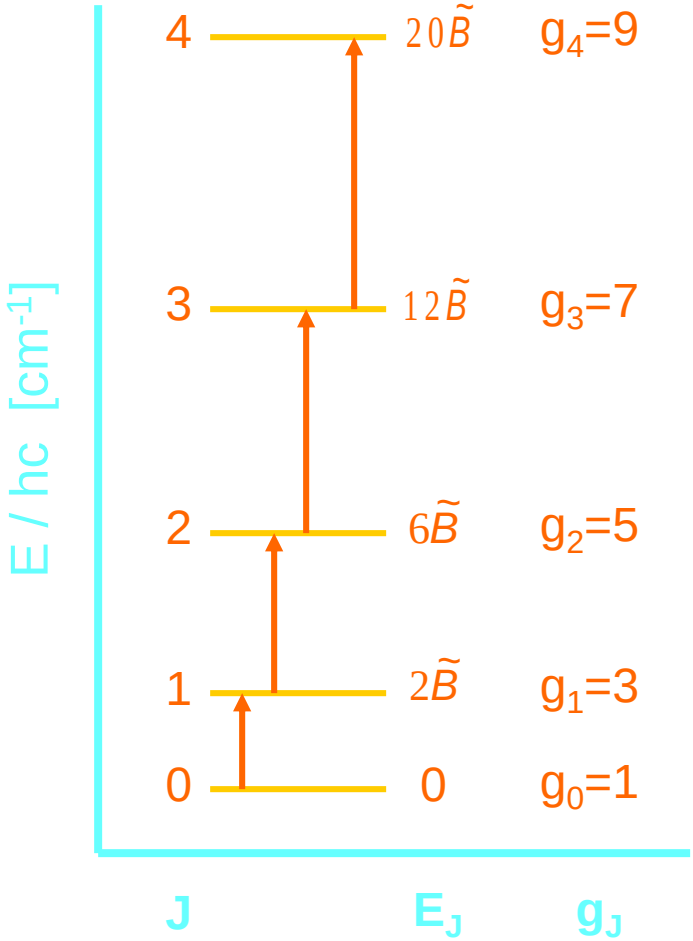
J' = J''+1

$$\Delta E = hc\tilde{B}(J''+1)(J''+2) - hc\tilde{B}J''(J''+1)$$

$$\Delta E = hc\tilde{B}(2J''+2) \quad J'' = 0, 1, 2, 3, \ldots$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = \tilde{B}(2J''+2) \quad J'' = 0, 1, 2, 3, \ldots$$





Rotational Raman Spectra

J'' → J'

$$\Delta E = E_{J'} - E_{J''}$$

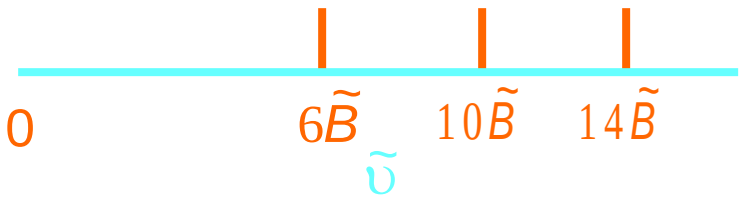
$$\Delta E = hc\tilde{B}J'(J'+1) - hc\tilde{B}J''(J''+1)$$

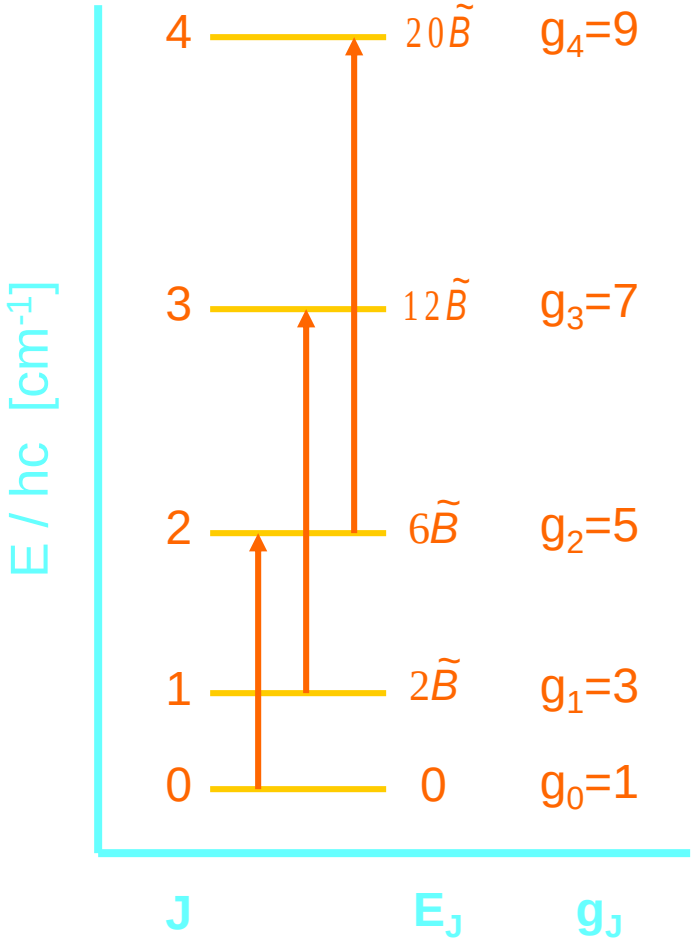
J' = J''+2

$$\Delta E = hc\tilde{B}(J''+2)(J''+3) - hc\tilde{B}J''(J''+1)$$

$$\Delta E = hc\tilde{B}(4J''+6) \quad J'' = 0, 1, 2, 3, \ldots$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = \tilde{B}(4J''+6) \quad J'' = 0, 1, 2, 3, \ldots$$





The HCl bond length is 0.127 nm.

Calculate the spacing between lines in the rotational microwave absorption spectrum of H-^{35}Cl, in cm^{-1}.

$h = 6.63x10^{-34}$ J•s
$c = 3.00x10^{8}$ m/s
$c = 3.00x10^{10}$ cm/s
$N_A = 6.02x10^{23}$ mol^{-1}
$k = 1.38x10^{-23}$ J/K
1 amu = $1.66x10^{-27}$ kg

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1amu)(35amu)}{1amu + 35amu} = 0.972\,amu$$

$$\mu = 0.972\,amu \cdot \frac{1.66x10^{-27}\,kg}{1amu} = 1.61x10^{-27}\,kg$$

$$I = \mu r^2 = (1.61x10^{-27}\,kg)(0.127x10^{-9}\,m)^2 = 2.60x10^{-47}\,kg \cdot m^2$$

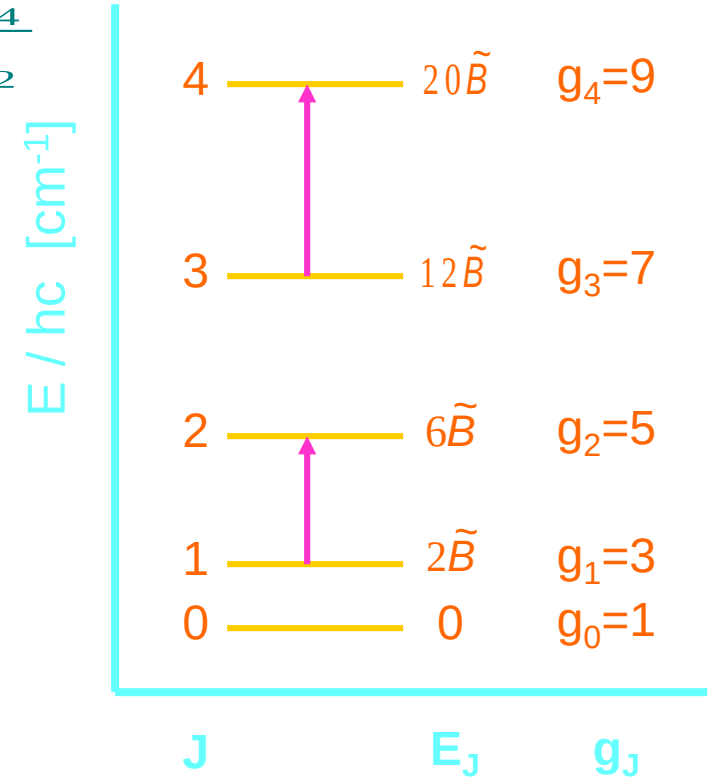
$$\tilde{B} = \frac{h}{8\pi^2 Ic} = \frac{6.63x10^{-34}\,J \cdot s}{8(3.14)^2(2.60x10^{-47}\,kg \cdot m^2)(3.00x10^{10}\,cm/s)} = 10.78\,cm^{-1} \approx 10.8\,cm^{-1}$$

As discussed above, microwave absorption lines occur at $2\tilde{B}$, $4\tilde{B}$, $6\tilde{B}$, ...
Therefore, the spacing is $2\tilde{B}$

$$Spacing = 2\tilde{B} = 2x10.8 = 21.6\,cm^{-1}$$

Calculate the ratio of intensities (at 25^{0}C): $\frac{I_{3\to4}}{I_{1\to2}}$

h = 6.63x10^{-34} J•s
c = 3.00x10^{10} cm/s
k = 1.38x10^{-23} J/K
$\tilde{B}$ = 10.8 cm^{-1}



$$\frac{I_{3\to4}}{I_{1\to2}} = \frac{N_3}{N_1} = \frac{g_3 e^{-E_3/kT}}{g_1 e^{-E_1/kT}} = \frac{7e^{-12hc\tilde{B}/kT}}{3e^{-2hc\tilde{B}/kT}} = \frac{7}{3}e^{-10hc\tilde{B}/kT}$$

$$\frac{I_{3\to4}}{I_{1\to2}} = \frac{7}{3}e^{-0.52} \approx 1.4$$

$$\boxed{\frac{10hc\tilde{B}}{kT} = \frac{10\left(6.63x10^{-34}\ J\cdot s\right)\left(3.00x10^{10}\ cm/s\right)\left(10.8\,cm^{-1}\right)}{\left(1.38x10^{-23}\ J/K\right)\left(298\,K\right)} = 0.52}$$

Note: This is equivalent to asking for the ratio of intensites of fourth line to the second line in the rotational microwave spectrum.

The first 3 Stokes lines in the rotational Raman spectrum of $^{12}C^{16}O_2$ are found at 2.34 cm^{-1}, 3.90 cm^{-1} and 5.46 cm^{-1}.

Calculate the C=O bond length in CO_2, in nm.

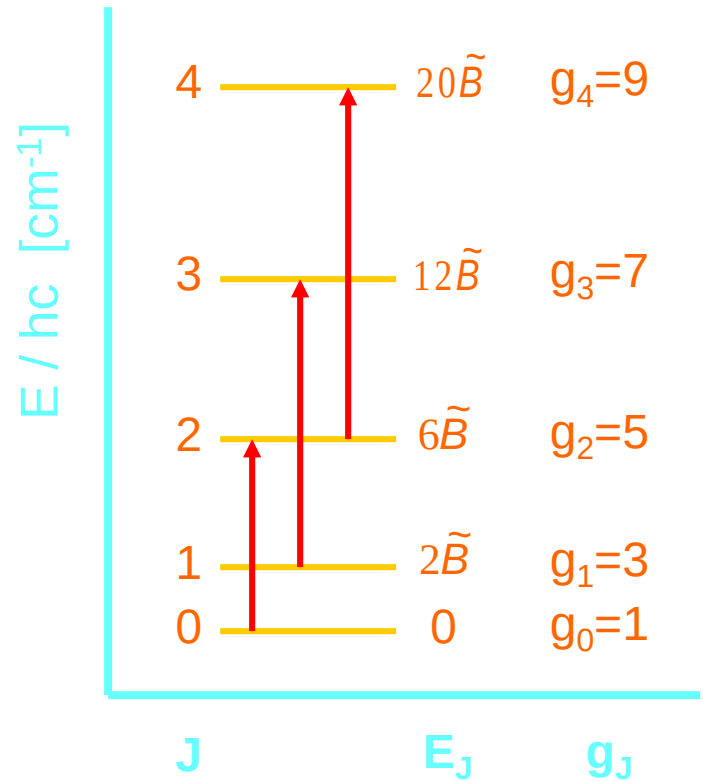
$h = 6.63x10^{-34}$ J•s
$c = 3.00x10^{10}$ cm/s
$k = 1.38x10^{-23}$ J/K
1 amu = $1.66x10^{-27}$ kg

$$2.34\,cm^{-1} = 6\tilde{B} - 0 = 6\tilde{B} \longrightarrow \tilde{B} = 0.39\,cm^{-1}$$

$$3.90\,cm^{-1} = 12\tilde{B} - 2\tilde{B} = 10\tilde{B} \longrightarrow \tilde{B} = 0.39\,cm^{-1}$$

$$5.46\,cm^{-1} = 20\tilde{B} - 6\tilde{B} = 14\tilde{B} \longrightarrow \tilde{B} = 0.39\,cm^{-1}$$

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \longrightarrow I = \frac{h}{8\pi^2 \tilde{B}c}$$



$$I = \frac{6.63x10^{-34}\,kg \cdot m^2/s}{8(3.14)^2(0.39\,cm^{-1})(3.00x10^{10}\,cm/s)} = 7.18x10^{-46}\,kg \cdot m^2$$

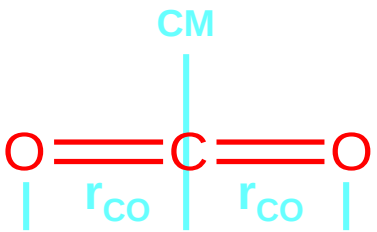
The first 3 Stokes lines in the rotational Raman spectrum of $^{12}C^{16}O_2$ are found at 2.34 cm^{-1}, 3.90 cm^{-1} and 5.46 cm^{-1}.

Calculate the C=O bond length in CO_2, in nm.

$h = 6.63x10^{-34}$ J•s
$c = 3.00x10^{10}$ cm/s
$k = 1.38x10^{-23}$ J/K
1 amu = $1.66x10^{-27}$ kg

$$I = 7.18x10^{-46}\ kg \cdot m^2$$

$$I = \sum_i m_i r_i^2 = m_O r_{CO}^2 + m_C (0)^2 + m_O r_{CO}^2 = 2 m_O r_{CO}^2$$



$$r_{CO} = \sqrt{\frac{I}{2m_O}}$$

$$m_O = 16\ amu \cdot 1.66x10^{-27}\ kg/amu = 2.66x10^{-26}\ kg$$

$$r_{CO} = \sqrt{\frac{7.18x10^{-46}\ kg \cdot m^2}{2 \cdot 2.66x10^{-26}\ kg}} = 1.16x10^{-10}\ m = 0.116\ nm = 1.16\ Angstroms$$

Calculate the initial state (i.e. J'') corresponding to the most intense line in the rotational Raman spectrum of $^{12}C^{16}O_2$ at 25°C.

Hint: Rather than calculating the intensity of individual transitions, assume that the intensity is a continuous function of J'' and use basic calculus.

$h = 6.63\times10^{-34}$ J•s
$c = 3.00\times10^{10}$ cm/s
$k = 1.38\times10^{-23}$ J/K
$\tilde{B} = 0.39$ cm^{-1}

$$I_{J''\to J''+2} \propto N_{J''} \propto (2J''+1)e^{-\frac{J''(J''+1)hc\tilde{B}}{kT}} \propto (2J''+1)e^{-\alpha\left(J''^2+J''\right)} \quad \alpha = \frac{hc\tilde{B}}{kT}$$

$N_{J''}$ is at a maximum for $dN_{J''}/dJ''=0$.

$$\frac{dN_{J''}}{dJ''} = 0 = (2J''+1)\frac{d}{dJ''}\left(e^{-\alpha\left(J''^2+J''\right)}\right) + \left(e^{-\alpha\left(J''^2+J''\right)}\right)\frac{d}{dJ''}(2J''+1)$$

$$0 = (2J''+1)\left(e^{-\alpha\left(J''^2+J''\right)}\right)(-\alpha)(2J''+1) + \left(e^{-\alpha\left(J''^2+J''\right)}\right)\cdot 2$$

$$0 = \left(e^{-\alpha\left(J''^2+J''\right)}\right)\left[-\alpha(2J''+1)^2+2\right]$$

$$0 = \left(e^{-\alpha\left(J''^2 + J''\right)}\right)\left[-\alpha\left(2J''+1\right)^2 + 2\right] \qquad \alpha = \frac{hc\tilde{B}}{kT}$$

$h = 6.63\text{x}10^{-34}$ J•s
$c = 3.00\text{x}10^{10}$ cm/s
$k = 1.38\text{x}10^{-23}$ J/K

$\tilde{B} = 0.39$ cm^{-1}

Therefore: $\left[-\alpha\left(2J''+1\right)^2 + 2\right] = 0 \longrightarrow 2J''+1 = \sqrt{\frac{2}{\alpha}}$

$$2J''+1 = \sqrt{\frac{2\left(1.38x10^{-23}\ J/K\right)\left(298\,K\right)}{\left(6.63x10^{-34}\ J\cdot s\right)\left(3.00x10^{10}\ cm/s\right)\left(0.39\,cm^{-1}\right)}} = \sqrt{1060} = 32.6$$

$$J'' = \frac{32.6-1}{2} = 15.8 \approx 16$$

Consider the linear molecule, H-C≡C-Cl.

There are two major isotopes of chlorine, ^{35}Cl (~75%) and ^{37}Cl (~25%). Therefore, one will observe two series of lines in the rotational spectrum, resulting from transitions of H-C≡C-^{35}Cl and H-C≡C-^{37}Cl.

Can the structure of H-C≡C-Cl be determined from these two series?

No. There are 3 bond distances to be determined, but only 2 moments of inertia.

What additional information could be used to determine all three bond distances?

The spectrum of D-C≡C^{35}Cl and D-C≡C^{37}Cl

3.9 The ladder operators

In general, assume L_x, L_y and L_z are operators with communications Relations:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar L_z \quad \left[\hat{L}_y, \hat{L}_x\right] = -i\hbar L_z \quad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar L_x \quad \left[\hat{L}_z, \hat{L}_y\right] = -i\hbar L_x$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar L_y \quad \left[\hat{L}_x, \hat{L}_z\right] = -i\hbar L_y$$

$$\left[\hat{L}_x, L^2\right] = \left[\hat{L}_y, L^2\right] = \left[\hat{L}_z, L^2\right] = 0$$

$$L^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Then we can introduce a new operators

$L_+ = \hat{L}_x + i\hat{L}y$ Raising Operator

$L_- = \hat{L}_x - i\hat{L}y$ Lowering Operator

Properties of Ladder operators

1) $\mathrm{L}_{+}\hat{L}_{-} = L^2 - L_z^2 + \hbar L_z$

2) $\mathrm{L}_{-}\hat{L}_{+} = L^2 - L_z^2 - \hbar L_z$

3) $[L_{+}, L_z] = -\hbar L_{+}$

if $L^2 Y(\theta,\phi) = cY(\theta,\phi)$ *and* $L_z Y(\theta,\phi) = bY(\theta,\phi)$

then

1) $L_z M_{+} Y(\theta,\phi) = (b+\hbar) L_{+} Y(\theta,\phi)$

Operating on the eigenfunction Y with raising operator L_+ convert Y into another eigenfunction of Lz with Eigen value $\hbar$ higher than the eigen value of Y

Properties of Ladder operators

2) $L_z L_+^2 Y(\theta,\phi) = (b+2\hbar) L_+^2 Y(\theta,\phi)$

$L_z L_+^k Y(\theta,\phi) = (b+k\hbar) L_+^k Y(\theta,\phi)$

3) $L_z L_- Y(\theta,\phi) = (b-\hbar) L_- Y(\theta,\phi)$

$L_z L_-^k Y(\theta,\phi) = (b-k\hbar) L_-^2 Y(\theta,\phi)$

$L_z L_\pm^k Y(\theta,\phi) = (b\pm k\hbar) L_\pm^2 Y(\theta,\phi)$

$L^2 L_\pm^k Y(\theta,\phi) = c L_\pm^k Y(\theta,\phi)$

4) $L_Z Y_{\max}(\theta,\phi) = b_{\max} Y_{\max}(\theta,\phi)$

$L_+ Y_{\max}(\theta,\phi) = zero$

$L_- Y_{\min}(\theta,\phi) = zero$

remmber $L^2 Y(\theta,\phi) = (j(j+1))\hbar^2 Y(\theta,\phi)$

$L_z Y(\theta,\phi) = m_j \hbar Y(\theta,\phi)$

By using the Raising and Lower operators on the on the eigenfunction with eigen value b, we generate a ladder of eigen values, step to difference =ħ

Important Notes

$\{A\}$

$$L^2Y(\theta,\phi) = (j(j+1))\hbar^2 Y(\theta,\phi)$$

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \frac{7}{2}, 4, ...$$

$$m_l = -j, ...0, .. + j$$

$$L_z Y(\theta,\phi) = m_j \hbar Y(\theta,\phi)$$

$\{\mathbf{B}\}$

$$L^2Y(\theta,\phi) = (l(l+1))\hbar^2 Y(\theta,\phi)$$

$$l = 0, 1, 2, 3, 4, ...$$

$$m_l = -l, ...0, .. + l$$

$$L_z Y(\theta,\phi) = m_l \hbar Y(\theta,\phi)$$

Comparison of A with B show that in addition to the integrated values of Angular momentum quantum mechanics (l=0,1,2,3,…) we have a possibility for half integrated values (j=0,1/2,1,3/2, 2,…) mean we have another kind of Angular momentum ,beside the orbital Angular momentum, l) can have half integral as well as integral called ***Spin Angular momentum***

Properties of Ladder operators

Find the following:

1) $\mathrm{L}_{+}\hat{L}_{-}$ 2) $\mathrm{L}_{-}\hat{L}_{+}$ 3) $[L_{+}, L_{z}]$ 4) $[L_{z}, L_{-}]$

5) *Later find*

Spin angular momentum (SPIN)

An electron spin s = 1/2 is an intrinsic property of electrons. Electrons have intrinsic angular momentum characterized by quantum number 1/2.

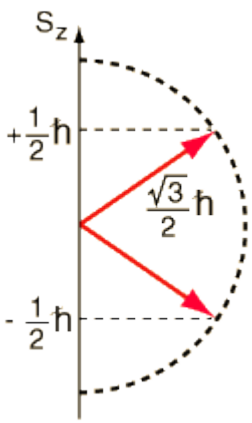
Experimental evidence like the hydrogen fine structure and the Stern-Gerlach experiment suggest that an electron has an intrinsic angular momentum, independent of its orbital angular momentum. These experiments suggest just two possible states for this angular momentum, and following the pattern of quantized angular momentum, this requires an angular momentum quantum number of 1/2.

The quantum numbers associated with electron spin follow the characteristic pattern:

$$S = \sqrt{s(s+1)}\hbar, \quad s = \frac{1}{2} \text{ and } m_{s=\pm\frac{1}{2}}$$

Example: An electron spin s = 1/2 is an intrinsic property of electrons. Electrons have intrinsic angular momentum characterized by quantum number 1/2. In the pattern of other quantized angular momenta, this gives total angular momentum $S = \sqrt{s(s+1}\hbar$ if s =1/2 so $S = \frac{\sqrt{3}}{2}\hbar$ the resulting fine structure which is observed corresponds to two possibilities for the z-component of the angular momentum.

$$S_Z = \pm\frac{1}{2}\hbar$$

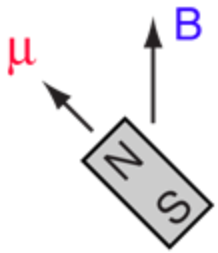


Spin "up" and "down" allows two electrons for each set of spatial quantum numbers:

n. l, ml

Spin-Orbit Interaction

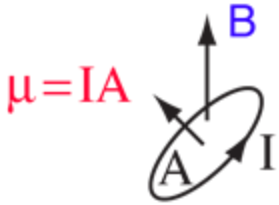
The energy levels of atomic electrons are affected by the interaction between the electron spin magnetic moment and the orbital angular momentum of the electron. It can be visualized as a magnetic field caused by the electron's orbital motion interacting with the spin magnetic moment. This effective magnetic field can be expressed in terms of the electron orbital angular momentum.



The interaction energy is of the form

$$E = \vec{\mu} \cdot \vec{B}$$

like a magnet in an applied magnetic field.



$$f(r)\ \vec{S} \cdot \vec{L}$$

Spin angular momentum

Orbital angular momentum

$$E = \vec{\mu} \cdot \vec{B}$$

From electron spin

From orbital motion

The interaction energy is that of a magnetic dipole in a magnetic field and takes the form. When atomic spectral lines are split by the application of an external magnetic field, it is called the Zeeman effect. The spin-orbit interaction is also a magnetic interaction, but with the magnetic field generated by the orbital motion of an electron within the atom itself. It has been described as an "internal Zeeman effect