Rotation as Translational Motion

For a particle of mass *m* moving in 3-D space

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(r,\theta,\phi) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right) + V(r,\theta,\phi)$$

where $\Lambda^2 = \frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$ Legendrian

Suppose the particle is confined to the surface of a sphere, i.e. $r = R$.

$$\hat{H} = -\frac{\hbar^2}{2mR^2}\Lambda^2$$

a function of θ and ϕ only

A rigid rotator is a pair of masses at a fixed distance apart (R), freely rotating about the centre of mass.

$$\hat{H} = -\frac{\hbar^2}{2\mu R^2}\Lambda^2 = -\frac{\hbar^2}{2I}\Lambda^2$$

$$I = \mu R^2$$

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

If the particle is confined to a ring (the equator), $\theta = \pi/2$.

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2\mu}\frac{d^2}{ds^2}$$

s is the distance along the circumference

Laplacian in Various Coordinate Systems *Enrichment*

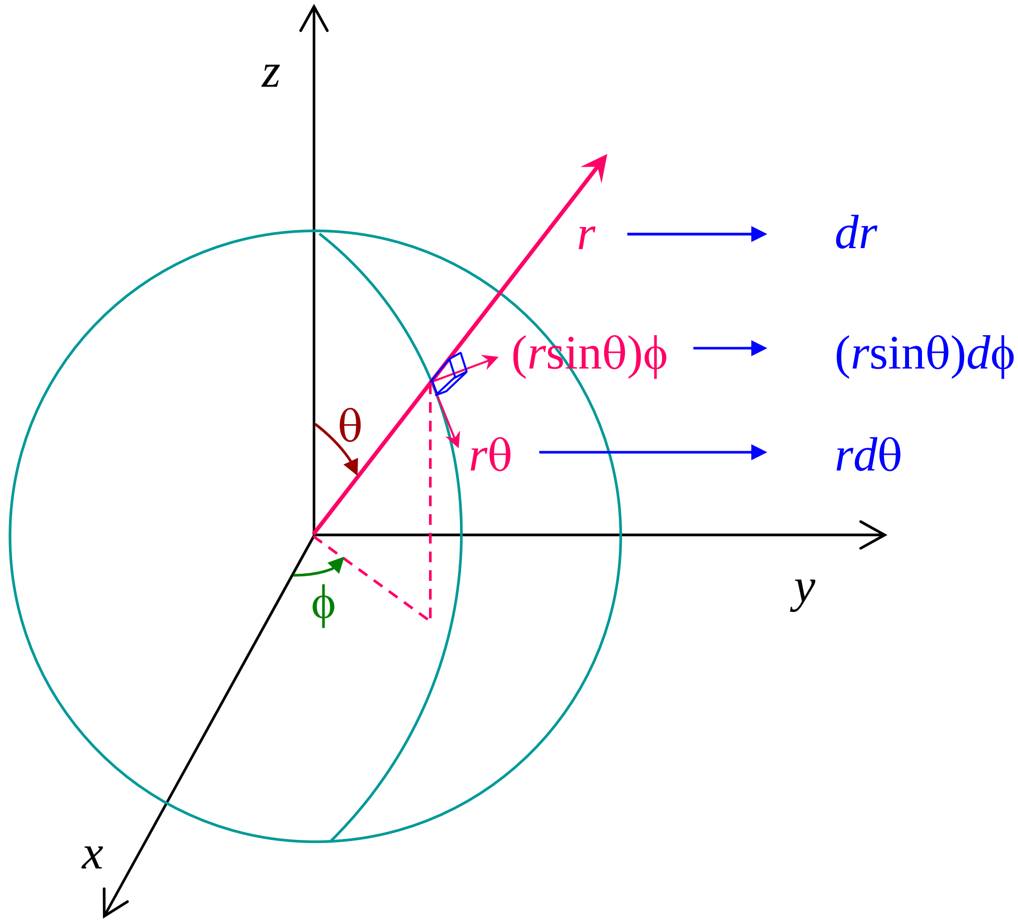
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ cartesian

$$= \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}$$ cylindrical

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$ spherical

where $$\Lambda^2 = \frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$ Legendrian

Spherical Polar Coordinates



$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\}$$

$$0 \leqslant r \leqslant R$$
$$0 \leqslant \phi \leqslant 2\pi$$
$$0 \leqslant \theta \leqslant \pi$$

$$\begin{aligned} d\tau &= dx\,dy\,dz \\ &= r^2 \sin\theta\, d\theta\, d\phi\, dr \end{aligned}$$

surface area

volume of sphere

$$\int d\tau = \int_0^R \int_0^{2\pi} \int_0^{\pi} r^2 \sin\theta\, d\theta\, d\phi\, dr = \int_0^R r^2 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta = \int_0^R 4\pi r^2 dr = \frac{4}{3}\pi R^3$$

Internal Coordinates and Reduced Mass

If the potential energy of a system depends only on the internal coordinates of the system, then the motion of the centre of mass can always be separated from the internal motion.

Consider two point masses m_1 and m_2, both in motion and interacting with each other.

$$E = \tfrac{1}{2} m_1 (\dot{x}_1^{\,2} + \dot{y}_1^{\,2} + \dot{z}_1^{\,2}) + \tfrac{1}{2} m_2 (\dot{x}_2^{\,2} + \dot{y}_2^{\,2} + \dot{z}_2^{\,2}) + V(x_1, y_1, z_1, x_2, y_2, z_2)$$

Define centre of mass coordinates: $X = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ $\quad Y = \dfrac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$ $\quad Z = \dfrac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$

and internal coordinates: $x = x_1 - x_2$ $\quad y = y_1 - y_2$ $\quad z = z_1 - z_2$

then

$$E = \underbrace{\tfrac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2)}_{\text{translational energy}} + \underbrace{\tfrac{1}{2}\mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + V(x, y, z)}_{\text{internal energy}}$$

where reduced mass

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

The Particle on a Ring

$$\hat{\mathrm{H}}\Phi = E\Phi \qquad \text{where} \qquad \hat{\mathrm{H}} = -\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$$

The Schrödinger Equation looks like that of the free particle, so the solutions are similar:

$$\Phi_m = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{im\phi} \qquad E_m = \frac{\hbar^2}{2I}m^2 \qquad m = 0, \pm 1, \pm 2, \ldots$$

quantum number not mass!

Quantization is due to a cyclic boundary condition: $\Phi(\phi) = \Phi(\phi + 2m\pi)$

Except for $m = 0$ the states are twofold degenerate.

Real functions can be constructed by taking linear combinations:

$$\Phi_m^+ = \frac{1}{\sqrt{2}}\left[\Phi_m + \Phi_{-m}\right] = \frac{1}{\sqrt{\pi}}\cos(|m|\phi)$$

$$\Phi_m^- = \frac{-i}{\sqrt{2}}\left[\Phi_m - \Phi_{-m}\right] = \frac{1}{\sqrt{\pi}}\sin(|m|\phi)$$

The Particle on a Ring – 2

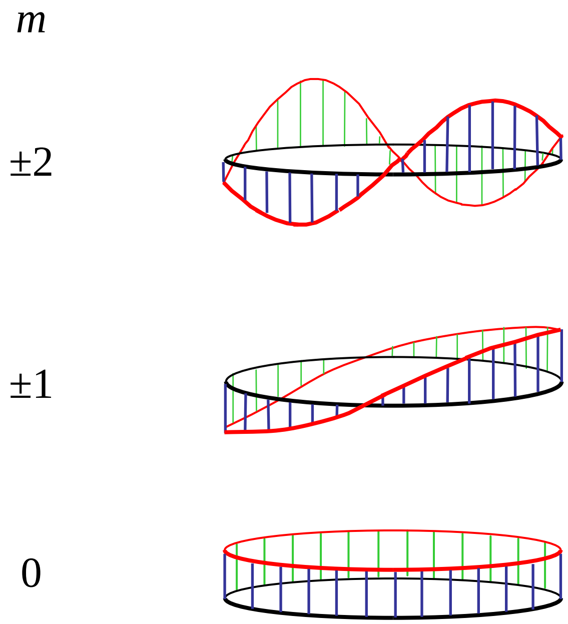
$$\Phi_m^+ = \frac{1}{\sqrt{\pi}}\cos(|m|\phi)$$

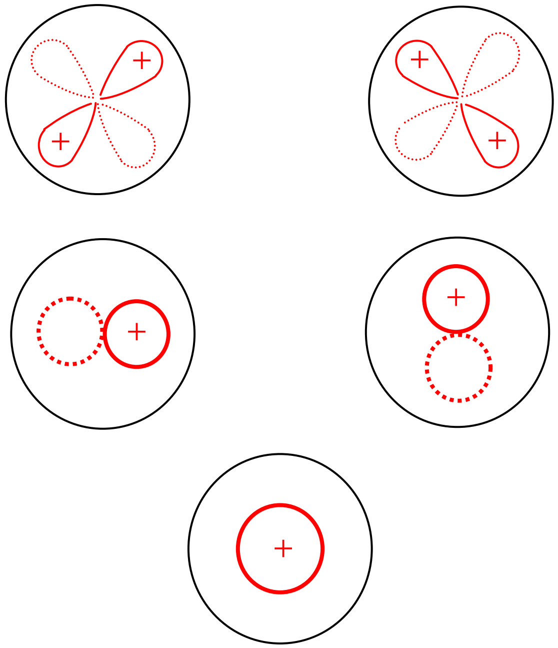
$$\Phi_m^- = \frac{1}{\sqrt{\pi}}\sin(|m|\phi)$$

Except for $m = 0$ the states are twofold degenerate.

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

polar plots





The Particle on a Sphere

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

This type of equation is "well known" (to applied mathematicians):

$$\Lambda^2\, Y_{lm}(\theta,\phi) = -l(l+1)\, Y_{lm}(\theta,\phi) \qquad \begin{cases} l = 0,1,2,\ldots \\ m = 0,\pm1,\pm2,\ldots,\pm l \end{cases}$$

The solutions are the spherical harmonics:

$$Y_{lm}(\theta,\phi) = \frac{1}{\sqrt{2\pi}}\,\Theta_{lm}(\theta)\, e^{im\phi}$$

where Θ_{lm} are the associated Legendre polynomials.

l	m	Θ_{lm}
0	0	$\sqrt{1/2}$
1	0	$\sqrt{3/2}\,\cos\theta$
1	±1	$\sqrt{3/4}\,\sin\theta$
2	0	$\sqrt{5/8}\,(3\cos^2\theta - 1)$
2	±1	$\sqrt{15/4}\,\sin\theta\cos\theta$
2	±2	$\sqrt{15/16}\,\sin^2\theta$

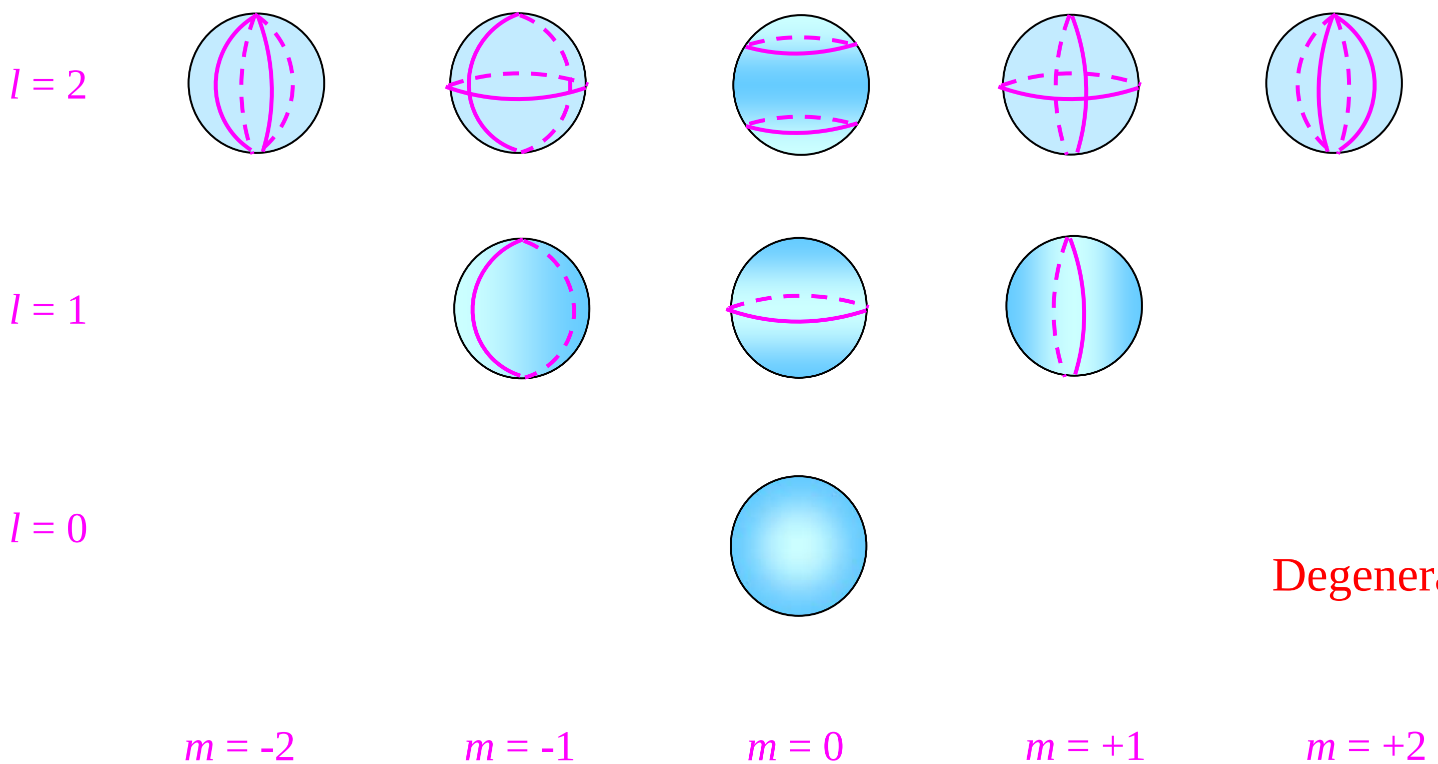
Comparing equations,

$$E_{lm} = \frac{\hbar^2}{2I}\, l(l+1)$$

Spherical Harmonics: Real Wavefunctions

$$Z^{+}_{l,m} = (1/\sqrt{2})\left[Y_{l,m} + Y_{l,-m}\right] = (1/\sqrt{\pi})\cos(|m|\phi)\Theta_{lm}(\theta)$$

$$Z^{-}_{l,m} = (-i/\sqrt{2})\left[Y_{l,m} - Y_{l,-m}\right] = (1/\sqrt{\pi})\sin(|m|\phi)\Theta_{lm}(\theta)$$



Degeneracy = $2l + 1$

Rotational/Orbital Angular Momentum

The energy of a rotating body (or particle in orbit) is quantized.

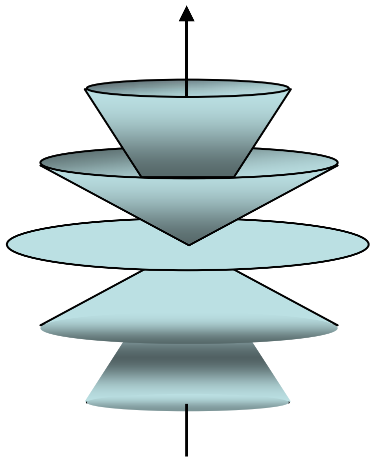
$$E_{lm} = \frac{\hbar^2}{2I} l(l+1) \qquad \begin{cases} l = 0, 1, 2, \ldots \\ m = 0, \pm 1, \pm 2, \ldots, \pm l \end{cases}$$

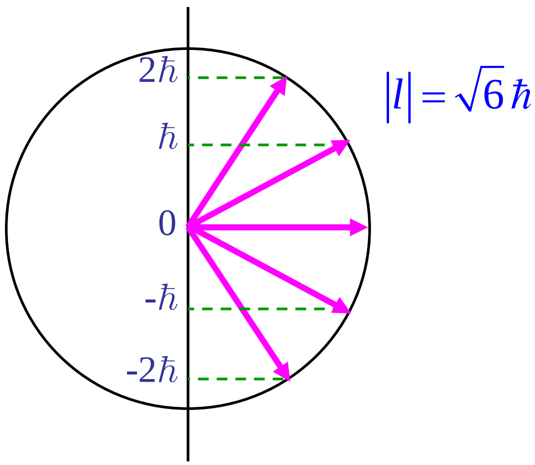
There are (2l+1) degenerate states which have the same energy determined by the quantum number l.

The different states, labelled by quantum numbers m, are related by simple symmetry transformations, i.e. they correspond to different orientations in space.

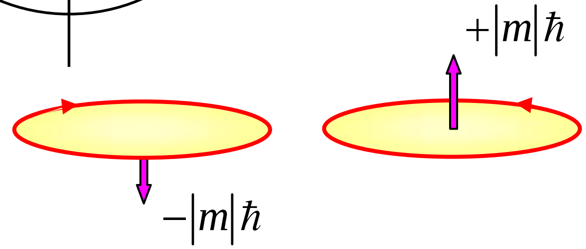
The orientation of a rotating body is quantized.

Example for l = 2:





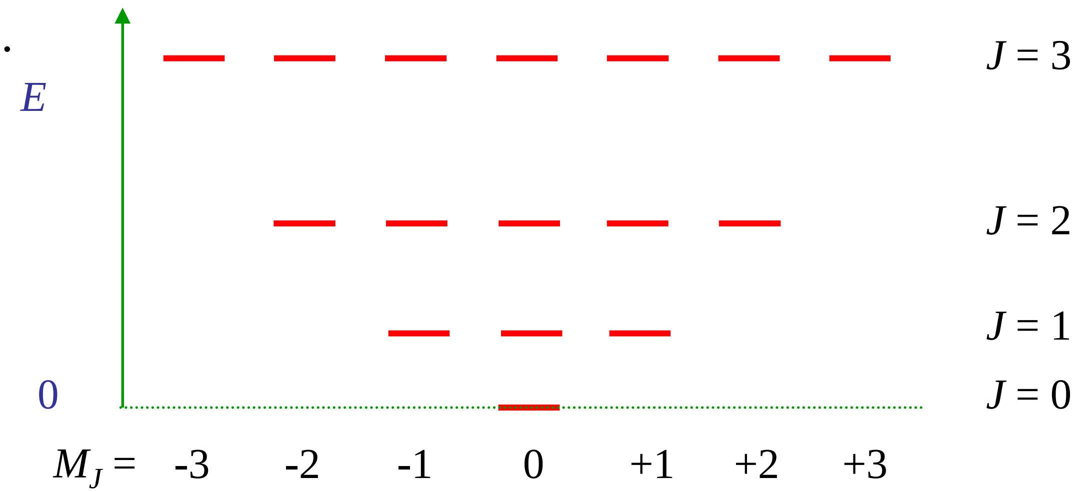
For the particle on a ring $E_m = \frac{\hbar^2}{2I} m^2 \qquad m = 0, \pm 1, \pm 2, \ldots$



Rotational Spectra of Diatomic Molecules

$$E_J = B\,J(J+1) \qquad J = 0, 1, 2, \ldots$$

$$B = \frac{\hbar^2}{2I}$$

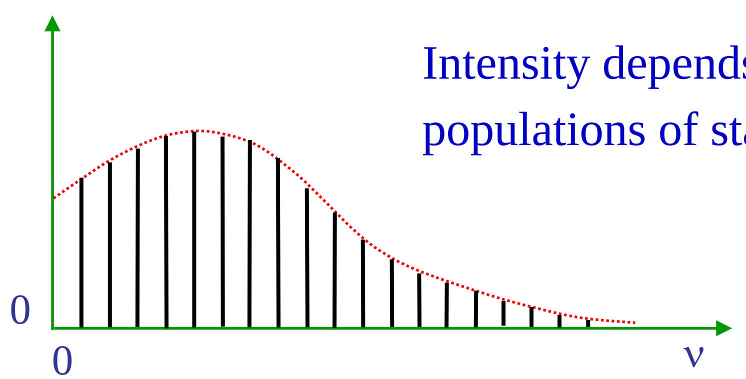


Selection Rules:

$$\Delta J = \pm 1 \qquad \Delta M_J = 0, \pm 1$$

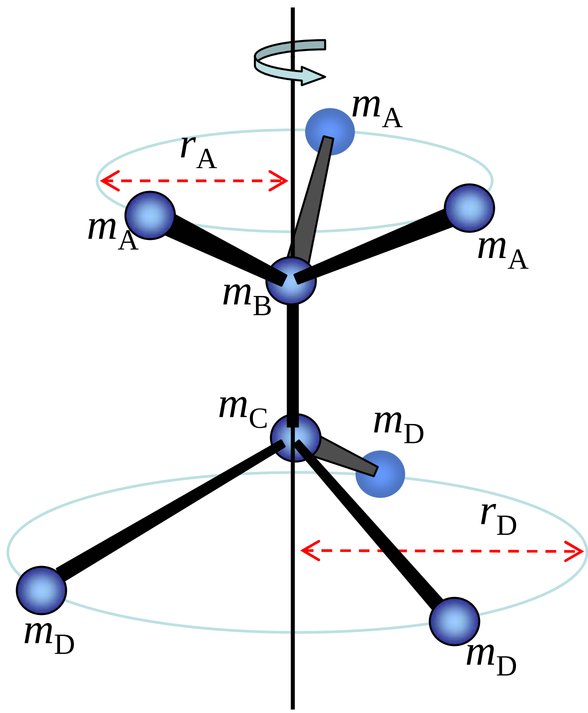
and the molecule must have a dipole moment.

Transitions: $\Delta E = E_{J+1} - E_J = 2B(J+1) = 2B, 4B, 6B, \ldots$



Intensity depends on degeneracy (1,3,5,…) and populations of states (Boltzmann distribution)

The Moment of Inertia of a Rotating Molecule



$$I = 3m_A r_A^{\,2} + 3m_D r_D^{\,2}$$

Moments of Inertia – Principal Axes

Consider a molecule as a system of point masses whose positions are fixed relative to each other.

Centre of gravity: $\vec{r}_0 = \dfrac{\sum_k m_k \vec{r}_k}{\sum_k m_k}$

Put a Cartesian coordinate system at this centre and define the three moments of inertia.

$$I_x = \sum_k m_k \, r_{kx}^{\;2} \quad \text{etc.}$$

r_{kx} is the perpendicular distance of nucleus k from the x axis

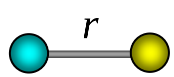
If $I_{xy} = m_k r_{kx} r_{ky} \neq 0$ etc. rotate the coordinate system until $I_{x'y'} = I_{y'z'} = I_{z'x'} = 0$ etc.

It is always possible to find unique principal axes and thus calculate principal moments of inertia (I_a I_b I_c).

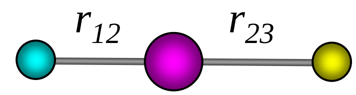
Linear Rotator	$I_a = I_b \neq 0$	$I_c = 0$
Spherical Top	$I_a = I_b = I_c$	$I_c \neq 0$
Symmetric Top	$I_a = I_b \neq I_c$	$I_c \neq 0$
prolate top	$I_a = I_b > I_c$	
oblate top	$I_a = I_b < I_c$	
Asymmetric Top	$I_a \neq I_b \neq I_c$	

Moments of Inertia

Linear Molecules



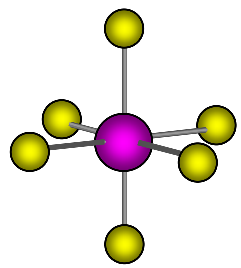
$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$



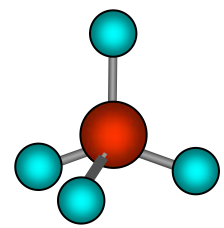
$$I = \frac{m_1 m_2 r_{12}^2 + m_2 m_3 r_{23}^2 + m_1 m_3 r_{13}^2}{m_1 + m_2 + m_3}$$

$$= 2 m_1 r_{12}^2 \quad \text{if} \quad m_1 = m_3$$

Spherical Tops

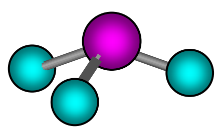


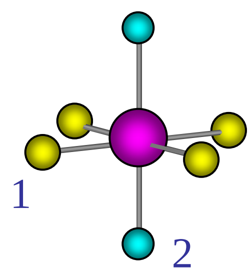
$$I = 4 m_1 r^2$$



$$I = \frac{8}{3} m_1 r^2$$

Symmetric Tops





$$I_{\parallel} = 4 m_1 r_1^2$$

$$I_{\perp} = 2 m_1 r^2 + 2 m_2 r_2^2$$