Chapter 3. Angular Momentum

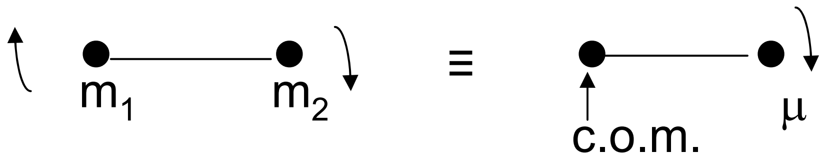
Nuclear Hamiltonian for a diatomic molecule

$H_{total} = H_{trans}(r_{cm}) + H_{vib}(q_{internal}) + H_{rot}(\theta, \phi)$

$E_{total} = E_{trans} + E_{vib} + E_{rot}$

$\psi_{tot} = \psi_{trans}\, \psi_{vib}\, \psi_{rot}$

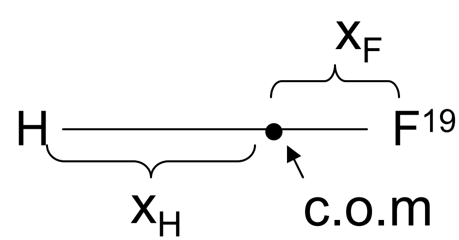
} separation of variables



reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} = \frac{1}{m_2}$$

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



$$x_H + x_F = .9168\text{Å}$$

$$x_H m_H = x_F m_F$$

$$x_F = .0458\text{Å}$$

$$x_H = .8710\text{Å}$$

Rotation in 2 dimensions

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

V(x,y) = 0 everywhere

Switch to polar coordinates: (x,y) $\rightarrow$ (r, ϕ)

$$x = r\cos\phi$$
$$y = r\sin\phi$$

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

$$\frac{\partial^2}{\partial r^2}\frac{1}{r}+\frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

if r fixed

$$\rightarrow \frac{1}{r^2}\frac{d^2}{d\phi^2}$$

This corresponds to the hamiltonian for a rigid rotor or for a particle on a ring.

Note that the original hamiltonian could correspond to a particle in a cylinder

$$\frac{-\hbar^2}{2\mu r^2}\frac{d^2\Phi}{d\phi^2} = E\Phi \longrightarrow \Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

$$0 \le \phi \le 2\pi$$

$$e^{im(\phi+2\pi)} = e^{im\phi} \quad \Rightarrow \quad e^{im2\pi} = 1$$

$$e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m = 1 \quad \Rightarrow \quad m = 0, \pm 1, \pm 2, \ldots$$

$$E = \frac{\hbar^2 m^2}{2\mu r_0^2} = \frac{\hbar^2 m^2}{2I}$$

$I = \mu r_0^2 =$ moment of inertia

quantization due to boundary condition $\Phi(0) = \Phi(2\pi)$

Note: there is no zero-point energy. Why?

Classically $E = \frac{|\vec{\ell}|^2}{2I} = \frac{1}{2} I\omega^2$

$\vec{\ell} =$ angular momentum

All energies possible

angular momentum in z direction: $\hat{\ell}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$

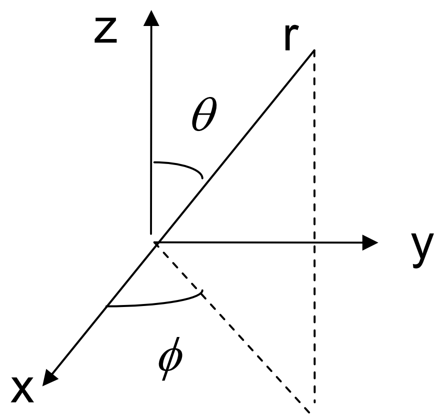
$$\hat{\ell}_z \Phi = \frac{\hbar}{i} \frac{1}{\sqrt{2\pi}} \frac{d}{d\phi} e^{im\phi} = m\hbar\Phi$$

$\hat{\ell}_z, \ \hat{\phi}$ do **<u>not</u>** commute

$$P(\phi)d\phi = \frac{d\phi}{2\pi},$$

all ϕ values equally probable
angular momentum in z direction precisely defined

On to 3 dimensions: (x, y, z) $\rightarrow$ (r, θ, ϕ)



$0 \le r \le \infty$

$0 \le \theta \le \pi$

$0 \le \phi \le 2\pi$

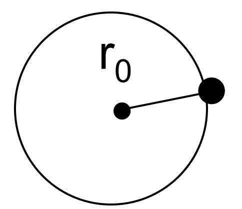
$x = r \sin\theta \cos\phi$
$y = r \sin\theta \sin\phi$
$z = r \cos\theta$

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

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

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

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



motion of particle on the surface of a sphere

≡ <u>Rigid rotor</u>

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

Y(θ, ϕ) = wave function

$$\beta=\frac{\partial\mu r_0^2}{\hbar^2}E$$

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

$$\Rightarrow Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

separation of variables

spherical harmonics

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

depends only on θ

depends only on ϕ

$\Rightarrow$ this must be equal to a constant

$$\begin{cases} \dfrac{1}{\Theta}\sin\theta\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)+\beta\sin^2\theta=m_\ell^2 \\ \dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2}=-m_\ell^2 \\ \Phi_{m_\ell}=Ae^{im_\ell\phi}, \qquad m_\ell=0,\pm1,\pm2,\ldots \end{cases}$$

$$\left.\begin{array}{l} \beta=\ell(\ell+1), \quad \ell=0,1,2,\ldots \\ m_\ell=-\ell,-\ell+1,\ldots0,\ldots,\ell-1,\ell \end{array}\right\} \text{quantization conditions}$$

$$\ell=0 \quad\rightarrow\quad m_\ell=0$$

$$\ell=1 \quad\rightarrow\quad m_\ell=-1,0,1$$

$$\ell=2 \quad\rightarrow\quad m_\ell=-2,-1,0,1,2$$

s
p
d } H atom

$$Y(\theta,\phi)=Y_\ell^{m_\ell}(\theta,\phi)=\Theta_\ell^{m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

two boundary conditions → two quantum #s

$$\beta = \frac{2\mu r_o^2 E}{\hbar^2} = \frac{2I}{\hbar^2}E$$

$$E = \frac{\hbar^2}{2I}\ell(\ell+1), \qquad \ell = 0, 1, 2, \ldots$$

$$\hat{H}Y_\ell^{m_\ell} = \frac{\hbar^2}{2I}\ell(\ell+1)Y_\ell^{m_\ell}$$

degeneracy = $2\ell+1$

$$\hat{\ell}^2 Y_\ell^{m_\ell} = \hbar^2\ell(\ell+1)Y_\ell^{m_\ell}$$

$\hat{\ell}^2$ and $\hat{H}$ obviously commute

$\hat{\ell}^2$: "angular momentum" operator

$$\left|\vec{\ell}\right| = \hbar\sqrt{\ell(\ell+1)}$$

components of the angular momentum operator

$$\hat{\ell}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\phi\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{\ell}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

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

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

$$\ell_z = xp_y - yp_x$$

$$= \frac{\hbar}{i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$\ell_z\Phi_m = m\hbar\Phi_m$$

$$\hat{\ell}_z Y_\ell^{m\ell} = m_\ell\hbar Y_\ell^{m\ell}$$

$$\left[\hat{\ell}_x, \hat{\ell}_y\right] = i\hbar\hat{\ell}_z$$

$$\left[\hat{\ell}_y, \hat{\ell}_z\right] = i\hbar\hat{\ell}_x$$

$$\left[\hat{\ell}_z, \hat{\ell}_x\right] = i\hbar\hat{\ell}_y$$

$$\left[\hat{\ell}^2, \hat{\ell}_z\right] = 0$$

Can simultaneously know the magnitude of the angular momentum and one of its components

Spherical harmonics

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$ spherically symmetric → s

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$ → p_z

$$Y_1^{\pm 1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$\left\{ \begin{array}{l} \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi \rightarrow p_x \\ \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi \rightarrow p_y \end{array} \right.$$

$$Y_2^0 \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$ → d_z^2

$$Y_2^{\pm 1} \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$$

$$\left\{ \begin{array}{l} \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi \rightarrow d_{xz} \\ \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi \rightarrow d_{yz} \end{array} \right.$$

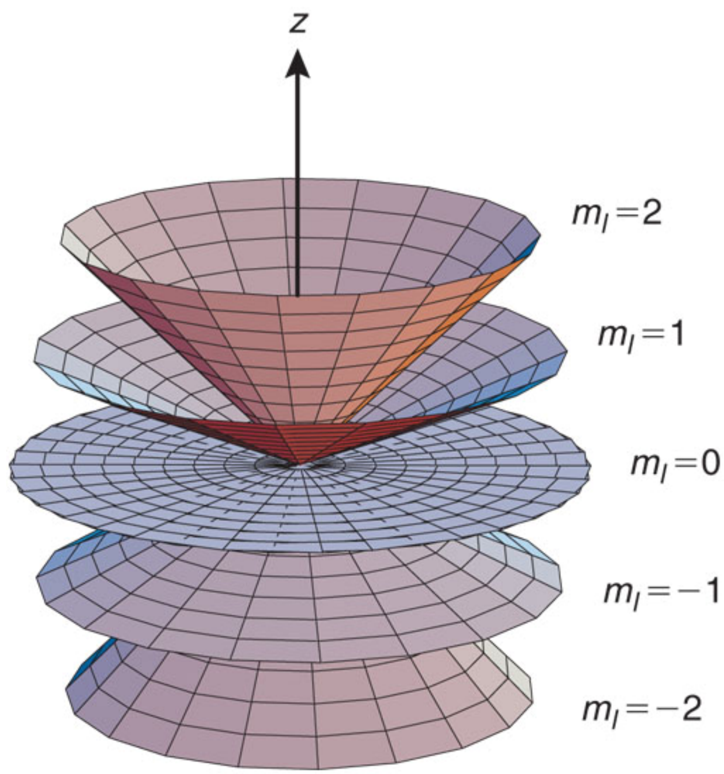
$$Y_2^{\pm 2} \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$\left\{ \begin{array}{l} \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi \rightarrow d_{x^2-y^2} \\ \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi \rightarrow d_{xy} \end{array} \right.$$

Consider a sphere of radius $\sqrt{\ell(\ell+1)}\hbar$

For ℓ=2, the allowed solutions can be represented as 4 cones and 1 disk.

Although the z component of the angular momentum is specified for each cone, the x and y components can take on any value.



$\ell = 2$

If the vector were parallel to the *z* axis, then ℓ_x and ℓ_y = 0.
But not possible