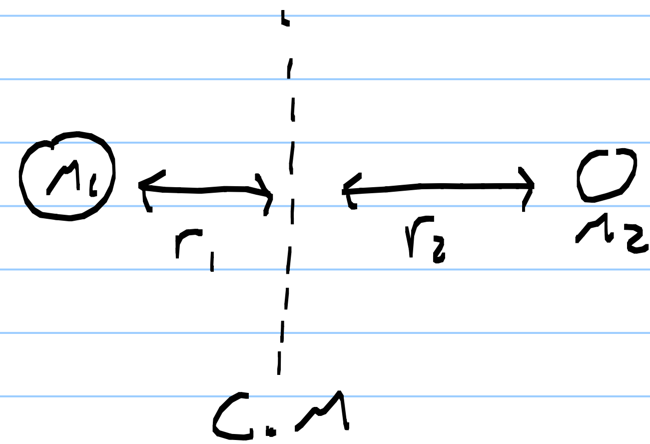
LECTURE 29: Angular Momentum (part 1)

What I expect you to learn:

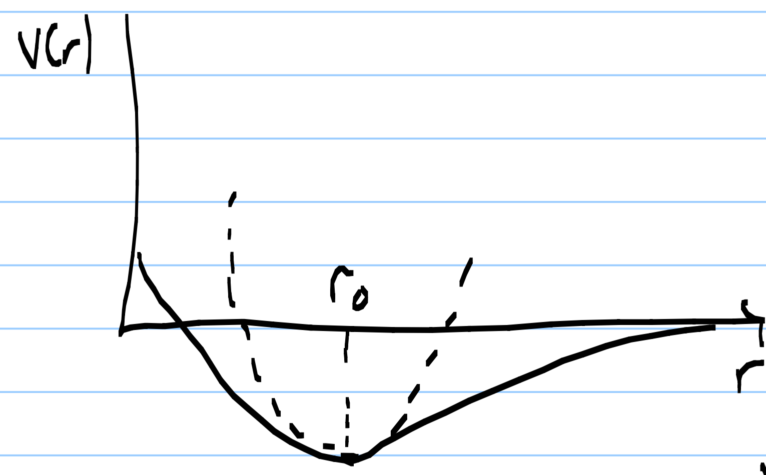
- The differences between angular momentum in CM and QM
- What are the relevant operators for working with angular momentum and how to derive them
- How this applies to Diatomic molecules

(Roughly covers chapter 6.1-6.3 of the textbook)

REMEMBER THE DIATOMIC MOLECULE:



POTENTIAL CURVE FOR DIATOMIC MOLECULE



V(r) for small oscillations will be approx. by harmonic potential

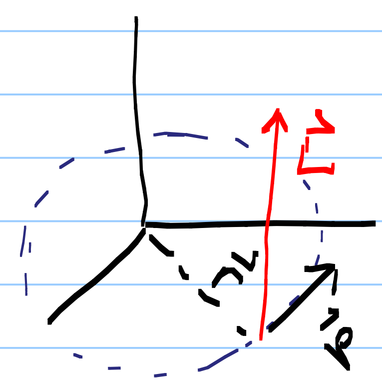
DIATOMIC MOLECULE ENERGY SPECTRUM:

→ ok, we understand where this comes from.

→ what about these levels?

They are not equally spaced

ANGULAR MOMENTUM IN CLASSICAL MECHANICS



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

$$\vec{L} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_z = (r \times p)_z = x p_y - y p_x$$

In QM, we replace p by its associated operator

$$p_{op} : \frac{\hbar}{i} \frac{\partial}{\partial r} \quad , \quad p_x{}_{op} : \frac{\hbar}{i} \frac{\partial}{\partial x}$$

with $\psi(x) = e^{iKx}$, $p_{op}\psi(x) = \frac{\hbar}{i}\frac{\partial}{\partial x} e^{iKx} = \frac{i}{i}\hbar K e^{iKx}$

$= p\,\psi(x)$

ANGULAR MOMENTUM IN QM

$L_z = x p_y - y p_x$ becomes $L_{z\,op} = \frac{\hbar}{i}\left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) \equiv \hat{L}_z$

$$L_{op} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x_{op} & y_{op} & z_{op} \\ \frac{\hbar}{i}\frac{\partial}{\partial x} & \frac{\hbar}{i}\frac{\partial}{\partial y} & \frac{\hbar}{i}\frac{\partial}{\partial z} \end{vmatrix}$$

$L_{x\,op} = \frac{\hbar}{i}\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right)$

$L_{y\,op} = \frac{\hbar}{i}\left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x}\right)$

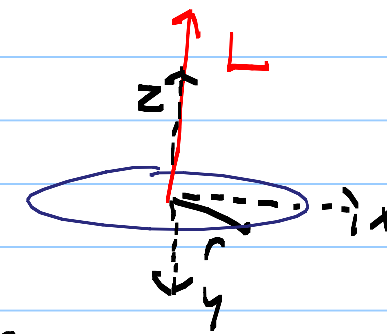
L_{op} : orbital angular momentum operator

L^2 will prove more useful later i.e.

$L^2 = L_{op} \cdot L_{op}$: squared magnitude of orbital angular momentum

Eigenvalue Equation for $\hat{L}_z$

Consider a particle in the x-y plane described by the 2-d wave function



$$\hat{L}_z \psi(x,y) = l_z \psi(x,y)$$

We can work in polar coordinates:

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

$$\frac{\partial}{\partial\varphi} = \frac{\partial y}{\partial\varphi}\frac{\partial}{\partial y} + \frac{\partial x}{\partial\varphi}\frac{\partial}{\partial x}, \qquad \frac{\partial x}{\partial\varphi} = -r\sin\varphi = -y$$
$$\frac{\partial y}{\partial\varphi} = r\cos\varphi = x$$

$$\frac{\partial}{\partial\varphi} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}$$

$$\boxed{\Rightarrow \hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \quad !}$$

Eigenvalue Equation for $\hat{L}_z$

$$\hat{L}_z \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial \varphi} = L_z \psi \qquad (1)$$

$\psi(x, y)$ is now $\psi(r, \varphi)$

solution to (1) will be : $e^{i(L_z \varphi/\hbar)}$

$$\psi(r, \varphi) = R(r)\, e^{i(L_z \varphi/\hbar)}$$

$\hookrightarrow$ A FUNCTION OF r ALONE

Now : $\psi(r, \varphi) = \psi(r, \varphi + 2\pi)$

i.e. $\exp\left[(iL_z/\hbar)(\varphi + 2\pi)\right] = \exp\left[(iL_z/\hbar)\,\varphi\right]$

or $\boxed{\exp\left[i(2\pi L_z/\hbar\right] = 1}$

Eigenvalue Equation for $\hat{L}_z$

$$\exp\left[i(2\pi L_z/\hbar)\right] = 1$$

$$\Rightarrow \frac{L_z}{\hbar} = m \qquad \text{where} \quad m = 0, \pm 1, \pm 2, \ldots$$

$$L_z = m\hbar \qquad \longrightarrow \qquad \psi(r, \varphi) = R(r)\, e^{im\varphi} \qquad (2)$$

Notes:

* – (2) is valid in a central potential

– WHEN ONE MEASURES THE COMPONENT OF THE ORBITAL ANGULAR MOMENTUM, ONE OBTAINS AN INTEGER MULTIPLE OF $\hbar$

COMMUTATION RELATIONS

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y L_x$$

$$\hat{L}_x \hat{L}_y \psi = -\hbar^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial z} \right)$$

$$= -\hbar^2 \left(y \frac{\partial \psi}{\partial x} + \cancel{yz \frac{\partial^2 \psi}{\partial z \partial x}} - \cancel{xy \frac{\partial^2 \psi}{\partial z^2}} - \cancel{z^2 \frac{\partial^2}{\partial y \partial x}} \psi + \cancel{zx \frac{\partial^2 \psi}{\partial y \partial z}} \right) \quad (3)$$

$$\hat{L}_y \hat{L}_x \psi = -\hbar^2 \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left(y \frac{\partial \psi}{\partial z} - z \frac{\partial \psi}{\partial y} \right)$$

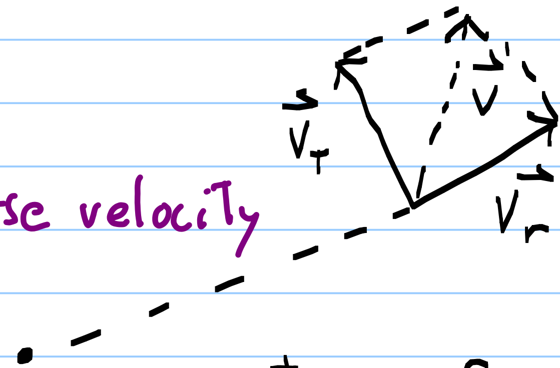
$$= -\hbar^2 \left(\cancel{zy \frac{\partial^2}{\partial x \partial z}} \psi - \cancel{z^2 \frac{\partial^2}{\partial x \partial y}} \psi - \cancel{xy \frac{\partial^2}{\partial z^2}} \psi + x \frac{\partial \psi}{\partial y} + \cancel{xz \frac{\partial^2}{\partial z \partial y}} \psi \right) \quad (4)$$

$$(3) - (4) = \hbar^2 \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \psi$$

$$= i\hbar \hat{L}_z$$

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

Transverse velocity



radial velocity

center of potential

Classical equation:

$$E = \frac{1}{2} m v_T^2 + \frac{1}{2} m v_r^2 + V(r)$$

→ Angular momentum is conserved

$L = m v_T r$

$$L = m v_T r \quad , \quad v_T = \frac{L}{mr} \quad , \quad v_r = \frac{p_r}{m}$$

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r) \qquad (5)$$

WHAT IS THE QM EQUIVALENT?

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

START FROM SCHRÖDINGER EQUATION WE KNOW (and love):

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\,\psi = E\,\psi \qquad (6)$$

IN SPHERICAL COORDINATES (6) CAN BE WRITTEN AS:

$$(7)\quad -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{1}{2mr^2}\cdot\left[-\hbar^2\left(\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\,\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right)\right] + V\psi = E\psi$$

$\rightarrow$ mult. (7) by r

$$-\frac{\hbar^2}{2m}\frac{\partial^2(r\psi)}{\partial r^2} + \frac{\hat{L}^2}{2mr^2}(r\psi) + V(r\psi) = E(r\psi)$$

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (8)$$

Note that r does not appear in (8)

$\rightarrow \psi(r, \theta, \varphi) = R(r)\, F(\theta, \varphi)$

$\Rightarrow \hat{L}^2 [R(r) \cdot F(\theta, \varphi)] = L^2 [R(r) \cdot F(\theta, \varphi)]$

$\hat{L}^2 F(\theta, \varphi) = L^2 F(\theta, \varphi)$

Note that $\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$ commutes with $\hat{L}^2$

$\rightarrow$ we have states that are eigenstates of both $\hat{L}_z$ and $\hat{L}^2$

$$\rightarrow \quad F(\theta, \varphi) = P(\theta)\, e^{im\varphi}, \quad \frac{\partial^2 F}{\partial \varphi^2} = -m^2 F \quad (9)$$

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

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

using (5) we have

$$\hat{L}^2 P = -\hbar^2\left[\frac{d^2P}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\,\frac{\partial P}{\partial\theta} - \frac{m^2}{\sin^2\theta}P\right] = L^2 P \qquad (10)$$

we'll write L^2 as $\lambda\hbar^2$

(10) becomes:

$$\frac{d^2P}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\,\frac{dP}{d\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)P = 0 \qquad (11)$$

Attempt to solve (11)

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

- FIRST TRY $P = \text{CONSTANT}$

$$\lambda - \frac{m^2}{\sin^2\theta} = 0$$

$\rightarrow$ FOR THIS TO BE TRUE FOR ALL θ,
$m = 0$, $\lambda = 0$

- SECOND TRY $P = \sin\theta$

$$-\sin\theta + \frac{\cos^2\theta}{\sin\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\sin\theta = 0$$

$$= -2\sin\theta + \frac{1}{\sin\theta} + \lambda\sin\theta - \frac{m^2}{\sin\theta} = 0$$

$$\lambda = 2 \qquad m^2 = 1 , \qquad m = \pm 1$$

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

- Third Try: $P = \cos\theta$

$$-2\cos\theta + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\cos\theta = 0$$

$$\lambda = 2 \quad , \quad m = 0$$

- FOURTH TRY: $P = \sin^2\theta$

$$4 - 6\sin^2\theta + \lambda\sin^2\theta - m^2 = 0$$

$$\lambda = 6 \quad , \quad m^2 = 4 \quad , \quad m = \pm 2$$

- FIFTH TRY: $P = \cos^2\theta$

$$2 - 6\cos^2\theta + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\cos^2\theta = 0$$

$m = 0$, $\lambda = 6$ would work but we are stuck with the "2".

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

- SIXTH TRY : $\cos^2 - 1/3$ removes the "2" that we had to cancel.

$$m = 0, \quad \lambda = 6$$

- 7th TRY : $\sin\theta \cos\theta$:

$$-6\sin\theta\cos\theta + \frac{\cos\theta}{\sin\theta} + \lambda\sin\theta\cos\theta - m^2\frac{\cos\theta}{\sin\theta}$$

$$\lambda = 6, \quad m^2 = 1, \quad m \pm 1$$

with more time, we'd find $\lambda = 12, 20, \ldots$

$$\lambda = 0, 2, 6, 12, 20$$

$$\lambda = \ell(\ell+1), \quad \ell = 0, 1, 2, 3, \ldots$$

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

we also Found:

$$\lambda = 0 \qquad m = 0$$
$$\lambda = 2 \qquad m = 0, -1, 1$$
$$\lambda = 6 \qquad m = 0, \pm 2, \pm 1$$

So:

$$L^2 = \ell(\ell+1)\hbar^2 \qquad (\ell = 0, 1, 2, 3)$$
$$L_z = m\hbar \qquad (|m| \leq \ell \text{ ; } m \text{ is an integer})$$

$$F = P_{\ell,m}(\theta)\, e^{im\varphi} \equiv Y_{\ell,m}(\theta,\varphi)$$

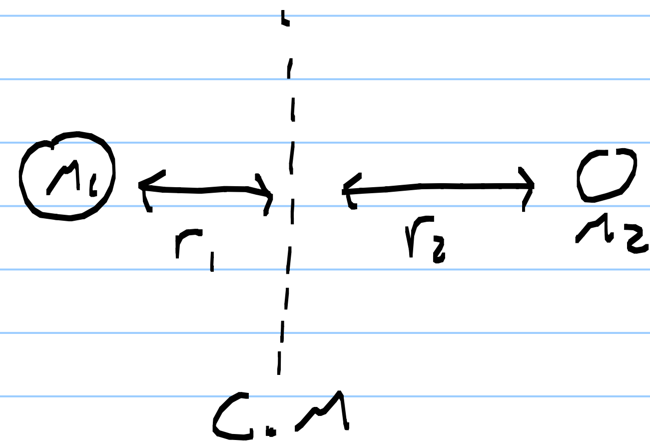
$Y_{\ell,m}(\theta,\varphi)$: SPHERICAL HARMONICS

ORBITAL MOMENTUM IN CENTRAL POTENTIALS

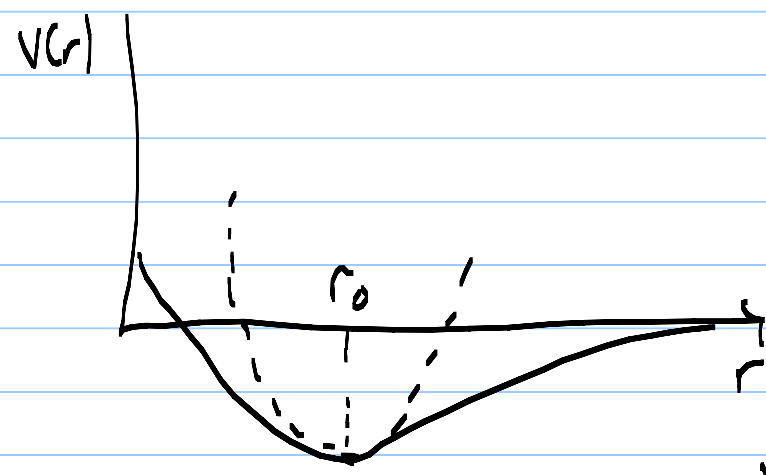
$Y_{l,m}(\theta, \varphi)$

l	m	$Y_{lm}(\theta, \varphi)$
0	0	$\frac{1}{\sqrt{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos\theta$
	± 1	$\mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\varphi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
	± 1	$\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \, e^{\pm i\varphi}$
	± 2	$\sqrt{\frac{15}{32}} \sin^2\theta \, e^{\pm 2i\varphi}$

ROTATIONAL STATES OF MOLECULES



POTENTIAL CURVE FOR DIATOMIC MOLECULE



$V(r)$ for small oscillations will be approx. by harmonic potential

ROTATIONAL STATES OF MOLECULES

$$r_0 = r_1 + r_2$$

$$L = m_1 v_{1T} r_1 + m_2 v_{2T} r_2$$

$$m_1 v_{1T} = m_2 v_{2T} \quad , \quad m_1 r_1 = m_2 r_2$$

$$E = \frac{1}{2} m_1 v_{1T}^2 + \frac{1}{2} m_2 v_{2T}^2$$ becomes

$$E = \frac{m_1 + m_2}{2 m_1 m_2} L^2 = \frac{L^2}{2 \mu r_0^2}$$

$$\rightarrow E = \frac{\ell(\ell+1)\hbar^2}{2 \mu r_0^2}$$

→ Rotational energy levels

In reality the diatomic molecule has rotational and vibrational energy levels.

To first approximation one can write:

$$E_{n,\ell} = (n + 1/2)\hbar\omega_0 + \frac{\ell(\ell+1)\hbar^2}{2\mu r_0^2}$$