Chapter 7, continued

Rotation in 2 dimensions

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

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

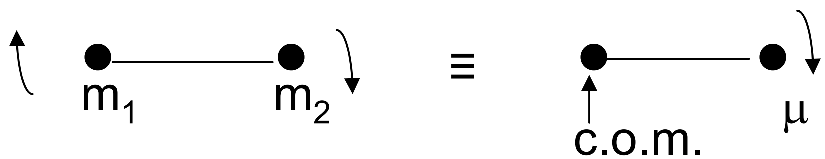
$\psi_{tot} = \psi_{trans}\, \psi_{vib}\, \psi_{rot}$

} separation of variables

reduced mass

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

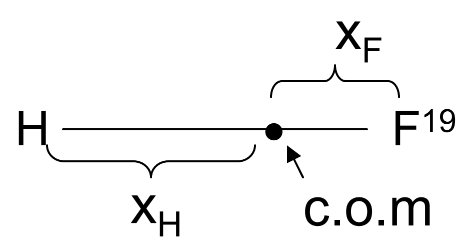
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



V(x,y) = 0 everywhere

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

↑ fixed radius



$$x_H + x_F = .9168\text{Å}$$

$$x_H m_H = x_F m_F$$

$$x_F = .0458\text{Å}$$

$$x_H = .8710\text{Å}$$

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

$$\frac{-\hbar^2}{2\mu r_0^2}\frac{d^2\Phi}{d\phi^2} = E\Phi \longrightarrow \quad \Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

$$0 \leq \phi \leq 2\pi$$

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

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

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

$$I = \mu r_0^2 =$$ 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

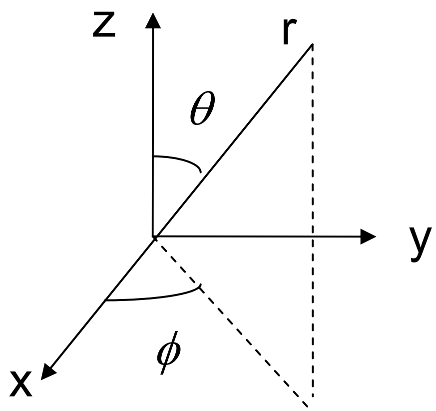
angular momentum in z direction: $\vec{\ell}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$

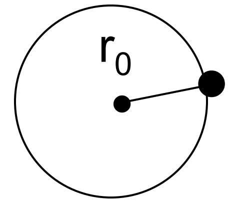
$$\vec{\ell}_z \Phi = \frac{\hbar}{i}\frac{1}{\sqrt{2\pi}}\frac{d}{d\phi}e^{im\phi} = m\hbar\Phi$$

$P(\phi)d\phi = \frac{d\phi}{2\pi}$, all ϕ values equally probable
angular momentum in z direction precisely defined

$\vec{\ell}_z, \; \hat{\phi}$ do **not** commute

On to 3 dimensions: $(x, y, z) \rightarrow (r, \theta, \phi)$





motion of particle on the surface of a sphere

≡ <u>Rigid rotor</u>

$0 \le r \le \infty$

$0 \le \theta \le \pi$

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

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

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

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

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