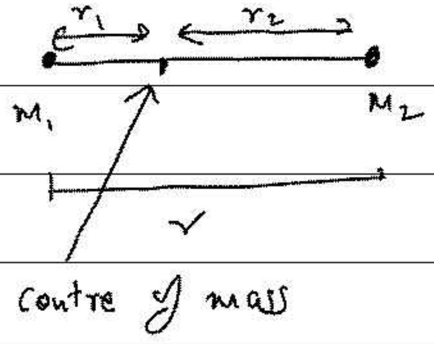
Note Title 08-11-2016

Rotational Motion

Still considering a rigid rotor!



at centre of mass: $m_1 r_1 = m_2 r_2$

also $r = r_1 + r_2$

$$I = m_1 r_1^2 + m_2 r_2^2$$
$$= \mu r^2$$

where $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$

reduced mass

$$E = \frac{\hbar^2}{2I} l(l+1) \quad \ldots \quad (1)$$

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

$I = \mu r^2$, $J = 0, 1, 2, 3, \ldots$

$J \Rightarrow$ rotational quantum number

$$\Delta E = E_{J+1} - E_J$$
$$= \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right]$$
$$= \frac{\hbar^2}{2I} 2(J+1) = \frac{\hbar^2}{I}(J+1)$$

$$\Delta E = \frac{h^2}{4\pi^2 I}(J+1) \quad \ldots \quad (3)$$

$$\Delta E = h\nu = \frac{h^2}{4\pi^2 I}(J+1)$$

$$\nu = \frac{h}{4\pi^2 I}(J+1)$$

$$\nu = 2\frac{h}{8\pi^2 I}(J+1)$$

$$\nu = 2B(J+1) \;; \quad B = \frac{h}{8\pi^2 I}$$

(Hz)

rotational constant

$$\Delta E = hc\tilde{\nu} = \frac{h^2}{4\pi^2 I}(J+1)$$

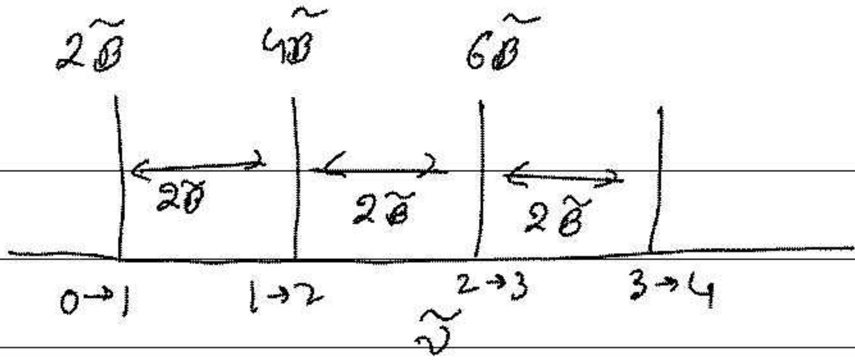
$$\tilde{\nu} = \frac{h}{4\pi^2 I c}(J+1)$$

$$\tilde{\nu} = 2\tilde{B}(J+1) \;; \quad \tilde{B} = \frac{h}{8\pi^2 I c}$$

(cm^{-1})

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

$J=3$	———	$\frac{12\hbar^2}{2I} = hc\tilde{\nu}$	$= 12\tilde{B}hc$
$J=2$	———	$6\frac{\hbar^2}{2I}$	$= 6\tilde{B}hc$
$J=1$	———	$2\frac{\hbar^2}{2I}$	$= 2\tilde{B}hc$
$J=0$	———	0	$= 0$



; $\Delta J = \pm 1$

Rotational lines $\Rightarrow$ equispaced

$$\text{spacing} = 2\tilde{B} \;;\quad \tilde{B} = \frac{h}{8\pi^2 I c}$$

bond distance !!

Central force problem!

$$\hat{H} = \frac{\hat{p}_M^2}{2M} + \underbrace{\left[\frac{\hat{p}_\mu^2}{2\mu} + V(r)\right]}_{\text{internal motion or relative motion}}$$

$(M = m_1 + m_2)$

central force potential!

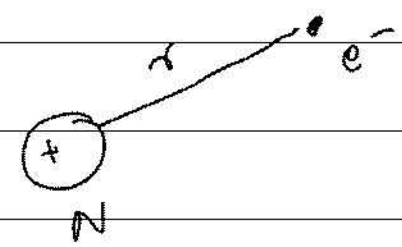
$$\hat{H}_1 \psi_{cM} = E_M \psi_{cM} \;;\quad \hat{H}_1 = \frac{\hat{p}_M^2}{2M} \quad \ldots (1)$$

$$\hat{H}_2 \psi_\mu = E_\mu \psi_\mu \;;\quad \hat{H}_2 = \frac{\hat{p}_\mu^2}{2\mu} + V(r) \quad \ldots (2)$$

free particle translation $\Rightarrow$ not interesting !!

Hydrogen atom or Hydrogen-like atom

Hydrogenic $\Rightarrow$ Hydrogen-like



$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \cdots \quad (3)$$

$$\hat{H} = \hat{T}_N + \hat{T}_e + V(r) \quad \cdots \quad (4)$$

$$\hat{H}\,\psi(r,\theta,\phi) = E\,\psi(r,\theta,\phi) \quad \cdots \quad (5)$$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r) \quad \cdots \quad (6)$$

$\Downarrow$ Centre of mass coordinates

$$\hat{H} = \left[-\frac{\hbar^2}{2M}\nabla^2\right] + \underbrace{\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]}_{\text{internal motion}}$$

$$M = m_e + m_N \; ; \quad \frac{1}{\mu} = \frac{1}{m_N} + \frac{1}{m_e}$$

$$\hat{H}\,\psi(r,\theta,\phi) = E\,\psi(r,\theta,\phi) \quad \cdots \quad (7)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \; ; \quad V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \quad \cdots \quad (8)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$+ V(r)$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]RY$$

$$+ V(r)\,RY = E\,RY \quad \cdots (9)$$

$$\underline{\Psi = RY}$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}RY - \frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]RY$$

$$+ V(r)RY = ERY \quad \cdots (10)$$

Second term $\equiv$ $-\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y$

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

$$I = \mu r^2$$

Divide (10) throughout by RY

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} - \frac{\hbar^2}{2\mu r^2}\frac{1}{Y}\Lambda^2 Y + V(r) = E$$

$$\cdots (11)$$

$$-\frac{\hbar^2}{2u}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}-\frac{\hbar^2}{2ur^2}l(l+1)+V(r)=E \quad (12)$$