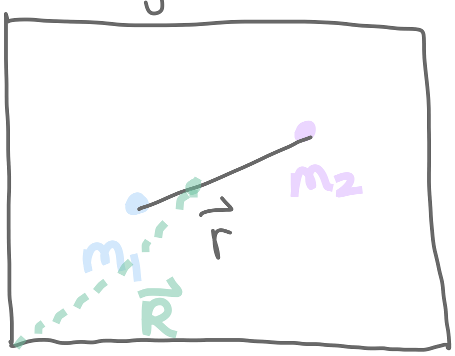
# Lecture 14

Tuesday, November 5, 2024 11:32

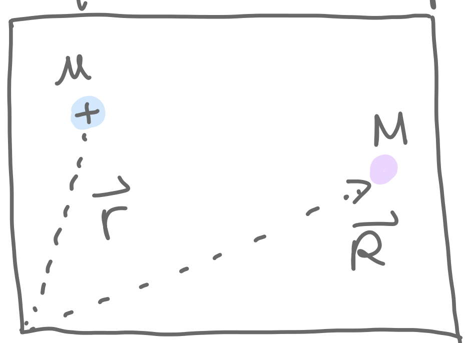
Last lecture :

$$\left[\frac{\hat{p}_\mu^2}{2\mu} + V(x,y,z)\right] + \frac{\hat{p}_M^2}{2M}$$

original




equivalent set-up

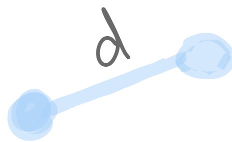



$$E = E_M + E_\mu$$

$$\frac{\hat{p}_M^2}{2M}\psi_M = E_M \psi_M$$

$$\left[\frac{\hat{p}_\mu^2}{2\mu} + V(x,y,z)\right]\psi_\mu = E_\mu \psi_\mu$$

## 6.4 The Two-Particle Rigid Rotor




The energy of the rotor is entirely kinetic, $V=0$

$$\hat{H} = \frac{\hat{p}_{\mu}}{2\mu} = -\frac{\hbar^2}{2\mu}\nabla^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Use spherical coordinates

$$\Psi = Y_J^m(\theta, \phi)$$

rotational angular momentum quantum number

$$\hat{H} = \frac{1}{2\mu d^2}\hat{L}^2$$

$$\hat{H}\Psi = E\Psi$$

$$\frac{1}{2\mu d^2}\hat{L}^2 Y_J^m(\theta,\phi) = E\, Y_J^m(\theta,\phi)$$

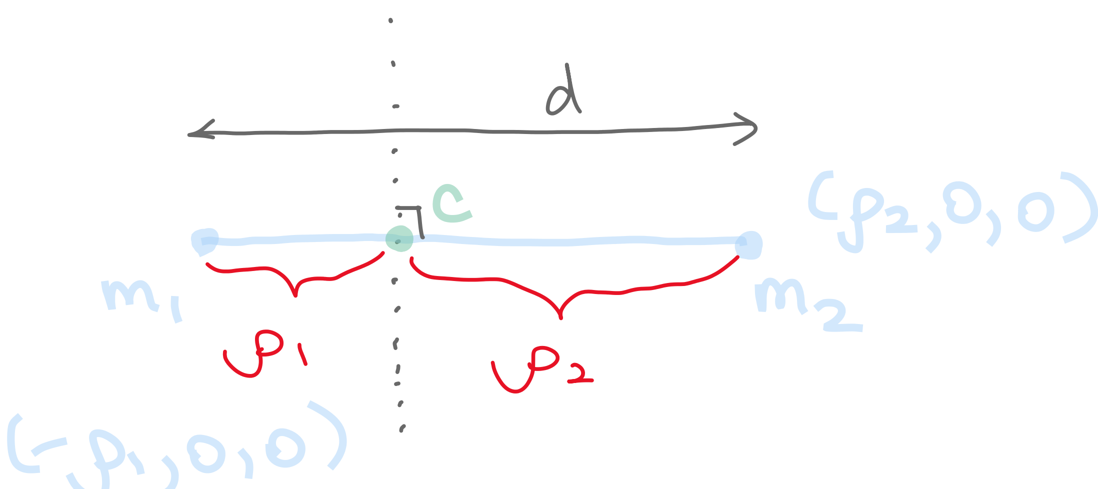
$$\frac{1}{2\mu d^2} J(J+1)\hbar^2 Y_J^m(\theta,\phi) = E Y_J^m(\theta,\phi)$$

$$E = \frac{J(J+1)\hbar^2}{2\mu d^2}, \quad J = 0, 1, 2, \ldots$$

Moment of inertia

$$I \equiv \sum_{i=1}^{n} m_i \rho_i^2$$

perpendicular distance from the particle to the axis




$$\boxed{m_1\rho_1 = m_2\rho_2}$$

$$I = m_1 \rho_1^2 + m_2 \rho_2^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad d = \rho_1 + \rho_2$$

$$I = \left(m_1 \rho_1^2 + m_2 \rho_2^2\right) \frac{m_1 + m_2}{m_1 + m_2}$$

$$= \frac{\boxed{m_1^2 \rho_1^2} + m_1 m_2 \rho_1^2 + m_1 m_2 \rho_2^2 + \boxed{m_2^2 \rho_2^2}}{m_1 + m_2}$$

$$= \frac{\boxed{m_1 m_2 \rho_1 \rho_2} + m_1 m_2 \rho_1^2 + m_1 m_2 \rho_2^2 + \boxed{m_1 m_2 \ldots}}{m_1 + m_2}$$

$$= \underbrace{\frac{m_1 m_2}{m_1 + m_2}}_{\mu} \rho_1^2 + 2 \underbrace{\frac{m_1 m_2}{m_1 + m_2}}_{\mu} \rho_1 \rho_2 + \underbrace{\frac{m_1 m_2}{m_1 + m_2}}_{\mu} \rho \ldots$$

$$= \mu(\rho_1 + \rho_2)^2$$

$$\boxed{I = \mu d^2}$$

$$\boxed{E = \frac{J(J+1)\hbar^2}{2I}, \quad J = 0, 1, 2, \ldots}$$

$J = 0, \quad E = 0$

no zero-point rotational energy

$E$ increases as $J^2 + J$; spacing between adjacent rotational levels increases as $J$ increases.

For each $J$, there are $(2J+1)$ values of $m_J$ the energy levels $(2J+1)$-fold degenerate are $(2J+1)$-fold degenerate.

N.B. For a single state, it is "nondegenerate" and <u>not</u> "singly degenerate".

Selection rule for rotational spectroscopy : $\Delta J = \pm 1$.

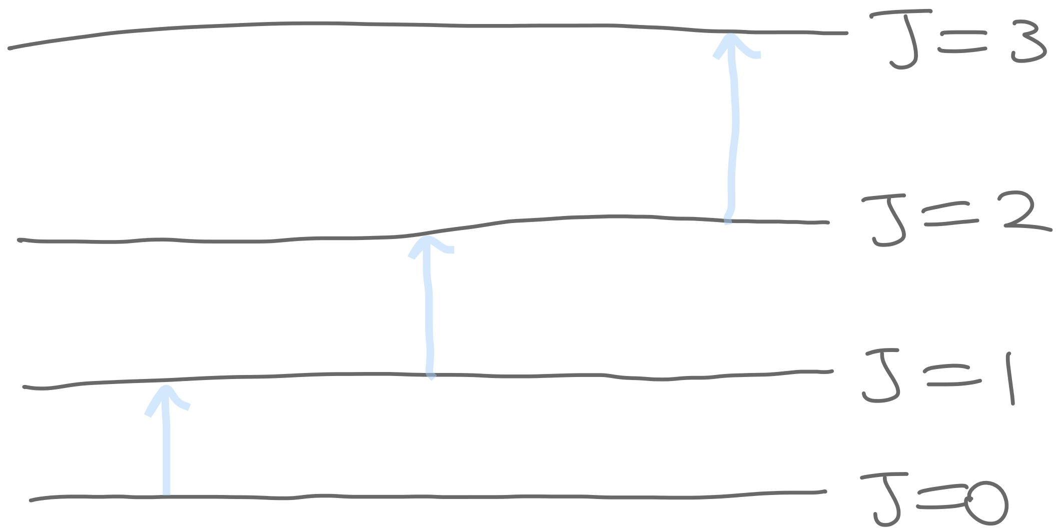
Pure rotational spectrum : a molec
must have a nonzero dipole mom

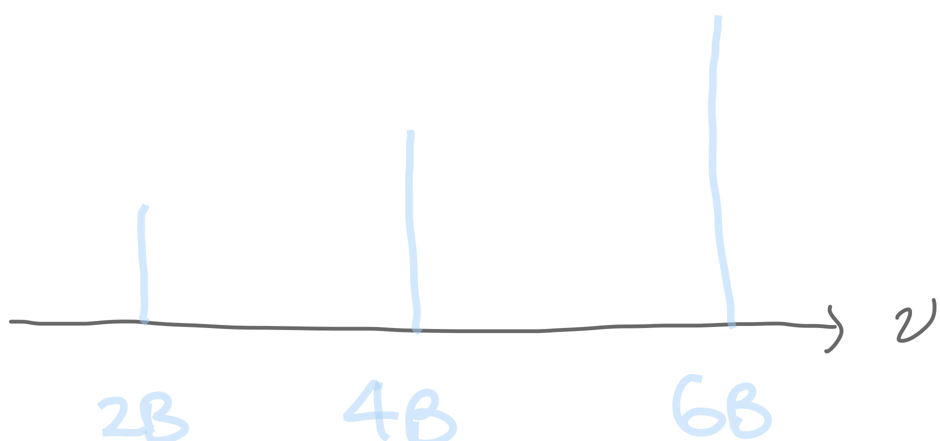
Microwave/infrared region; microw
works by rotating water molecules –

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

$$\nu = 2(J+1)B, \quad B = \frac{h}{8\pi^2 I}, \quad J = 0$$

rotational constant




intensity comes fr
degenera

**Exercise:** The lowest-frequency absorp
line of $^{12}C^{32}S$ occurs at 48991.0 M
Find the bond distance of $^{12}C^{32}S$.

Solution : lowest-frequency transiti

is $J=0 \rightarrow J=1$.

$$h\nu = E_{upper} - E_{lower}$$

$$h\nu = \frac{1(2)\hbar^2}{2\mu d^2} - \cancel{\frac{0(1)\hbar^2}{2\mu d^2}}$$

$$d^2 = \frac{2\hbar^2}{2\mu h\nu}$$

$$\hbar = \frac{h}{2\pi}$$

$$\hbar^2 = \frac{h^2}{4\pi^2}$$

$$d^2 = \frac{h^{\cancel{2}}}{4\pi^2 \cancel{h}\mu\nu}$$

$\xi$ $\zeta$

$$d = \left(\frac{h}{4\pi^3\mu\nu}\right)^{\frac{1}{2}}$$

$$m_C = 12\ g\cdot mol^{-1}$$

$$m_S = 31.91207\ g\cdot mol^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12(31.97207)}{12 + 31.97207}\ g\cdot mol^{-1}$$

1

$$\cdot\ 6.02214 \times 10^{23}\ \text{mol}^{-1}$$

$$\mu = 1.44885 \times 10^{-23}\ \text{g}$$

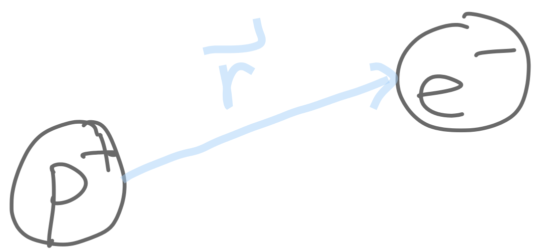
$$d = \frac{1}{2\pi}\left(\frac{h}{\nu\mu}\right)^{\frac{1}{2}}$$

$$= \frac{1}{2\pi}\left[\frac{6.62607 \times 10^{-34}\ \text{J}\cdot\text{s}}{(48991.0 \times 10^{6}\ \text{s}^{-1})(1.44885 \times 10^{-26}\ldots}\right.$$

$$d = 1.5377 \times 10^{-10}\ \text{m}$$

$$\boxed{d = 1.5377\ \text{Å}}$$

# 6.5 The Hydrogen Atom



hydrogen-like atoms: just one electro
with different nuclei

$H$, $He^+$, $Li^{2+}$, ..., $Au^{78+}$, ...

orbital: one-electron spatial wavefunct

Let $(x, y, z)$ be the coordinates of
the electron relative to the nucleus
and let $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$. The
Coulomb's law force on the electron
in the hydrogenlike atom is:

$$\boxed{\vec{F} = -\frac{Ze^2}{4\pi\varepsilon_0 r^2}\frac{\vec{r}}{r}}$$

$$\frac{dV(r)}{dr} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

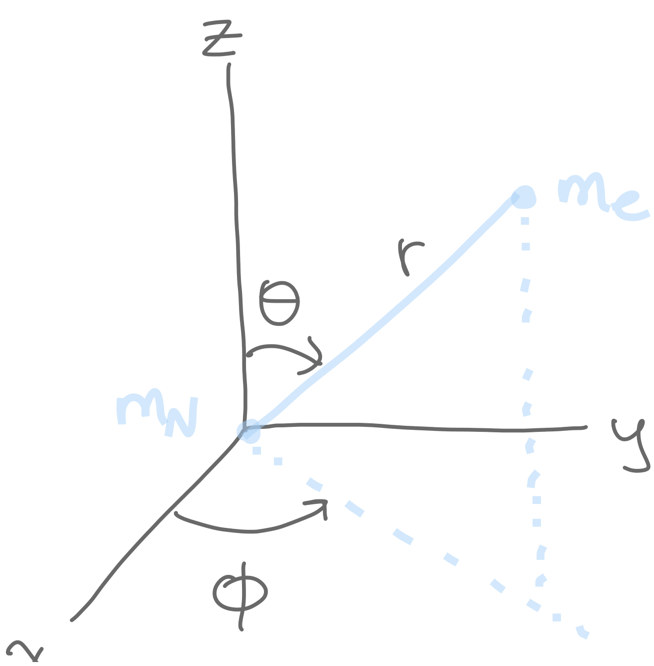
$$\int x^{-2}dx = -x^{-1} + C$$

$$\int dV(r) = \frac{Ze^2}{4\pi\varepsilon_0}\int \frac{1}{r^2}dr$$

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

$$\boxed{V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_{12}}}$$

general form



$$\mu = \frac{m_e m_N}{m_e + m_N}$$

$m_e$ : electronic mass

$m_N$ : nuclear mass

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\psi = R(r)\,Y_\ell^m(\theta,\phi),$$

$$\ell = 0, 1, 2, \dots, \quad |m| \le \ell$$

$R(r)$ has to satisfy

$$-\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}R - \frac{Ze^2}{4\pi\varepsilon_0 r}R =$$

$$a \equiv \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$R'' + \frac{2}{r}R' + \left[\frac{8\pi\varepsilon_0 E}{ae^2} + \frac{2Z}{ar} - \frac{\ell(\ell+1)}{r^2}\right.$$