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Q3) Born Oppenheimer approximation. is the assumption that for molecules, the electronic and nuclear motions (vibrational and rotational) can be separated. It is based on the fact that nuclei are much heavier than the electrons

In molecular spectroscopy using the Born Oppenheimer approximation means considering molecular energy as a sum of independent terms.

i.e $E_{total} = E_{elec} + E_{vib} + E_{rot}$

This approximation is widely used to speed up the computation of molecular wavefunctions

We can invoke Born Oppenheimer approximation to separate $\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$

as if a Hamiltonian is separable into 2 or more terms then the total eigenfunctions are products of individual eigenfunctions of the separated Hamiltonian terms.

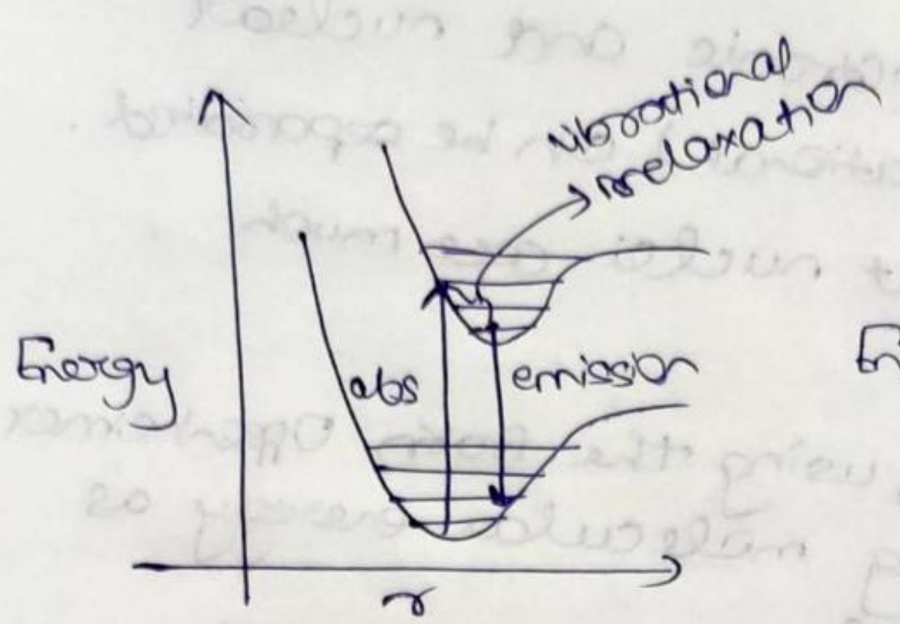
Q6) → In fluorescence the excess vibrational energy is lost by intermolecular collisions.

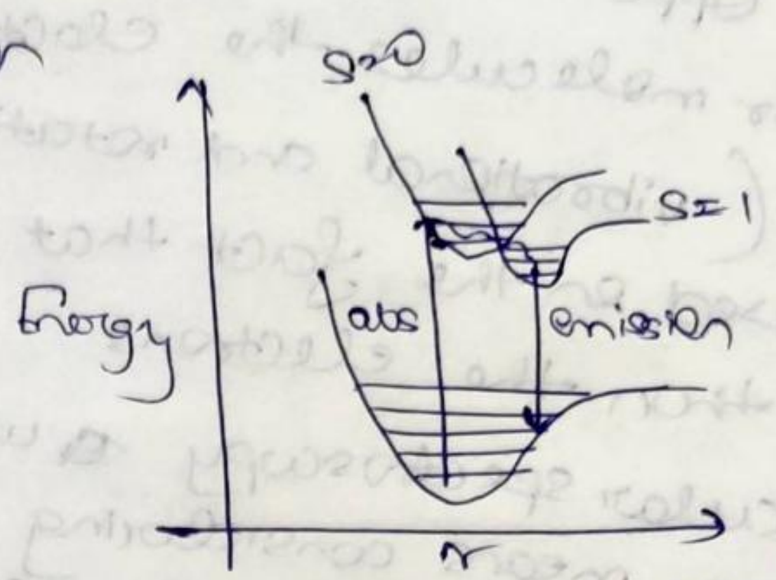
Vib Energy → Kinetic energy (Radiationless Energy transfer)

It reaches lowest vibrational state and then reverts back to the electronic ground state.

→ In phosphorescence there is an intersystem crossing b/w 2 excited states of different total spin with comparable energies. (singlet → triplet)

Jablonski Diagrams





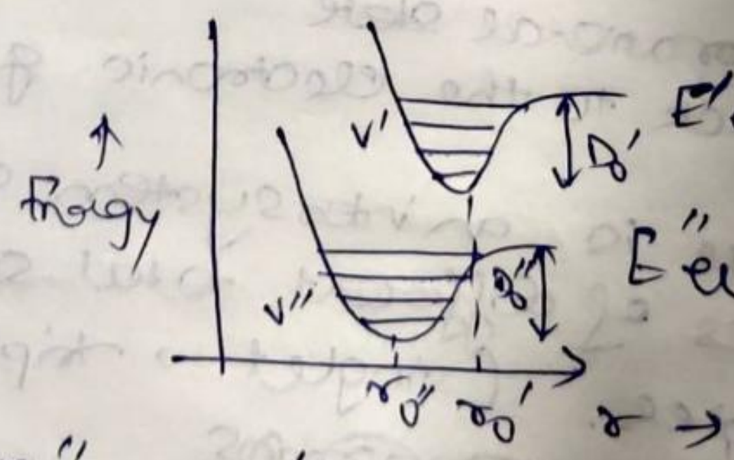
fluorescence

phosphorescence

Q8) Franck condon principle :

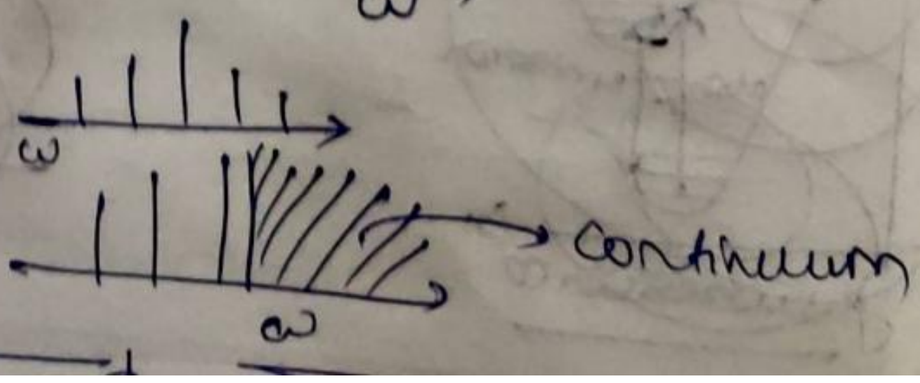
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition. The resulting state is called a Franck condon state and the transition involved a vertical transfer.

The principle relates to the interaction between the electronic and vibrational motions and like the Born Oppenheimer approximation follows from the fact that the nuclear mass is much larger than the electronic mass.



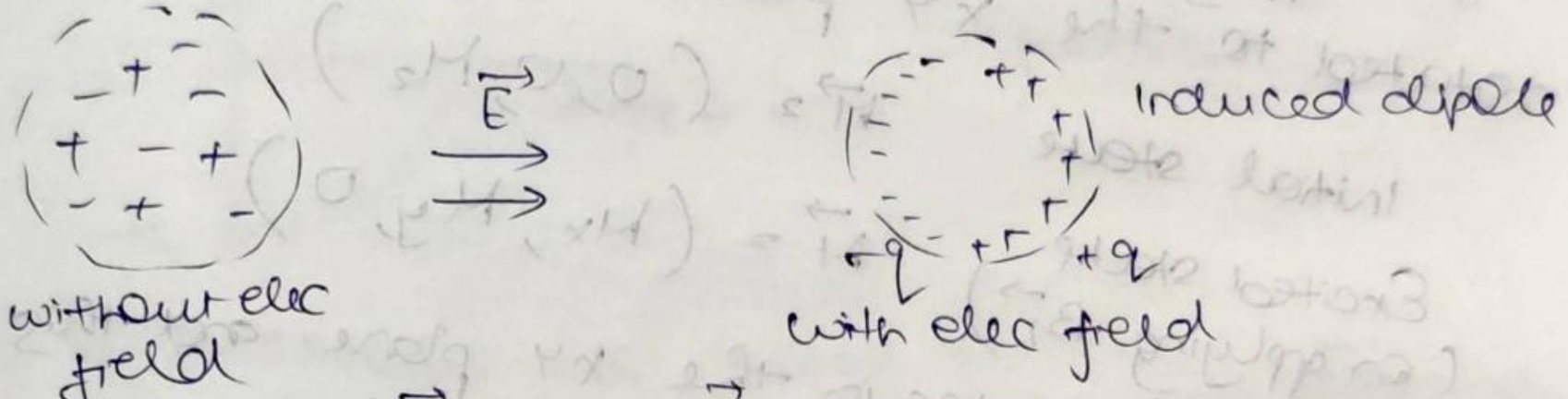
Case 1 : $r_0'' = r_0'$ → (0,0) is strongest spectral line

Case 2 : $r_0'' < r_0'$



Case 3 : $r_0'' << r_0'$

89) ~~When~~ Raman spectroscopy's classical theory is the polarisability of the molecule. When a molecule is put in any electric field, the positive charges get attracted to the negative pole of the field and vice versa. Therefore a separation of charges takes place causing the molecule to develop induced electric dipole hence polarising it



$\vec{\mu}_I = \alpha \vec{E}$

induced dipole ↳ polarisability

∴ when monochromatic radiation is incident upon a sample then it may get reflected, absorbed or scattered. If the frequency of this scattered radiation is analyzed, then we see 3 wavelengths. (frequencies). One corresponding to the incident wavelength (Rayleigh scattering) and, one ~~~~ less than the incident (Antistokes) and one with wavelength greater than the incident (Stokes)

$\mu_I = \alpha(x_0) E_0 \cos(2\pi \nu_0 t)$ → Rayleigh scattering

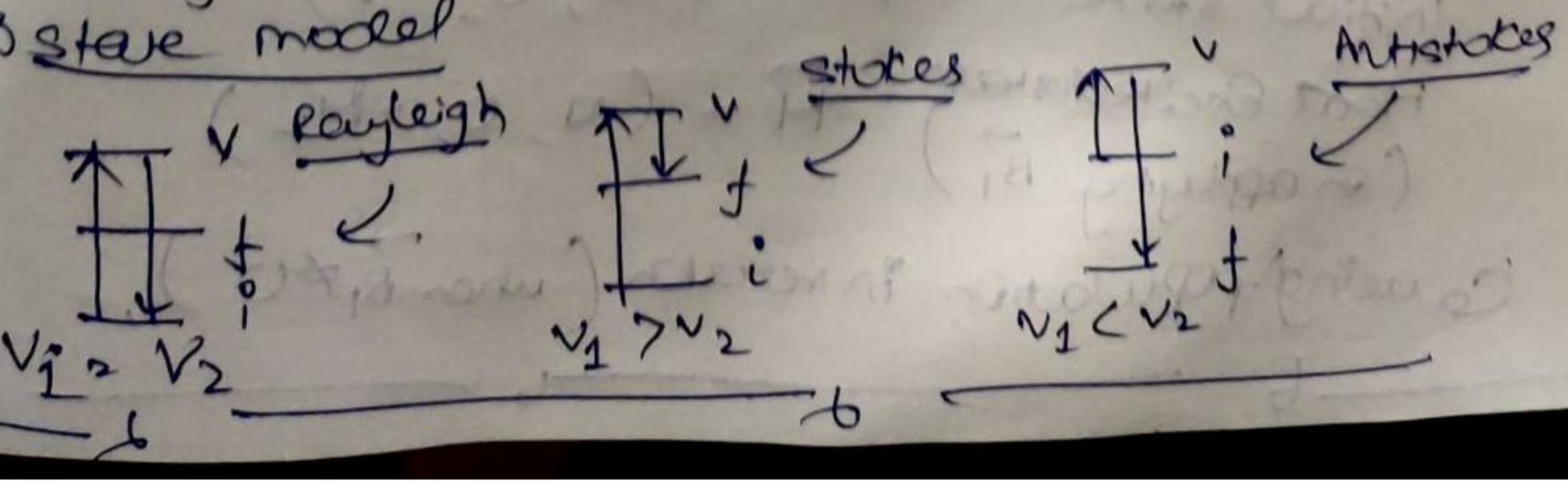
$+ \left(\frac{\partial \alpha}{\partial x}\right)_{x_0} \left(\frac{x_0 E_0}{2}\right) \cos(2\pi(\nu_0 - \nu_m)t)$ → stokes scattering

$+ \left(\frac{\partial \alpha}{\partial x}\right)_{x_0} \left(\frac{x_0 E_0}{2}\right) \cos(2\pi(\nu_0 + \nu_m)t)$ → Antistokes scattering.

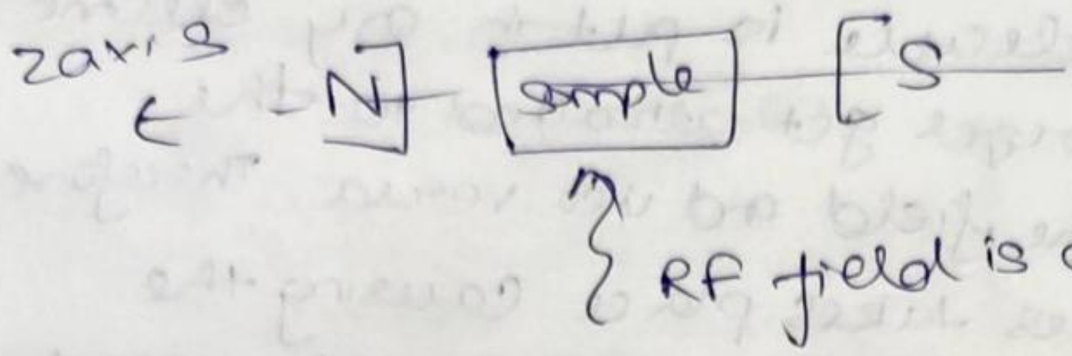
Condition for Raman scattering → $\left(\frac{\partial \alpha}{\partial x}\right)_{x_0} \neq 0$

then only is a molecule Raman active

3 state model



Q7) a) In pulse techniques in NMR



i) 90° RF PULSE

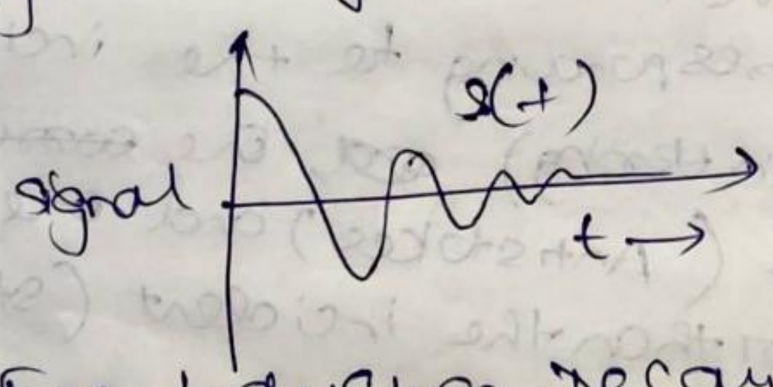
are apply $\vec{B}$ and B_1 such that $\vec{M}$ is rotated to the xy plane

Initial state $\vec{M}_2 (0, 0, M_2)$

Excited state (on applying B_1) $\vec{M} = (M_x, M_y, 0)$

$\vec{M}$ rotates in the xy plane and this rotating $\vec{M}$ induces current in a coil around it, and this current can be amplified and measured.

Once B_1 is closed, $\vec{M}$ returns from excited state to equilibrium state called spin Relaxation (energy exchange takes place as well).



the projection of $\vec{M}$ on xy plane decreases with time as $\vec{M}$ relaxes

Free Induction Decay (FID)

We can perform fourier transform of s(t) to get I(ν) which is dependent on nuclei as well as its local environment which can help us in identification.

ii) 180° RF Pulse

B_1 is applied such that $\vec{M}$ rotates 180°.

Initial state $\vec{M} = (0, 0, M_2)$

Excited state (on applying B_1) $\vec{M} = (0, 0, -M_2)$

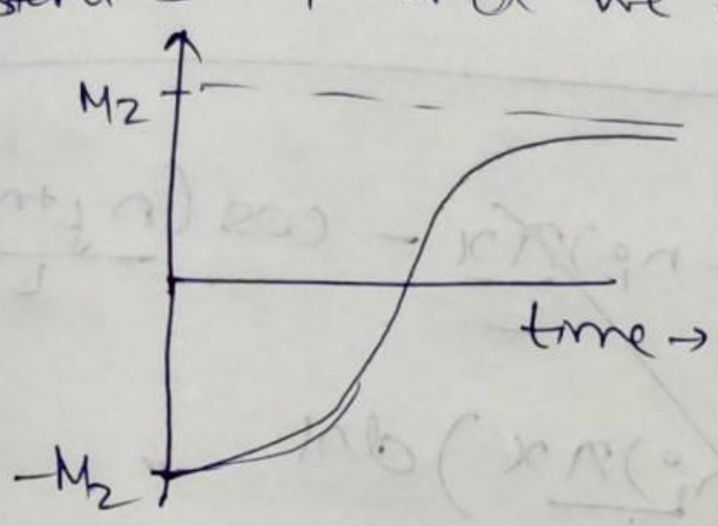
Causing population inversion (when $\vec{B}_1 \neq 0$).

~~also causes population inversion~~

b) T_1 and T_2 relaxations are 2 types of spin relaxations.

a) T_1 relaxation (also called spin-lattice relaxation or longitudinal relaxation)

occurs when 180° pulse is applied. The time constant is T_1 and we investigate M_z with time

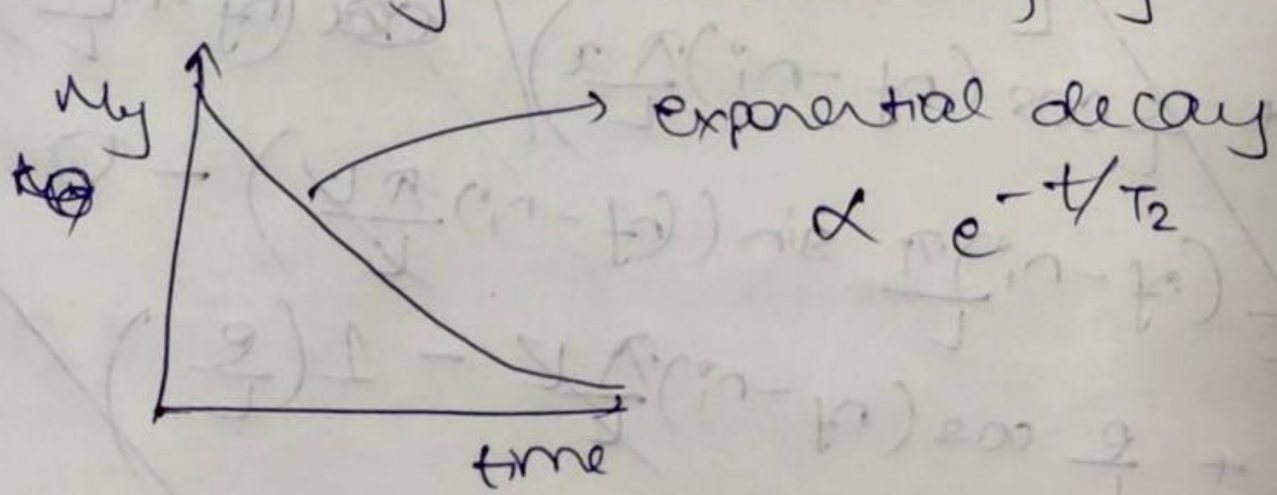


time starts on closing (B) the pulse

a) T_2 relaxation (also called spin spin relaxation or transverse relaxation)

occurs when 90° pulse is applied. Time constant is T_2

Here we investigate variation of M_y with time



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31) 1D infinite potential well:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

as we know

$T_{i \to f} \neq 0$ for valid transition

where $T_{i \to f} = \langle \psi_f | \hat{\mu} | \psi_i \rangle$

$$= \int_{\vec{\sigma}} \psi_f^*(\vec{r}) \vec{\mu} (\psi_i(\vec{r}) \, d\vec{r}$$

$$t_{i\to f} = \int_x \psi_f^*(x)\,(ex)\,\psi_i(x)\,dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n_f \pi}{L} x\right)(ex)\sqrt{\frac{2}{L}} \sin\left(\frac{n_i \pi}{L} x\right)$$

$$= \frac{2e}{L} \int_0^L \sin\left(n_i \frac{\pi x}{L}\right) \sin\left(n_f \frac{\pi x}{L}\right) x\,dx$$

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taking

$$= \frac{2e}{L} \int_0^L \frac{x}{2}\left(\cos(n_f - n_i)\frac{\pi x}{L} - \cos\left(\frac{n_f + n_i}{L}\right)\right)$$

$$= \frac{e}{L}\int_0^L x\cos\left((n_f - n_i)\frac{\pi x}{L}\right)dx$$

$$- \frac{e}{L}\int_0^L x\cos\left((n_f + n_i)\frac{\pi x}{L}\right)dx$$

$$= \int \frac{e}{L}(n_f - n_i)\pi \times \sin\left((n_f - n_i)\frac{\pi x}{L}\right) + \frac{e}{L}\cos\left((n_f - n_i)\frac{\pi x}{L}\right) \Big/ \left(\frac{n_f - n_i}{L}\pi\right)^2$$

$$= 0 - \left(\frac{e}{L}\right)\left(\frac{L}{\pi}\right)^2 \cos\left((n_f - n_i)\frac{\pi x}{L}\right) + \frac{e}{L}\cos\left((n_f - n_i)\frac{\pi x}{L}\right) - 1$$

given $n_f - n_i = 1$

$$\therefore = \frac{e}{L}\left(\frac{L}{\pi}\right)\sin(\pi) + \frac{e}{L}\left(\frac{L}{\pi}\right)\cos(\pi)$$

$$= -\frac{2eL}{\pi}$$

for $n_f + n_i$ we get

(i) contd)

$$\frac{2}{2L}\int x\left(\cos\left(\frac{nf-n_i}{2}\right)\frac{\pi x}{L} - \cos\left(\frac{nf+n_i}{2}\right)\frac{\pi x}{L}\right)dx$$

$$\Rightarrow \int x\cos\left(\frac{nf-n_i}{2}\frac{\pi x}{L}\right)dx$$

$$= \left(\frac{nf-n_i}{2}\right)\pi\, x\left[\sin\left(\frac{nf-n_i}{2L}\right)\pi x\right) + \cos\left(nf-\frac{n_i}{2L}\right)\pi x\Big]$$

$(nf-n_i) = 1$ → odd

$\therefore (nf-n_i)\pi = \pi$

$\therefore$ ⓐ $= \frac{-1}{\pi}$

similarly ⓑ $\frac{2e}{2L}\int x\left(\cos\left(\frac{nf+n_i}{2L}\pi x\right)dx\right.$

$\left. + \cos\left(\frac{nf+n_i}{2L}\pi x\right)dx\right)$

given $nf-n_i = 1$ (odd)

therefore transition is allowed as

Ti → is non zero

8.4) $\mu_z = \int \psi_1^* \mu_z \psi_1 \, d\tau$.

for transition $(\mu_z)_{12} = \int \psi_1^* \mu_z \psi_2 \, d\tau$.

using transition moment and spherical harmonics.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'*}(\theta,\phi)\, \mu_z\, Y_J^M(\theta,\phi) \sin\theta \, d\phi \, d\theta$$

where $Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$

using $x = \cos\theta$.

$$(\mu_z) = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{i(M-M')\phi} d\phi \int_{-1}^{1} P_{J'}^{|M'|} P_J^{|M|} dx$$

for integral over the function to be non zero we need $M = M'$ or $\Delta M = 0$. integrating over gives us 2π.

$$\therefore (\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|} P^{|M|}_{0} \, dx$$

using the identity

$$(2J+1)\, x\, P_J^{|M|}(x) = (J-|M|+1) P_{J+1}^{|M|}(x) + (J-|M|) P_{J-1}^{|M|}(x)$$

substituting into the integral the integrals vanish unless $J' = J+1$ or $J' = J-1$

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J-|M|+1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J-|M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx$$

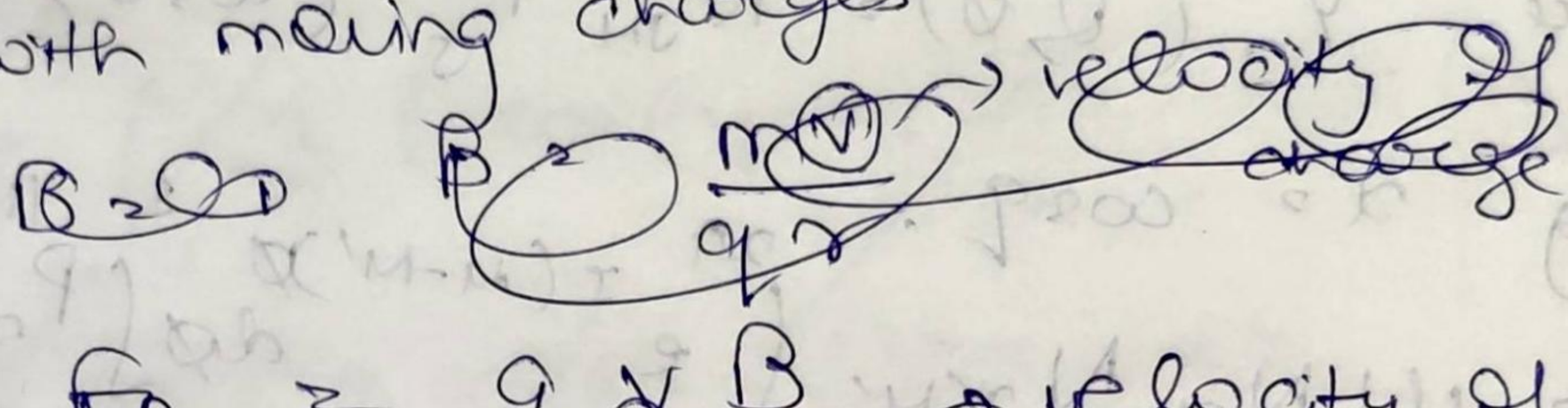
This gets us $\Delta J = \pm 1$ as the selection rule for rigid rotor problem

$\therefore$ $J = 0 \rightarrow J = 1$ $\Delta J = +1$ is allowed while

$J = 0 \rightarrow J = 2$ $\Delta J = +2$ is forbidden

Qs) a) we can ignore the spatial variation of these fields as long as our particle is stationary. we assumed our particle is stationary that's we we need not consider the spatial variations

b) we can ignore the interactions with magnetic fields as the charge is not moving. magnetic field only interacts with moving charges.



$F_B = qvB$ → velocity of charge

83) we have

$$U(R) = De\left[1 - e^{-a(R-R_0)}\right]^2$$

$$F(r) = -\frac{dU}{dR} = -De\left(-a(R-R_0)^2\right)\times$$
$$-a(R-R_0)^2 \times (2(R-R_0))$$

$$F(r) = -k(R-R_0)$$

$$\therefore k = -De\,a(R-R_0)^2$$

$$f(r) = -\frac{dU}{dR} = De\left(2\left(1-e^{-a(R-R_0)}\right)\times\right.$$
$$\left.\left(-(-a)(R-R_0)e^{-a(R-R_0)}\times 1\right)\right)$$

$$F(R) = -k(R-R_0)$$

$$= 2aDe\left(1-e^{-a(R-R_0)}\right)e^{-a(R-R_0)}\left[R-R_0\right]$$

get force constant.

then we get frequency $(w) = \sqrt{k/\mu}$

so we assumed harmonicity.

for anharmonic we will have to take more higher order terms (3rd and 4th power) into consideration and therefore k will change and ultimately ω will change