$$\hat{H}\,\Psi(x,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,t)$$

$$\Psi(x,t) = a_0(t)\,\phi_0(x)\,e^{i\frac{E_0}{\hbar}t} + a_1(t)\,\phi_1(x)\,e^{i\frac{E_1}{\hbar}t}$$

$$\hat{H} = \hat{H}_0 + \hat{H}_s(t)$$

$$\hat{H}_0 \phi_i = E_i \phi_i$$

$$\hat{H}_s(t) = \underset{\sim}{\mu} \cdot \underset{\sim}{E}(t)$$

$$= \underset{\sim}{\mu} \cdot \underset{\sim}{E_0} \cos(\omega t)$$

FIRST APPROXIMATION

$$a_0(t) \simeq 1$$
$$a_1(t) \simeq \frac{h_{10}}{i\hbar} G_{10}(t,0;\omega)$$

THEREFORE THE OCCUPATION PROBABILITY OF THE EXCITED STATE IS GIVEN BY:

$$\boxed{P_1^{(1)}(t,\omega) = \frac{|h_{10}|^2}{\hbar^2} |G_{10}(t,0;\omega)|^2}$$

WITH

$$G_{10}(t,0;\omega) = \int_0^t f_\omega(s)\, e^{i\omega_{10} s}\, ds$$

WHERE

$$f_\omega(s) = \frac{1}{2}\left[e^{i\omega s} + e^{-i\omega s}\right] = \cos(\omega s)$$

$$\hbar\omega = E = h\nu$$
$$\hbar\omega_{10} = E_{10}$$

$$G_{10}(t,0;\omega) = \frac{1}{2i}\left[\frac{e^{i(\omega_{10}+\omega)t} - 1}{\omega_{10}+\omega} + \frac{e^{i(\omega_{10}-\omega)t} - 1}{\omega_{10}-\omega}\right]$$

$$G_{10}(t,0;E) = \frac{\hbar}{2i}\left[\frac{e^{i(E_{10}+E)\frac{t}{\hbar}}-1}{E_{10}+E} + \frac{e^{i(E_{10}-E)\frac{t}{\hbar}}-1}{E_{10}-E}\right]$$

$$(E_{10}+E)\frac{t}{\hbar} = 2\pi(\cancel{1}+x)\frac{E_{10}t}{h}$$

$$= 2\pi(1+x)\frac{t}{(h/E_{10})} = 2\pi(1+x)\tau$$

$$ut \equiv \frac{h}{E_{10}} = \frac{4.\ eV\,fs}{E_{10}} \simeq \frac{4}{3}\frac{eV}{eV}fs$$

$$ut \simeq fs \qquad x = E/E_{10}$$

$$\boxed{G_{10}(\tau,0;x) = \left(\frac{h}{E_{10}}\right)\left(\frac{1}{4\pi i}\right)\left[\frac{e^{i2\pi(1+x)\tau}-1}{1+x} + \frac{e^{i2\pi(1-x)}-1}{1-x}\right]}$$

$$\tau = \frac{t}{ut} \sim \text{time in } fs$$

$$x = \frac{E}{E_{10}}$$

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

$$\hat{H}_0 = \hat{H}_{VIB} + \hat{H}_{ROT}$$

$$E_{n\ell m} = \hbar\omega(\tfrac{1}{2}+n) + \hbar^2 \ell(\ell+1)$$

(I) $H_I^{VIB} \sim \underset{\sim}{E}\cdot\underset{\sim}{\mu} \sim |E_0|\,\mu_x(x)$ VIB

(II) $H_I^{ROT} \sim \underset{\sim}{E}\cdot\underset{\sim}{\mu} \sim |E_0|\,\mu_z(x)$ ROT

<u>TRANSITIONS</u>

$$\langle n'|H_I^{VIB}|n\rangle \quad \text{OR} \quad \langle \ell', m'|H_I^{ROT}|\ell, m'\rangle$$

I) Vibrational

$$h_{10} \equiv \int_{\Omega} \phi_1^*(x) \left(\hat{h}(x)\, \phi_0(x)\right) dx \equiv \langle 1 | \hat{h} | 0 \rangle$$

$$H_f(x,t) = -g\, \underset{\sim}{\mu} \cdot \underset{\sim}{E}(t) = -g\, \underset{\sim}{\mu} \cdot \underset{\sim}{E}_0 \cos(\omega t)$$

$$\boxed{\hat{h}(x)} \equiv g\, \underset{\sim}{\mu} \cdot \underset{\sim}{E}_0 = \underline{\overline{g\, |E_0|\, \mu_x(x)}} \quad \text{if } \underset{\sim}{E}_0 = \hat{\imath}\, |E_0|$$

$$h_{10} = g|E_0| \int_{\Omega} \phi_1^*(x) \left(\mu_x(x)\, \phi_0(x)\right) dx \equiv g|E_0| \langle 1 | \hat{\mu}_x | 0 \rangle$$

$$\mu_x(x) = \mu_x^0 + \left.\frac{d\mu_x}{dx}\right|_0 x + \frac{1}{2} \left.\frac{d^2\mu_x}{dx^2}\right|_0 x^2 + \cdots$$

Transitions

$$\langle n' | \hat{\mu}_x | n \rangle = \mu_x^0 \langle n' | n \rangle + \left.\frac{d\mu_x}{dx}\right|_0 \langle n' | \hat{x} | n \rangle + \frac{1}{2} \left(\left.\frac{d^2\mu_x}{dx^2}\right|_0 \right) \langle n' | \hat{x}^2 | n \rangle + \cdots$$

Permanent dipole $\Rightarrow$ $\mu_x^0 \neq 0$

IF $n' \neq n$ AND $\left.\frac{d\mu_x}{d\lambda}\right|_0 \neq 0$ (SR ACTIVE)

$$\langle n' | n \rangle = 0$$

AND

Vib

$$\langle n' | \hat{x} | n \rangle \neq 0$$

WHERE

$$|n\rangle \sim H_n(x)\, e^{-\frac{\alpha x^2}{2}}$$

We KNOW THAT

$$x H_n(x) \sim a\, H_{n-1}(x) + b\, H_{n+1}(x)$$

THEREFORE

$$\langle n' | \hat{x} | n \rangle \sim a \langle n' | n-1 \rangle + b \langle n' | n+1 \rangle$$

$$\Rightarrow \quad \Delta n' = \pm 1$$

OR

$$n \longrightarrow n+1$$
$$n \longrightarrow n-1$$

ANYTHING ELSE IS FORBIDDEN IN THE HO APPROXIMATION