

## d) General Solution for the Oscillating Perturbation

Similar to spatial functions it can be shown that any periodic function of time  $f(t)$  can be expressed as a sum of oscillating functions.

$$\text{e.g. } f(t) = a_0 + \sum_{i=1}^{\infty} a_i \cos(\omega_i t) \quad = \text{cosine Fourier expansion}$$

$$\text{More general: } f(t) = \sum_{j=1}^{\infty} a_j e^{i\omega_j t} \quad = \text{Fourier expansion}$$

or

any function (as the period goes to infinity)

$$f(t) = \int a(\omega) e^{i\omega t} d\omega \quad = \text{Fourier transform}$$

Thus, if we can solve a simple oscillating perturbation, then in principle we can actually solve the first-order time dependent perturbation theory problem for any periodic perturbation.

Fortunately, the simplest and most significant perturbation for spectroscopy is light = oscillating perturbation

Consider therefore:

$$\begin{aligned}\hat{H}^{(1)}(t) &= 2\hat{H}^{(1)} \cos(\omega t) \\ &= \hat{H}^{(1)}(e^{i\omega t} + e^{-i\omega t})\end{aligned}$$

Then:

$$\begin{aligned}H_{qj}^{(1)}(t) &= \langle \psi_q(\vec{r}) | \hat{H}^{(1)}(e^{i\omega t} + e^{-i\omega t}) | \psi_j(\vec{r}) \rangle \\ &= \langle \psi_q(\vec{r}) | \hat{H}^{(1)} | \psi_j(\vec{r}) \rangle (e^{i\omega t} + e^{-i\omega t}) \\ &= H_{qj}^{(1)}(e^{i\omega t} + e^{-i\omega t})\end{aligned}$$

$$\Rightarrow a_q^{(1)}(t) = -\frac{i}{\hbar} H_{qj}^{(1)} \int_0^t (e^{i\omega t} + e^{-i\omega t}) e^{i\omega_{qj}t} dt$$

So:

$$\begin{aligned}
a_q^{(1)}(t) &= -\frac{i}{\hbar} H_{qj}^{(1)} \int_0^t \left[ e^{i(\omega_{qj} + \omega)t} + e^{i(\omega_{qj} - \omega)t} \right] dt \\
&= -\frac{i}{\hbar} H_{qj}^{(1)} \left[ \frac{e^{i(\omega_{qj} + \omega)t} - 1}{i(\omega_{qj} + \omega)} + \frac{e^{i(\omega_{qj} - \omega)t} - 1}{i(\omega_{qj} - \omega)} \right] \\
&= \frac{H_{qj}^{(1)}}{\hbar} \left[ \frac{1 - e^{i(\omega_{qj} + \omega)t}}{i(\omega_{qj} + \omega)} + \frac{1 - e^{i(\omega_{qj} - \omega)t}}{(\omega_{qj} - \omega)} \right]
\end{aligned}$$

where

$$H_{qj}^{(1)} = \langle \psi_q | \hat{H}^{(1)} | \psi_j \rangle \quad \text{static term}$$

$$\omega_{qj} = \frac{(E_q^{(0)} - E_j^{(0)})}{\hbar}$$

Note:  $0 \leq 1 - e^{i(\omega_{qj} + \omega)t} \leq 1 \quad (\because e^{ix} = \cos(x) + i \sin(x))$

$$\omega_{qj} + \omega \gg 1 \quad \omega \sim 10^6 \text{ s}^{-1} - 10^{15} \text{ s}^{-1}$$

However,  $\omega_{qj} - \omega \rightarrow 0$

Thus, for  $\omega \sim \omega_{qj}$  the first term is small and

$$a_q^{(1)}(t) = \frac{H_{qj}^{(1)}}{\hbar} \left[ \frac{1 - e^{i(\omega_{qj} - \omega)t}}{(\omega_{qj} - \omega)} \right]$$

This describes absorption.

$$\begin{aligned} \therefore P_q(t) &= |a_q^*(t)a_q(t)| \\ &= \frac{H_{jq}^{(1)}H_{qj}^{(1)}}{\hbar^2} \left\{ \frac{1 - e^{-i(\omega_{qj} - \omega)t}}{(\omega_{qj} - \omega)} \cdot \frac{1 - e^{i(\omega_{qj} - \omega)t}}{(\omega_{qj} - \omega)} \right\} \end{aligned}$$

**Note:**  $(1-e^{-ia})(1-e^{ia})=1-e^{-ia}-e^{ia}+1$   
 $=2-[\cos(a)-i\sin(a)]-[\cos(a)+i\sin(a)]=2-2\cos(a)$   
 $=2(1-\cos(a))=2(2\sin^2(a/2))$

$$\Rightarrow P_q(t) = \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} \frac{4 \sin^2\left(\frac{1}{2}(\omega_{qj} - \omega)t\right)}{(\omega_{qj} - \omega)^2}$$

Let  $x = \frac{1}{2}(\omega_{qj} - \omega)t \Rightarrow x^2 = \frac{1}{4}(\omega_{qj} - \omega)^2 t^2 \Rightarrow \frac{4}{(\omega_{qj} - \omega)^2} = \frac{t^2}{x^2}$

$$\therefore P_q(t) = \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} \frac{\sin^2(x)t^2}{x^2}$$

Now: the series expansion for  $\sin(x)$  is:  $\sin(x) = x - \frac{1}{3!}x^3 + \dots$

$$\begin{aligned}
\therefore P_q(t) &= \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} \frac{\left(x - \frac{1}{3!} x^3 + \dots\right)^2 t^2}{x^2} \\
&= \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} \frac{\left(x^2 - O(x^4) + \dots\right)^2 t^2}{x^2} \\
&= \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} \left(t^2 - O(x^2) t^2 + \dots\right) \\
&= \lim_{\substack{x \rightarrow 0 \\ (\text{resonance})}} \frac{|H_{jq}^{(1)} H_{qj}^{(1)}|}{\hbar^2} t^2
\end{aligned}$$

$$\Rightarrow P_q(t) \rightarrow \infty \quad \text{when} \quad t \rightarrow \infty \quad ???!$$

Probabilities can't be  $> 1$  (100%) therefore this result is just an approximation and must be used with caution. The formula can be used to derive selection rules.

**Selection Rules:** The strongest transitions in spectroscopy arise when the electric vector of the light interacts with the dipole moment of the charge distribution of the molecule. This is called the **electric dipole approximation**

Here: 
$$H_{qj}^{(1)} = \frac{1}{2} \langle \psi_q | -e\vec{r} | \psi_j \rangle \vec{E}_o = \frac{1}{2} \vec{\mu}_{qj} \vec{E}_o$$

$\vec{E}_o$  is the amplitude of the electric field vector and  $\vec{\mu}$  is the dipole moment (also a vector).

$$\vec{\mu}_{qj} = \mathbf{0} \leftarrow \text{Electric dipole transition forbidden}$$

$$\neq \mathbf{0} \leftarrow \text{Electric dipole transition allowed}$$