

Module 3 : Nonlinear susceptibilities of materials

Lecture 15 : Optical Response of an Atomic System

Objectives

In this lecture you will learn the following

- Density matrix formulation.
- Perturbation theory for optical response of a quantum system.
- Thermal and non thermal population distribution effects on linear optical response.

Atomic system describe by Hamiltonian H_0

$$H_0 |\alpha\rangle = E_\alpha |\alpha\rangle \quad (15.1)$$

Light- atom interaction has harmonic form

$$H'(t) = \left(H'(\omega) e^{i\omega t} + c.c. \right) e^{\varepsilon t} \quad (15.2)$$

where $e^{\varepsilon t}$ adiabatic switching factor and ε can be absorbed in ω as a small imaginary part. This trick is used to calculate "steady state" response. In physical terms it means we are looking for optical response to pulses for which rise and fall are much slower than are response times in the system.

We use density –matrix formulation, to accommodate mixed state *i.e.* states which are incoherent superposition of several pure states [e.g. a system in thermal equilibrium]

We define a density matrix operator as

$$\hat{\rho} = \sum_n p_n |n\rangle \langle n| \quad (15.3)$$

where p_n is the probability of finding the system in state $|n\rangle$. Note the operator $|n\rangle \langle n|$ is a projection operator which projects the component of any state vector $|\psi\rangle$ which since $|n\rangle \langle n| \psi\rangle$ is the projection of $|\psi\rangle$ along $|n\rangle$

$$\hat{\rho} |m\rangle = p_m |m\rangle \quad (15.4)$$

is a vector along $|m\rangle$ but with amplitude equal to the probability p_m . The density operator satisfies

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [H, \hat{\rho}] \quad (15.5)$$

where H is the Hamiltonian of the system which governs the time evolution of states $|n\rangle$. To see that this equation of motion is consistent with the Schrodinger equation, we note that

$$\begin{aligned} i\hbar \frac{\partial \hat{\rho}}{\partial t} &= i\hbar \sum_n p_n \left\{ \frac{\partial \hat{\rho} |n\rangle}{\partial t} \langle n| + |n\rangle \frac{\partial \hat{\rho} \langle n|}{\partial t} \right\} \\ &= \sum_n p_n \{ |n\rangle \langle n| - |n\rangle \langle n| H \} \\ &= [H, \hat{\rho}] \end{aligned}$$

Expectation value $\langle \theta \rangle$ in a mixed state is given by

$$\begin{aligned}
\sum_n p_n \langle n | \theta | n \rangle &= \text{Tr} [\hat{\rho} \theta] \\
&= \sum_n p_n \langle n | \hat{\rho} \theta | n \rangle \\
&= \sum_{n,m} \langle n | p_m | m \rangle \langle m | \theta | n \rangle \\
&= \sum_n \langle n | \theta | n \rangle p_n
\end{aligned} \tag{15.6}$$

To calculate the perturbative response of the optical field on the atomic system we write a perturbation series in H'

$$\hat{\rho} = \hat{\rho}^{(0)} + \hat{\rho}^{(1)} + \hat{\rho}^{(2)} + \dots \tag{15.7}$$

where the superscript denotes the order of the term in H' . In the unperturbed state, we have

$$i\hbar \frac{\partial \hat{\rho}^{(0)}}{\partial t} = [H_0, \hat{\rho}^{(0)}] \tag{15.8}$$

$$i\hbar \frac{\partial \hat{\rho}^{(1)}}{\partial t} = [H_0, \hat{\rho}^{(1)}] + [H', \hat{\rho}^{(0)}] \tag{15.9}$$

$$\hat{\rho}^{(0)} |\alpha\rangle = p_\alpha |\alpha\rangle \tag{15.10}$$

where $|\alpha\rangle$ are eigen states of H_0 as given by Eq (15.1)

$$i\hbar \frac{\partial}{\partial t} \langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle = (E_\alpha - E_{\alpha'}) \langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle + (p_{\alpha'} - p_\alpha) \langle \alpha | H' | \alpha' \rangle \tag{15.11}$$

This is a linear differential equation for $\langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle$ with an inhomogeneous term composed of two terms- one varying like $e^{-i\omega t}$ and another like $e^{+i\omega t}$. So the solution for $\langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle$ also has two terms. The term varying like $e^{-i\omega t}$ is

$$\langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle_\omega = \frac{p_{\alpha'} - p_\alpha}{\hbar\omega - (E_\alpha - E_{\alpha'})} \langle \alpha | H'(\omega) | \alpha' \rangle \tag{15.12}$$

It is convenient to write

$$E_{\alpha\alpha'} \equiv E_\alpha - E_{\alpha'} = \hbar\omega_{\alpha\alpha'} \tag{15.13}$$

$$H'_{\alpha\alpha'}(\omega) = \langle \alpha | H'(\omega) | \alpha' \rangle \tag{15.14}$$

and

$$\hat{\rho}_{\alpha\alpha'}^{(1)}(\omega) = \langle \alpha | \hat{\rho}^{(1)} | \alpha' \rangle_\omega = \frac{p_{\alpha'} - p_\alpha}{\hbar\omega - E_{\alpha\alpha'}} H'_{\alpha\alpha'}(\omega) \tag{15.16}$$

For atoms or molecules where the polarizable units are much smaller than the wave length of light, the interaction Hamiltonian is limited to the electric dipole term

$$H'_{\alpha\alpha'}(\omega) = -\vec{d} \cdot \vec{E}(\omega) \tag{15.17}$$

where $\vec{d} = \sum_i \vec{q}_i \vec{r}_i$ (i runs over all particles) is the electric dipole operator.

Now, the induced polarization density (dipole moment per unit value), oscillating at frequency ω is given by the expectation value of \vec{d} for a polarization unit (atom, molecule, bond....) multiplied by the density of such units.

Thus, the polarization, (induced dipole moment per unit volume) is given by

$$\begin{aligned}\vec{P}(\omega) &= N \langle \vec{d} \rangle_{(\omega)} \\ &= N \text{Tr}(\hat{\rho}(\omega) \vec{d}) \\ &= N \sum_{\alpha' \alpha} \rho_{\alpha \alpha'}(\omega) \vec{d}_{\alpha' \alpha}\end{aligned}\quad (15.18)$$

where $\vec{d}_{\alpha' \alpha} = \langle \alpha | \vec{d} | \alpha' \rangle$, N is the density of polarizable units and angular bracket denotes expectation value.

$P^i(\omega)$, the i th component of $\vec{P}(\omega)$ is given by

$$P^i(\omega) = -N \sum_{\alpha \alpha'} \frac{p_{\alpha'} - p_{\alpha}}{\hbar \omega - E_{\alpha \alpha'}} d_{\alpha \alpha'}^j d_{\alpha' \alpha}^i \quad (15.19)$$

If we denote, as before, the proportionality factor between polarization and field $\chi_{ij}(\omega)$ the linear susceptibility tensor:

$$P^i(\omega) = \chi_{ij}(\omega) E^j(\omega). \quad (15.20)$$

then

$$\chi_{ij}(\omega) = N \sum_{\alpha \alpha'} \frac{p_{\alpha'} - p_{\alpha}}{E_{\alpha \alpha'} - \hbar \omega} d_{\alpha \alpha'}^j d_{\alpha' \alpha}^i \quad (15.21)$$

Recall that inclusion of adiabatic switching factor makes all frequencies complex we write $\omega \rightarrow \omega + i\varepsilon$

$$\frac{1}{E_{\alpha \alpha'} - \hbar \omega} \rightarrow \frac{(E_{\alpha \alpha'} - \hbar \omega)}{(E_{\alpha \alpha'} - \hbar \omega)^2 + \varepsilon^2} + \frac{i\varepsilon}{(E_{\alpha \alpha'} - \hbar \omega)^2 + \varepsilon^2}$$

In isotropic media χ_{ij} has only diagonal elements. Then, the real and imaginary parts of χ_{ii} corresponding to the first and second factors in this energy denominator are:

$$\text{Im}(\chi_{ij}(\omega)) = N \sum_{\alpha \alpha'} (p_{\alpha'} - p_{\alpha}) d_{\alpha \alpha'}^j d_{\alpha' \alpha}^i \cdot \frac{\varepsilon}{(E_{\alpha \alpha'} - \hbar \omega)^2 + \varepsilon^2} \quad (15.22)$$

$$\text{Re}(\chi_{ij}(\omega)) = N \sum_{\alpha \alpha'} (p_{\alpha'} - p_{\alpha}) d_{\alpha \alpha'}^j d_{\alpha' \alpha}^i \cdot \frac{E_{\alpha \alpha'} - \hbar \omega}{(E_{\alpha \alpha'} - \hbar \omega)^2 + \varepsilon^2} \quad (15.23)$$

We note that the adiabatic switching factor serves to dampen the resonances. In real systems there are a variety of relaxation mechanisms. To account for these a damping term is introduced in the Liouville's equation which is now modified to

$$i\hbar \frac{d\hat{\rho}}{dt} = [H, \hat{\rho}] - i\hbar \Gamma \hat{\rho} \quad (15.24)$$

where Γ denotes the damping or dissipation operator. It describes the interaction of the system with the perturbing environment. For example, when H_0 describes the motion of electrons in a solid the damping term describes the relaxation due to interaction of electrons with phonons and defects and impurities. In this case, the susceptibility tensor becomes

$$\chi_{ij}(\omega) = N \sum_{\alpha \alpha'} \frac{p_{\alpha'} - p_{\alpha}}{E_{\alpha \alpha'} - \hbar \omega - i\hbar \Gamma_{\alpha \alpha'}} d_{\alpha \alpha'}^j d_{\alpha' \alpha}^i \quad (15.25)$$

In thermal equilibrium, a lower energy state has a higher probability of occupation i.e. $p_u < p_l$ with

$E_u > E_l$ where the indices u and l refer to upper and lower energy levels

Then, the corresponding term in

$$\text{Im} \chi_{ij}(\omega) > 0$$

which corresponds to absorption or attenuation of the incident wave. When population inversion

between two levels u, i exists $p_u < p_i$ with $E_u > E_i$.

The corresponding contribution to

$$\text{Im } \chi_{ij}(\omega) < 0$$

and an incident wave at ω will show exponential gain growth.

At room temperature kT is much smaller than the electronic energy separations, so that levels other than the ground state are all empty. Such a system would show absorption only from ground state. However, at higher temperature such higher state get populated and can also contribute to absorption /emission spectra.

Recap

In this lecture you have learnt the following

- Density matrix formulation introduced to describe systems interacting with environment.
- Linear response calculated.
- Imaginary part of susceptibility peaks when photon energy matches a transition energy in the system.
- Real and imaginary parts of susceptibility are related.