

Module 3 : Nonlinear susceptibilities of materials

Lecture 16 : Nonlinear Optical Susceptibilities

Objectives

In this lecture you will learn the following

- Quantum mechanical expressions are derived for nonlinear optical susceptibilities.

We have seen earlier that second order nonlinear susceptibilities play an important role in determining the efficiencies of nonlinear frequency conversion devices. In the early days of nonlinear optics formal expressions were derived for nonlinear response of materials. In this lecture we derive formal expressions for $\chi^{(2)}$ and $\chi^{(3)}$ and discuss their relationship to transitions in an atomic or molecular system. We do this by extending the calculations of the previous lecture 15 to the nonlinear case. We start with the equation of motion for the density matrix $\hat{\rho}$.

$$i\hbar \frac{d\hat{\rho}}{dt} = [H, \hat{\rho}] - i\hbar\Gamma\hat{\rho} \quad (16.1)$$

where $i\hbar\Gamma\hat{\rho}$ is the phenomenological relaxation term which represents the interaction of the quantum system with the "environment" which is a euphemism for all interactions not included in the Hamiltonian. Since frequency mixing is anticipated we now write the field to contain a number of frequencies:

$$H'(t) = \sum_i H'(\omega_i) e^{i\omega_i t} \quad (16.2)$$

where, as mentioned in earlier lectures, the sum extends over positive as well as negative frequencies. As before, the expansion for the density matrix is

$$\hat{\rho} = \hat{\rho}^{(0)} + \hat{\rho}^{(1)} + \hat{\rho}^{(2)} + \dots \quad (16.3)$$

and we take each to have a Fourier decomposition like eq (16.2)

$$\hat{\rho}^{(n)}(t) = \sum_i \hat{\rho}^{(n)}(\omega_i) e^{-i\omega_i t} \quad (16.4)$$

we obtain equations of motion for successive orders in the perturbation series:

$$i\hbar \frac{\partial \hat{\rho}^{(1)}}{\partial t} - [H_0, \hat{\rho}^{(1)}] - i\hbar\Gamma\hat{\rho}^{(1)} = [H', \hat{\rho}^{(0)}], \quad (16.5)$$

in first order. In the second order, we obtain

$$i\hbar \frac{\partial \hat{\rho}^{(2)}}{\partial t} - [H_0, \hat{\rho}^{(2)}] - i\hbar\Gamma\hat{\rho}^{(2)} = [H', \hat{\rho}^{(1)}] \quad (16.6)$$

and similarly in the n^{th} order

$$i\hbar \frac{\partial \hat{\rho}^{(n)}}{\partial t} - [H_0, \hat{\rho}^{(n)}] - i\hbar\Gamma\hat{\rho}^{(n)} = [H', \hat{\rho}^{(n-1)}] \quad (16.7)$$

In each order, the left hand side is linear in the unknown $\hat{\rho}^{(n)}$ while the right hand side has quantities obtained in the previous order. So the equations can be solved successively. The first order solutions were already given in the previous lecture and can be written as follows in a shortened notation

$$\rho_{rs}^{(1)}(\omega_\lambda) = H'_{rs}(\omega_\lambda)(\rho_{ss}^{(0)} - \rho_{rr}^{(0)}) / D_r(\omega_\lambda) \quad (16.8)$$

where the denominator $D_{rs}(\omega)$ is given by

$$D_{rs}(\omega) = E_r - E_s - \hbar\omega - i\hbar\Gamma_{rs} \quad (16.9)$$

with Γ_{rs} representing the broadening parameter for the transition between levels r and s . In the second order, we obtain from eq (16.6)

$$\begin{aligned} \rho_{iu}^{(2)}(\omega_i + \omega_j) = & \frac{1}{D_{iu}(\omega_i + \omega_j)} \sum_r (H'_{ir}(\omega_i) H'_{ru}(\omega_j) \frac{(\rho_{uu}^{(0)} - \rho_{rr}^{(0)})}{D_{ru}(\omega_i)} + \\ & H'_{ir}(\omega_i) H'_{ru}(\omega_j) \frac{(\rho_{rr}^{(0)} - \rho_{ii}^{(0)})}{D_{ir}(\omega_j)} + \text{terms obtained by exchanging indices } i \text{ and } j) \end{aligned} \quad (16.10)$$

Similarly, we obtain an expression for the third order contribution to the density matrix.

The n^{th} order contribution to the polarization is obtained by using the standard form for the expectation value

$$\vec{P}^{(n)} = N \text{Tr}(\vec{d} \rho^{(n)}) \quad (16.11)$$

where, N denotes the density of molecules, \vec{d} denotes the electric dipole operator and Tr denote the trace or sum of diagonal matrix elements of a dynamical variable, here the product $\vec{d} \rho^{(n)}$.

The polarizations in order is related to the susceptibility tensor by equation (8.10). We obtain:

$$\epsilon_0 \chi_{\mu\alpha}^{(1)}(\omega) = N \sum_{i,j} \left(\frac{d_{\mu,ij} d_{\alpha,ji}}{\hbar(\omega_{ji} + \omega - i\Gamma_{ij})} - \frac{d_{\alpha,ij} d_{\mu,ji}}{\hbar(\omega_{ji} - \omega + i\Gamma_{ij})} \right) \quad (16.12)$$

for the linear susceptibility. Here $d_{\mu,ij} = \langle i | d_{\mu} | j \rangle$ is the matrix element of the electric dipole operator in the states $|i\rangle$ and $|j\rangle$.

Note here that the second term is obtained by interchanging the indices i and j . So in the summation there are no terms corresponding to both states being occupied or both states being empty. The second order susceptibility is given by

$$\begin{aligned} \epsilon_0 \chi_{\mu\alpha\beta}^{(2)}(\omega_\alpha, \omega_\beta) = & NP(\alpha, \beta) \sum_{i,j} \rho_{ii}^{(0)} \left(\frac{d_{\mu,ij} d_{\alpha,jk} d_{\beta,ki}}{D_{ji}(\omega_\alpha + \omega_\beta) D_{ki}(\omega_\beta)} \right) \\ & - \frac{d_{\beta,ij} d_{\mu,jk} d_{\alpha,ki}}{D_{jk}(\omega_\alpha + \omega_\beta) D_{ik}(\omega_\beta)} \\ & - \frac{d_{\alpha,ij} d_{\mu,jk} d_{\beta,ki}}{D_{jk}(\omega_\alpha + \omega_\beta) D_{ji}(\omega_\beta)} \\ & - \frac{d_{\mu,ij} d_{\alpha,jk} d_{\beta,ki}}{D_{ij}(\omega_\alpha + \omega_\beta) D_{ik}(\omega_\beta)} \end{aligned} \quad (16.13)$$

where the symbol $P(\alpha, \beta)$ means that terms obtained by permutations of distinct frequencies have to be added.

Similarly, one can obtain higher order susceptibilities.

Away from resonances the damping can be neglected. The expression for the second order susceptibility simplifies to:

$$\epsilon_0 \chi_{\mu\alpha\beta}^{(2)}(\omega_\alpha, \omega_\beta) = NP(\alpha, \beta) \sum_{i,j} \rho_{ii}^{(0)} \left(\begin{aligned} & \frac{d_{\mu,ij} d_{\alpha,jk} d_{\beta,ki}}{\hbar^2 (\omega_{ji} + \omega_\alpha + \omega_\beta)(\omega_{ki} + \omega_\beta)} \\ & + \frac{d_{\beta,ij} d_{\alpha,jk} d_{\mu,ki}}{\hbar^2 (\omega_{ji} - \omega_\alpha - \omega_\beta)(\omega_{ki} - \omega_\alpha)} \\ & + \frac{d_{\alpha,ij} d_{\mu,jk} d_{\beta,ki}}{\hbar^2 (\omega_{ki} - \omega_\alpha)(\omega_{ji} + \omega_\beta)} \end{aligned} \right) \quad (16.14)$$

Higher order calculations proceed in the same way and produce longer expressions. This appears a bit tedious but the picture that emerges is profound and easy to understand. Infact, a very compact form for nth order susceptibility can be written as

$$\epsilon_0 \chi_{\mu\alpha_1\alpha_2\ldots\alpha_n}^{(2)}(-\omega_\mu, \omega_1, \ldots, \omega_n) = (N/n!) \sum_{\text{all permutations}} P(-\omega_\mu, \omega_1, \ldots, \omega_n) \sum_{i,j,\ldots,n} \rho_{ii}^{(0)} \left(\frac{d_{\mu,ij} d_{\alpha_1,jk} \ldots d_{\alpha_n,ni}}{\hbar^n (\omega_{ji} - \omega_1 - \ldots - \omega_n)(\omega_{ji} - \omega_2 - \omega_n) \ldots (\omega_{ni} - \omega_n)} \right)$$

This has the interpretation that nth order response involves n+1 virtual electric dipole transitions from initial state i back to the state i . Corresponding to each such virtual transition a dipole matrix element there is a corresponding dipole matrix element in the numerator and an energy denominator in the denominator. Since, different frequency fields can be combined in any order to produce the same frequency we need to add all such amplitudes.

- For example, the term

$$\frac{d_{\mu,ij} d_{\alpha,jk} d_{\beta,ki}}{\hbar^2 (\omega_{ji} - \omega_\alpha - \omega_\beta)(\omega_{ki} - \omega_\beta)}$$

- in $\chi^{(2)}$ corresponds to a virtual transition from state i to state j by an electric dipole transition by a field at frequency ω_β polarized in direction β , followed by a transition from state k to j by a field at ω_α and finally a deexcitation of the state j back to i emitting a field at frequency $\omega_\alpha + \omega_\beta$.
- when one of the energy denominators goes to zero we hit a resonance. Then it is important to include the damping terms and this simple form is not sufficient. It is tempting to follow the prescription from linear response theory

where in we replace $\frac{1}{(\omega_{ki} - \omega_\beta)}$ by $\frac{1}{(\omega_{ki} - \omega_\beta - i\gamma)}$ which produces a Lorentzian peak in the

imaginary part of susceptibility. The problem with this prescription is that in the nonlinear response two denominators can simultaneously go to zero. Then one can get new structures in the susceptibilities. More important it can give resonances between two unoccupied states. We will illustrate this in different experimental situations in later lectures.

- with the availability of modern computers their evaluation is easy if we know all the eigen states of the system. Of course, we generally do not! That is why very accurate calculations have not had a very significant impact on nonlinear materials.
- On the other hand, nonlinear response often is more sensitive to certain features in the eigen states and therefore provides more stringent test of our understanding of a system.
- There are additional resonances in nonlinear response. A study of these resonances gives rise to a very significant enhancement to spectroscopy.
- A somewhat subtle point is that a nonlinear response can see resonances between two occupied levels or two empty levels.
- The symmetry relations discussed earlier are built in the expressions. For example, for systems with inversion symmetry $\chi_{\mu\alpha\beta}^{(2)}(\omega_\alpha, \omega_\beta)$ vanishes because the product of matrix elements

$d_{\mu,ij} d_{\alpha,jk} d_{\beta,ki}$ vanishes because for such systems the eigen states can be chosen to be eigen states of parity operator i.e. every state satisfies $\psi(-\vec{r}) = \pm \psi(\vec{r})$ dipole operator has nonzero matrix elements only between states of opposite parity.

In the next two lectures we describe simple model calculations of susceptibilities of various materials.

Recap

In this lecture you have learnt the following

- Expressions for nonlinear susceptibilities are obtained by perturbation theory.
- Some of the key features of these expressions are discussed.