

## 12. Quantum-classical theory of linear and non-linear spectroscopy

In the quantum-classical formalism, we treat the electric field classically as in eq. 10-17 or Appendix B. The electric field becomes a time-dependent external perturbation, and can be treated by perturbation theory. Photons are absent from this formalism.

Here we expand the treatment to arbitrary interactions with multi-level molecules. We will proceed by expanding the total density matrix in a perturbation series. In lowest order, absorption and stimulated emission are predicted. In higher orders, multiphoton processes or multi-quantum coherences can be calculated, including optical effects such as coherent anti-Stokes Raman scattering, degenerate four wave mixing, or harmonic generation.

Before dealing with the density matrix expansion, we discuss the Hamiltonian, develop a few more properties of the wave equation for electric fields by introducing the polarization and molecular susceptibility, and derive formulas for the absorption coefficient and refractive index in terms of molecular parameters. We then derive general formulas for any  $n^{\text{th}}$  order absorption/emission/scattering experiment in terms of the  $n^{\text{th}}$  order molecular susceptibility  $\chi_{ij\dots}^{(n)}$ . Finally, the density matrix expansion is a general way of obtaining  $\chi_{ij\dots}^{(n)}$ .

### 12.1 Hamiltonian and limitations

In the quantum-classical approximation, the molecule is treated quantum-mechanically, and the field classically. Furthermore, we will use the electric dipole approximation and neglect  $H^{(2)}$  as well as any magnetic field effects. This can still accurately predict one- and higher-order photon processes not involving spontaneous effects such as spontaneous emission or spontaneous Raman scattering. Spontaneous emission can be reintroduced by an *ad-hoc* modification of the molecular susceptibility. The Hamiltonian becomes

$$H_{tot} = H_{mol} + H^{(1)}(t) = H_{mol} - \boldsymbol{\mu}_{mol} \cdot \mathbf{E}(t), \quad 12-1$$

where the quantized expression  $\sum_{\mathbf{k}\lambda} \langle N' | E_{\mathbf{k}\lambda} | N \rangle \hat{e}_{\mathbf{k}\lambda}$  has simply been replaced by the time-dependent electric field.

### 12.2 Fourier expansion of the field and power series expansion of the polarization.

It will be convenient to represent the electric field in both the frequency and time domains. For a monochromatic wave,

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_c \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) + \mathbf{E}_s \sin(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad 12-2$$

If many frequency components are involved,  $\mathbf{E}(t)$  can be expressed in terms of a Fourier integral:

$$\begin{aligned} \mathbf{E}(\mathbf{r},t) &= \int_0^{\infty} d\omega \int_{-\infty}^{\infty} d\mathbf{k} (\mathbf{E}_c \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) + \mathbf{E}_s \sin(\mathbf{k} \cdot \mathbf{r} - \omega t)) \\ &= \int_0^{\infty} d\omega \int_{-\infty}^{\infty} d\mathbf{k} (\mathbf{E}_c \frac{1}{2} \{ e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \} + \mathbf{E}_s \frac{1}{2i} \{ e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} - e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \}) \\ &= \int_0^{\infty} d\omega \int_{-\infty}^{\infty} d\mathbf{k} (\frac{\mathbf{E}_c}{2} + \frac{\mathbf{E}_s}{2i}) e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + \int_0^{\infty} d\omega \int_{-\infty}^{\infty} d\mathbf{k} (\frac{\mathbf{E}_c}{2} - \frac{\mathbf{E}_s}{2i}) e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \end{aligned} \quad 12-3$$

where the triple integral over  $d\mathbf{k} = dk_x dk_y dk_z$  has been symbolized by a single integration sign. Letting

$$\mathbf{k} \rightarrow -\mathbf{k} \text{ and } \omega \rightarrow -\omega \text{ so the second integration is over } \int_{-\infty}^0 d\omega \int_{-\infty}^{\infty} d\mathbf{k}, \quad 12-4$$

one obtains

$$\mathbf{E}(\mathbf{r}, t) = \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\mathbf{k}^3 \mathbf{E}(\mathbf{k}, \omega) e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t} \text{ where } \mathbf{E}(-\mathbf{k}, -\omega) = \mathbf{E}^*(\mathbf{k}, \omega) \text{ so } \mathbf{E}(t) \text{ is real.} \quad 12-5$$

$\mathbf{E}(\mathbf{k}, \omega)$ , represents the electric field as a function of propagation direction and frequency. Note that both positive and negative frequencies are allowed in the Fourier-transform expression because  $\exp[-i\omega t]$  is complex.

Consider now the wave equation for  $\mathbf{E}(\mathbf{r}, t)$  derived in section 2:

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E}(\mathbf{r}, t) = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}(\mathbf{r}, t). \quad 12-6$$

$\mathbf{P}$  is a time varying dipole located in the space that  $\mathbf{E}$  is passing through.  $\mathbf{P}$  can act as a source (emission) or sink (absorption) for the field. For a dilute macroscopic sample of molecules such as a gas,  $\mathbf{P}$  is just the sum of all the molecular time-dependent dipole moments:  $\mathbf{P} = \sum \boldsymbol{\mu}_i(t)$ . For a dense liquid or solid,  $\mathbf{P}$  is the overall macroscopic dipole moment, which depends on intermolecular properties as well. Fourier transforming only with respect to  $t$ , and using  $\partial/\partial t \rightarrow -i\omega$ , it follows that

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) - \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}, \omega) = +\frac{4\pi\omega^2}{c^2} \mathbf{P}(\mathbf{r}, \omega) \quad 12-7$$

or

$$-\nabla^2 \mathbf{E}(\mathbf{r}, \omega) - \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}, \omega) = +\frac{4\pi\omega^2}{c^2} \mathbf{P}(\mathbf{r}, \omega) \quad 12-8$$

for a plane wave. Clearly, this equation is completely local in  $\boldsymbol{\omega}$ .  $\mathbf{E}$  can interact with the polarizability (or dipole density) only at the same frequency. For example,  $\mathbf{E}(\boldsymbol{\omega})$  can only be absorbed by molecules with a component of  $\mathbf{P}$  at  $\boldsymbol{\omega}$ . In what follows, we will generally suppress both  $\mathbf{k}$  and  $\mathbf{r}$  for simplicity; the same Fourier-transform relationships as between  $\omega$  and  $t$  hold for them also. By not explicitly treating  $\mathbf{k}$  or  $\mathbf{r}$ , the resulting formulas will not be applicable to spatially inhomogeneous samples or for phase-matching calculations.

Due to the locality of eq. 12-8, we can expand  $\mathbf{P}(\boldsymbol{\omega})$  in a power series in  $\mathbf{E}(\boldsymbol{\omega})$ :

$$\begin{aligned} \mathbf{P}(\boldsymbol{\omega}) &= \mathbf{P}^{(0)}(\boldsymbol{\omega}) + \mathbf{P}^{(1)}(\boldsymbol{\omega}) + \mathbf{P}^{(2)}(\boldsymbol{\omega}) + \dots \\ &= \chi^{(0)}(\boldsymbol{\omega}) + \chi^{(1)}(\boldsymbol{\omega}) \cdot \mathbf{E}(\boldsymbol{\omega}) + \chi^{(2)}(\boldsymbol{\omega} = \boldsymbol{\omega}_1 + \boldsymbol{\omega}_2): \mathbf{E}(\boldsymbol{\omega}_1) \mathbf{E}(\boldsymbol{\omega}_2) \\ &\quad + \chi^{(3)}(\boldsymbol{\omega} = \boldsymbol{\omega}_1 + \boldsymbol{\omega}_2 + \boldsymbol{\omega}_3): \mathbf{E}(\boldsymbol{\omega}_1) \mathbf{E}(\boldsymbol{\omega}_2) \mathbf{E}(\boldsymbol{\omega}_3) + \dots \end{aligned} \quad 12-9$$

The coefficients  $\chi^{(n)}$  are the molecular susceptibility tensors of  $n^{\text{th}}$  order and contain all the dependence of  $\mathbf{P}$  on molecular properties. Since the electric fields are vectors, and the resulting  $\mathbf{P}$  must also be a vector, for  $n=0$   $\chi$  is a vector, for  $n=1$  it is a matrix, for  $n=2$  it is a third rank tensor, and so forth. In the higher order terms, the frequencies of the fields must add up exactly to the frequency  $\omega$ , since a product of harmonic waves only contains frequency components at the various sums and differences of the individual frequencies (e.g.  $\cos(\omega_1 t) \cos(\omega_2 t) = \{\cos([\omega_1 + \omega_2]t) + \cos([\omega_1 - \omega_2]t)\}/2$ . Tensor products of higher order than "matrix times vector" are indicated by a ":" symbol. Figs. 12-9 and 12-11 later on will provide a pictorial description of eq. 12-9

The first term in eq. 12-9 is usually zero. For example, for a dilute gas of randomly oriented rotating molecules, each individual vector  $\boldsymbol{\mu}(t)$  will rotate and be nonzero, but the sum over all  $\boldsymbol{\mu}(t)$  will be macroscopically negligible. There are exceptions such as electrets, which have macroscopic dipole moments. An example would be a quartz crystal, which becomes charged at

its ends when subjected to pressure. In general, all electric fields with  $\Sigma\omega_i=\omega$  can contribute to a given order, so one should let

$$\mathbf{P}(\omega) = \chi^{(0)}(\omega) + \chi^{(1)}(\omega)\mathbf{E}(\omega) + \int_0^{\infty} \int_0^{\infty} d\omega_1 d\omega_2 \delta(\omega - \omega_1 - \omega_2) \chi^{(2)}(\omega = \omega_1 + \omega_2) \mathbf{E}(\omega_1) \mathbf{E}(\omega_2) + \dots \quad 12-10$$

We will use the simpler expansion in eq. 12-9 to avoid additional integrals in the derivations.  $\mathbf{P}(\omega)$  and  $\chi(\omega)$  are related to  $\mathbf{P}(t)$  and  $\chi(t)$  by Fourier transform also, since  $\mathbf{P}(\omega)$  was obtained from  $\mathbf{P}(t)$  by Fourier transforming equation 12-6, and  $\chi^{(n)}(\omega)$  and  $\mathbf{P}^{(n)}(\omega)$  are linearly related in eq. 12-9:

$$P^{(n)}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega P^{(n)}(\omega) e^{-i\omega t} \quad 12-11$$

$$\chi^{(n)}(t_1 \dots t_n) = \frac{1}{(2\pi)^n} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} d\omega_1 \dots d\omega_n e^{-i(\omega t_1 + \dots + \omega_n t_n)} \chi^{(n)}(\omega = \omega_1 + \omega_2 \dots \omega_n) \quad 12-12$$

$\chi(t)$  depends on a several time variables since  $\chi(\omega)$  depends on several frequencies  $\omega_1, \omega_2, \dots$  and the two are related by a multiple Fourier transform. Note that because of eq. 12-9,  $\mathbf{P}(\omega)$  and  $\chi^{(n)}(\omega)$ , just like  $\mathbf{E}(\omega)$ , can be complex. On the other hand, since  $\mathbf{E}(t)$  is real,  $\mathbf{P}(t)$  and  $\chi^{(n)}(t)$  must also be real due to eqs. 12-8 and 12-9. Therefore we again have

$$\mathbf{P}(-\omega) = \mathbf{P}^*(\omega) \text{ and } \chi(-\omega) = \chi^*(\omega). \quad 12-13$$

This is equivalent to requiring that the real parts of  $\mathbf{P}$  and  $\chi$  must be even functions, and that their imaginary parts must be odd functions.

There should be an expression analogous to eq. 12-10 in the time domain. From the convolution theorem in appendix A, eq. 12-10 is the Fourier transform of

$$\mathbf{P}^{(n)}(t) = \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \chi^{(n)}(t_1 \dots t_n) \mathbf{E}(t - t_1 - t_2 \dots - t_n) \dots \mathbf{E}(t - t_n) \quad 12-14$$

In particular, the linear response of the polarization is given by

$$P^{(1)}(t) = \int_{-\infty}^{\infty} dt' \chi^{(1)}(t') \mathbf{E}(t - t') \quad 12-15$$

For positive values of  $t'$ ,  $\mathbf{P}(t)$  clearly depends on the past history of the electric field it interacts with. For negative  $t'$ ,  $\mathbf{P}(t)$  would depend on the future of the electric field. This would violate the causality principle, so  $\chi(t') = 0$  if  $t' < 0$ .

### 12.3 Computing the refractive index, dielectric constant, and absorption coefficient from $\chi$

Once  $\chi$  is known, one can solve any spectroscopy problem except those involving spontaneous emission in the quantum-classical approximation: insert eq. 12-14 into eq. 12-6 (time domain), or insert eq. 12-10 into eq. 12-8 (frequency domain) to eliminate  $\mathbf{P}$  and solve for  $\mathbf{E}$ . In section f), a general density matrix formalism for  $\chi$  will be derived.

As an example of how any spectroscopic quantity can be expressed in terms of  $\chi$ , we truncate the susceptibility at first order such that  $\mathbf{P}$  depends linearly on  $\mathbf{E}$ . This approximation is valid for low field intensities, such that higher powers of  $\mathbf{E}$  in eq. 12-14 are small. It allows one to express the refractive index  $n$ , dielectric constant  $\epsilon$ , and absorption coefficient  $\alpha$  to lowest order as functions of  $\chi$ .

Inserting the  $\chi^{(1)}$  part of eq. 12-10 into the wave equation 12-8,

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) - \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}, \omega) = \frac{\omega^2}{c^2} 4\pi\chi^{(1)}(\omega) \cdot \mathbf{E}(\mathbf{r}, \omega) \quad 12-16$$

and thus

$$\left\{ \nabla \times \nabla \times - \frac{\omega^2}{c^2} [I + 4\pi\chi^{(1)}(\omega)] \right\} \mathbf{E}(\mathbf{r}, \omega) = 0 \quad 12-17$$

where I is the identity matrix. For simplicity, assume that  $\chi$  is independent of polarization and coordinate  $\mathbf{r}$  on a length scale of the wavelength, i.e. corresponds to a homogeneous molecular ensemble such as a gas or liquid. In that case,  $\chi$  is a multiple of the identity matrix with three equal diagonal elements  $\chi^{(1)}(\omega)$ .

In an isotropic medium, we can also take  $\mathbf{k}$  along the z-axis, and  $\mathbf{E} = E\hat{\mathbf{i}}$  as x-polarized. As the wave propagates along the z direction it may be amplified or attenuated, but will not change in the x or y directions, so  $\partial E/\partial x = \partial E/\partial y = 0$ . The cross products in eq. 12-17 therefore become

$$\nabla \times \mathbf{E} = \begin{pmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ E & 0 & 0 \end{pmatrix} = \frac{\partial E}{\partial z} \hat{\mathbf{j}} \quad \text{and} \quad \nabla \times \nabla \times \mathbf{E} = \begin{pmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ 0 & \partial E/\partial z & 0 \end{pmatrix} = -\frac{\partial^2 E}{\partial z^2} \hat{\mathbf{i}}. \quad 12-18$$

and eq. 12-17 can be rewritten as

$$\frac{\partial^2}{\partial z^2} E(z, \omega) + \frac{\omega^2}{c^2} (1 + 4\pi\chi^{(1)}(\omega)) E(z, \omega) = 0 \quad 12-19$$

The solution of this equation is given by

$$E(z, \omega) = E(\omega) e^{ikz}, \quad 12-20$$

as can easily be verified by insertion into 12-19 with

$$k = \omega \frac{(1 + 4\pi\chi^{(1)}(\omega))^{1/2}}{c} \quad 12-21$$

$$= \omega \frac{n(\omega)}{c} = \omega \frac{\epsilon^{1/2}(\omega)}{c} = \frac{\omega}{c_{local}}. \quad 12-22$$

This is a plane monochromatic wave propagating in the z direction. In order for  $\mathbf{E}(\mathbf{r}, t)$  to be real after Fourier transforming 12-20, it must also be true that

$$E(z, -\omega) = E^*(\omega) e^{-ik^*z} \quad 12-23$$

holds for the negative frequency component of the complex field amplitude, as noted after eq. 12-5. This is indeed satisfied by the k in eq. 12-21 due to eq. 12-13.

Eq. 12-22 defines the values of the refractive index  $n(\omega)$  and the dielectric constant  $\epsilon(\omega)$  in terms of the molecular linear susceptibility  $\chi$ . The refractive index is defined as usual as the ratio between the vacuum and local speeds of light. Thus, the speed of light through a molecular medium can be calculated once the susceptibility  $\chi$  is known.

$\chi^{(1)}(\omega)$  is generally a complex quantity, and therefore we can write k as

$$\begin{aligned} k &= \frac{\omega}{c} [1 + 4\pi\chi_r^{(1)}(\omega) + 4\pi i\chi_i^{(1)}(\omega)]^{1/2} = \frac{\omega}{c} [1 + 2\pi\chi_r^{(1)}(\omega) + 2\pi i\chi_i^{(1)}(\omega)] \\ &= \frac{\omega}{c} n_r(\omega) + 2\pi \frac{\omega}{c} i\chi_i^{(1)}(\omega). \end{aligned} \quad 12-25$$

Inserting eq. 12-25 into the electric field eq. 12-20,

$$E(z, \omega) = E(\omega) e^{\frac{i \sin(\omega) z}{c} - \frac{2\pi \omega}{c} \chi_i^{(1)}(\omega) z} \quad 12-26$$

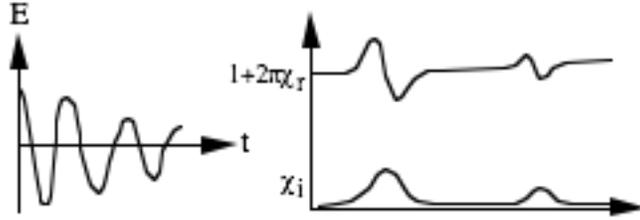


Fig. 12-1. Electric field as a function of  $z$  for positive  $\chi_i$ , and real and ima-

For a plane electromagnetic wave in an isotropic medium of index  $n$ ,  $u=(\mathbf{E}\mathbf{D}+\mathbf{B}\mathbf{H})/8\pi=n^2|\mathbf{E}|^2/8\pi$ ,  $v=c/n$  and  $I=uv$  is therefore  $nc|\mathbf{E}|^2/4\pi$ . Taking into account  $\pm\omega$  components,

$$\begin{aligned} I &= nc |\mathbf{E}(\omega)|^2/4\pi + nc |\mathbf{E}(-\omega)|^2/4\pi \\ &= nc \mathbf{E}(\mathbf{r},\omega) \cdot \mathbf{E}^*(\mathbf{r},\omega)/2\pi, \end{aligned} \quad 12-27$$

where the fact that  $\mathbf{E}(\mathbf{r},\omega)=\mathbf{E}^*(\mathbf{r},-\omega)$  has been used. Note that to obtain the total intensity at a frequency  $\omega$ , both the positive and negative frequency components must be added in the Fourier domain. Inserting eq. 12-26,

$$I = \frac{nc}{2\pi} E(\omega)E^*(\omega)e^{-\alpha z} = I_0 e^{-\alpha z} \quad 12-28$$

where

$$\alpha = \frac{4\pi\omega}{c} \chi_i^{(1)}(\omega) \quad 12-29$$

is the absorption coefficient encountered in section 10. Eq. 12-28 is Beer's law as derived from the quantum-classical molecule-field interaction.

$\chi^{(1)}(\omega)$  is an analytic complex function (appendix A), so by the residue theorem,

$$\chi^{(1)}(\omega) = \frac{1}{2\pi i} \oint \frac{\chi^{(1)}(\omega')}{\omega' - \omega} d\omega' \quad 12-30$$

$$\chi_r^{(1)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\chi_i^{(1)}(\omega')}{\omega' - \omega} d\omega' \quad \text{and} \quad \chi_i^{(1)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\chi_r^{(1)}(\omega')}{\omega' - \omega} d\omega' \quad 12-31$$

Thus, if we can determine  $\chi_i^{(1)}$  (i.e. the absorption coefficient  $\alpha$  according to eq. 12-29), we know everything about the linear optical properties of a chemical substance, since the real part of the susceptibility can be deduced from 12-31: the refractive index and absorption coefficients of materials are not independent, but rather correlated as shown in fig. 12-1. A practical and often overlooked way of evaluating eq. 12-31 by fast Fourier transform has been given by Peterson and Knight, *J. Opt. Soc. Am.* (1973).

#### 12.4 Density matrix perturbation series for $\chi^{(n)}$

The output field of any  $n^{\text{th}}$  order scattering or absorption/emission process can be related to  $\mathbf{P}$  and hence to  $\chi^{(v)}$ .  $\chi^{(v)}$  can be computed from molecular properties such as transition dipole moments or energy level differences, which can be evaluated from the molecular Hamiltonian and its eigenfunctions.

The most systematic way of deriving  $\chi$  to any order is by a perturbation expansion of the molecular density matrix. However, perturbation series do not always converge, and particularly for condensed phase systems, empirical adjustments are often used to estimate  $\chi$ , in lieu of a formidable computational problem. Nevertheless, we will pursue the perturbation approach here as it often does converge, and provides a useful starting point for other treatments.

Let

$$H = H_{\text{mol}} + H_{\text{int}} = H^{(0)} + H^{(1)} \quad 12-32$$

where

$$H^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E}(t) \text{ and } H^{(0)} |n\rangle = \hbar\omega_n |n\rangle. \quad 12-33$$

$\{|n\rangle\}$  are the eigenstates of the molecular system interacting with the field  $\mathbf{E}$ , and the density matrix is written in terms of these eigenstates. Splitting the density matrix into terms with different orders  $n$ , and sorting the resulting Liouville equation by order,

$$\rho(t) = \sum_n \rho^{(n)}(t) \text{ and } \frac{\partial \rho}{\partial t} = \frac{i}{\hbar} [\rho, H] \Rightarrow \quad 12-34$$

$$\frac{\partial}{\partial t} \sum_n \rho^{(n)} = \frac{i}{\hbar} \left\{ \left[ \sum_n \rho^{(n)}, H^{(0)} \right] + \left[ \sum_n \rho^{(n)}, H^{(1)} \right] \right\}$$

Collecting terms by order one obtains a recursive relationship for  $\rho^{(n)}$  to all orders.

$$\frac{\partial \rho^{(n)}}{\partial t} = \frac{i}{\hbar} [\rho^{(n)}, H^{(0)}] + \frac{i}{\hbar} [\rho^{(n-1)}, H^{(1)}]. \quad 12-35$$

Without loss of generality, the input field in eq. 12-48 can be constructed from  $n$  discrete frequency components, or

$$\mathbf{E}(\mathbf{r}, t) = \sum_{i=1}^n E(\mathbf{r}, \omega_i) e^{-i\omega_i t} + E^*(\mathbf{r}, \omega_i) e^{+i\omega_i t} \quad 12-36$$

if results up to  $n$ th order (i.e.  $\chi^{(n)}$  and  $\mathbf{P}^{(n)}$ ) are desired. The reason this can be done without loss of generality is because the wave equations 12-9 and equations 12-10/11 connecting  $\mathbf{E}$  and  $\mathbf{P}$  are local and linear: any desired field  $\mathbf{E}$  and polarization  $\mathbf{P}$  can be constructed by superimposing the simple harmonic solutions above: the sum in eq. 12-36 would simply be replaced by an integration over all frequencies, and turn into the standard Fourier transform expression for the field, eq. 12-5. In the case of a series of near-monochromatic fields at  $\omega_1, \omega_2, \dots$  eq. 12-36 yields the desired answer without any further superposition or integration.

Because eq. 12-34 is linear and its only time dependence comes from  $\mathbf{E}(t)$ , expansion 12-36 implies that  $\rho^{(n)}$  will be of the form

$$\rho^{(n)}(\mathbf{r}, t) = \sum_i \rho_i^{(n)}(\mathbf{r}, \omega_1, \dots, \omega_n) e^{-i(\omega_1 \pm \omega_2 \pm \dots \pm \omega_n) t} + c.c. \quad 12-37$$

where the sum over  $i$  is over all the possible  $\pm$  combinations of frequencies that result from  $n$  electric fields of type 12-51 being multiplied together.

Once the density matrix to  $n^{\text{th}}$  order has been evaluated, one can use it to obtain  $\mathbf{P}^{(n)}$  and  $\chi^{(n)}$ . In practice, one starts with the unperturbed density matrix  $\rho^{(0)}$  of the system before the field is applied, calculates  $\rho^{(1)}$ , then  $\rho^{(2)}$ , and so forth from 12-35. The observed polarization is (section 3)

$$\mathbf{P} = \text{Tr}\{\rho \hat{\mathbf{P}}\} = \sum \mathbf{P}^{(n)} = \sum \text{Tr}\{\rho^{(n)} \hat{\mathbf{P}}\}, \quad 12-38$$

where  $\hat{\mathbf{P}}$  is the dipole polarization operator for the ensemble of molecules. Taking one term out of the perturbation series yields the  $n$ th order polarization

$$\mathbf{P}^{(n)} = \text{Tr}\{\rho^{(n)} \hat{\mathbf{P}}\}. \quad 12-39$$

As will be seen, if we start with electric fields at a discrete set of frequencies, the polarization  $\mathbf{P}^{(n)}$  by construction depends on the electric fields to the overall  $n$ th power, and  $\chi^{(n)}$  at a specific set of frequencies can be obtained by inverting eq. 12-10 to yield

$$\chi_{j \dots k}^{(n)}(\omega = \omega_1 + \omega_2 + \dots + \omega_{n-1}) = \frac{P_j^{(n)}}{E_j(\omega_1) \dots E_k(\omega_{n-1})} \quad 12-40$$

the desired final result.

In the calculation of  $\chi$ , we will apply four boundary conditions and simplifying assumptions, which could be relaxed if necessary. The general procedure of the derivation is identical if these conditions are relaxed, but will generally be more involved.

1) The initial state is thermalized:  $\rho^{(0)} = \frac{1}{Z} e^{-\beta H^{(0)}}$  (section 3). 12-41

2) The ensemble polarization can be written as the sum of the individual molecular polarizations:

$$P^{(n)} = \text{Tr}(\rho^{(n)} \hat{P}) = N \text{Tr}(\rho^{(n)} \hat{\mu}) \quad 12-42$$

where  $\hat{P} = N\hat{\mu}$ , and  $\hat{\mu}$  is the dipole operator for a single molecule. This is only valid in the weakly interacting limit, such as in a gas or for an uncoupled crystal phonon mode. Or of course, one can just compute the complete polarization operator  $P$  for the complex overall system.

3) The vector nature of  $\mathbf{E}$  will be neglected: in eq. 12-36,  $\mathbf{E}(\mathbf{r},t)$  is replaced by  $E(t)$ . This is sufficient for a single polarization in isotropic media, but neglects the phase matching conditions which arise in anisotropic media, as well as polarization effects. The same derivation could be done by Fourier-transforming both  $\mathbf{r} \rightarrow \mathbf{k}$  and  $t \rightarrow \omega$  and treating  $\mathbf{E}$  as a vector.

Phase matching can actually be calculated 'after the fact' by requiring momentum conservation:

$$\hbar \sum \mathbf{k}_{\text{input}} + \mathbf{p}_{\text{molecule, in}} = \hbar \sum \mathbf{k}_{\text{output}} + \mathbf{p}_{\text{molecule, out}} \quad 12-43$$

$\hbar \mathbf{k}$  is the photon momentum, and  $\mathbf{p}_{\text{molecule}}$  the molecular momentum. In many processes, no momentum is transferred to the molecular system, and the output wavevectors must simply add up to the same as the input wavevectors. Fig. 12-5 shows this in the example of second harmonic generation, a  $\chi^{(2)}$  effect. Since  $|\mathbf{k}_i| = \omega_i n(\omega_i)/c$ , condition 12-58 in this particular case becomes

$$\omega_1 n(\omega_1) + \omega_2 n(\omega_2) = \omega_3 n(\omega_3) \quad 12-44$$

in addition to energy conservation

$$\omega_1 + \omega_2 = \omega_3 \quad 12-45$$

One case where the molecular momentum must be included in eq. 12-43 is laser cooling, where a molecule is braked by absorbing a photon, and braked again by emitting the photon by stimulated emission in the same direction in which the absorbed photon was moving ( $\Delta p_{\text{molecule}} = 2\hbar k$ ).

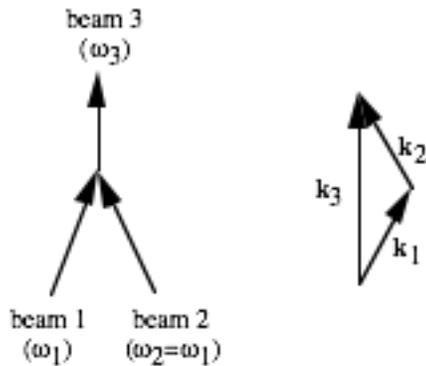


Fig. 12-5. Phase matching for noncollinear second harmonic generation (SHG). Since the length of  $\mathbf{k}_3$  is less than twice the lengths of  $\mathbf{k}_1$  and  $\mathbf{k}_2$ ,  $n(\omega_3)$  must be smaller than  $n(\omega_1)$ : anomalous dispersion or a birefringent crystal are required for phasematching.

4) Perturbation expansion lineshapes always diverge on resonance due to the energy denominator. In section 10 we saw that the quantum field theory (e.g. a set of  $\infty$  many harmonic

oscillators) yields correct decay behavior. The lineshape is Lorentzian for spontaneous emission or any Markov process. This can be enforced *ad hoc* in any perturbation expression by adding a  $\pm i\Gamma$  term to the denominator to make the energy complex. Then 'eigenstates' propagate as  $\exp[-i\omega t - \Gamma t]$   $|i\rangle$  or  $\langle i| \exp[+i\omega t - \Gamma t]$  and decay exponentially with time. A finite linewidth of excited states implies that some relaxation process restores the ground state density towards its equilibrium value  $\rho^{(0)}$ , and some other (or the same) process causes the off-diagonal coherences to decay to zero, as described under 2). Consider the example of a density matrix element oscillating at frequency  $\omega_0$  and decaying towards equilibrium at a rate  $\Gamma = 1/2T_1$ :

$$\begin{aligned}
 (\rho(t > 0) - \rho^{(0)}) &= ae^{-\Gamma t} \sin \omega_0 t \Rightarrow \\
 \rho(\omega) &= a \int_0^{\infty} dt e^{i\omega t} e^{-\Gamma t} \frac{1}{2i} (e^{i\omega_0 t} - e^{-i\omega_0 t}) \\
 &= \frac{a}{2i} \int_0^{\infty} dt e^{i(\omega + \omega_0 + i\Gamma)t} - e^{i(\omega - \omega_0 + i\Gamma)t} \\
 &= \frac{a}{2i} \left\{ -\frac{1}{i(\omega + \omega_0 + i\Gamma)} + \frac{1}{i(\omega - \omega_0 + i\Gamma)} \right\} \\
 &= \frac{a}{2} \left\{ \frac{1}{(\omega + \omega_0 + i\Gamma)} - \frac{1}{(\omega - \omega_0 + i\Gamma)} \right\}
 \end{aligned} \tag{12-46}$$

The perturbation expressions will be similar to the last line, but lack the  $\pm i\Gamma$  factor, which should be added to prevent  $\rho$  from diverging as  $\omega \rightarrow \pm\omega_0$ . Note that in contrast to section 10, we are assuming that the amplitude decays as  $\exp[-\Gamma t]$ , not  $\exp[-\Gamma t/2]$ , in order to avoid many factors of 2 in the notation. That is why  $\Gamma = 1/2T_1$  while  $\Gamma = 1/\tau_{\text{spont}}$  in section 10.

### 12.5 First iteration: calculation of $\chi^{(1)}$

We now have all the ingredients to calculate higher order correction to  $\rho^{(0)}$ . Starting with  $\rho^{(1)}$  in eq. 12-35

$$\frac{\partial \rho^{(1)}}{\partial t} = \frac{i}{\hbar} [\rho^{(1)}, H^{(0)}] + \frac{i}{\hbar} [\rho^{(0)}, H^{(1)}] \tag{12-47}$$

inserting the Fourier expansions 12-36 and 12-37 for  $E(t)$  and  $\rho^{(1)}(t)$ ,

$$-i\omega \rho^{(1)}(\omega) e^{-i\omega t} + c.c. = \frac{i}{\hbar} [\rho^{(1)}(\omega) e^{-i\omega t} + c.c., H^{(0)}] - \frac{i}{\hbar} [\rho^{(0)}, \hat{\mu} E(\omega) e^{-i\omega t} + c.c.] \tag{12-48}$$

The complex conjugate *c.c.* can be dropped since it contains redundant information: all the  $\exp[+i\omega t]$  terms are matched by an equivalent  $\exp[-i\omega t]$  term, and we already know that  $\chi(-\omega)$  is given by  $\chi^*(\omega)$ . Equating the terms in  $\exp[-i\omega t]$  and dividing out the common exponential factor, 12-48 becomes

$$-\omega \rho^{(1)} = \frac{1}{\hbar} (\rho^{(1)} H^{(0)} - H^{(0)} \rho^{(1)} - \rho^{(0)} \hat{\mu} E(\omega) + \hat{\mu} E(\omega) \rho^{(0)}) \tag{12-49}$$

The  $\langle i| |j\rangle$  matrix element of this equation is

$$\begin{aligned}
 -\hbar\omega \langle i| \rho^{(1)} |j\rangle &= \langle i| \rho^{(1)} H^{(0)} |j\rangle - \langle i| H^{(0)} \rho^{(1)} |j\rangle - \langle i| \rho^{(0)} \hat{\mu} E(\omega) |j\rangle + \langle i| \hat{\mu} E(\omega) \rho^{(0)} |j\rangle \\
 &= \langle i| \rho^{(1)} |j\rangle \hbar\omega_j - \hbar\omega_i \langle i| \rho^{(1)} |j\rangle - \rho_{ii}^{(0)} \langle i| \hat{\mu} |j\rangle E(\omega) + \langle i| \hat{\mu} |j\rangle E(\omega) \rho_{jj}^{(0)}
 \end{aligned}$$

or

$$-\hbar\omega \rho_{ij}^{(1)} = \rho_{ij}^{(n)} \hbar\omega_j - \rho_{ij}^{(n)} \hbar\omega_i - \mu_{ij} \rho_{ii}^{(0)} E(\omega) + \mu_{ij} E(\omega) \rho_{jj}^{(0)} E(\omega). \tag{12-50}$$

We can now solve for  $\rho^{(1)}$  in terms of the known equilibrium  $\rho^{(0)}$ :

$$\begin{aligned}\rho_{ij}^{(1)}(\omega) &= \frac{1}{\hbar} \frac{[H^{(1)}(\omega), \rho^{(0)}]_{ij}}{\omega_{ij} - \omega} = \frac{1}{\hbar} \frac{\mu_{ij}(\rho_{jj}^{(0)} - \rho_{ii}^{(0)})}{\omega_{ij} - \omega} \\ &= \frac{1}{\hbar} \left\{ \frac{-\mu_{ij}\rho_{jj}^{(0)}}{\omega - \omega_{ij}} + \frac{\mu_{ij}\rho_{ii}^{(0)}}{\omega - \omega_{ij}} \right\} E(\omega)\end{aligned}\quad 12-51$$

where  $\omega_{ij} = \omega_i - \omega_j$  is the molecular transition frequency between levels  $E_i = \hbar\omega_i$  and  $E_j = \hbar\omega_j$ . Inserting into eq. 12-42

$$\begin{aligned}P^{(1)}(\omega) &= N \text{Tr}_i \{ \rho^{(1)}(\omega) \hat{\mu} \} \\ &= N \sum_i \left\{ \sum_j \rho_{ij}^{(1)} \mu_{ji} \right\} \\ &= \frac{N}{\hbar} \sum_{i,j} \left( \frac{-\mu_{ij}\rho_{jj}^{(0)}}{\omega - \omega_{ij}} \mu_{ji} + \frac{\mu_{ij}\rho_{ii}^{(0)}}{\omega - \omega_{ij}} \mu_{ji} \right) E(\omega) \\ &= \frac{N}{\hbar} \sum_{i,j} \left( \frac{-\mu_{ji}\rho_{ii}^{(0)}}{\omega - \omega_{ji}} \mu_{ij} + \frac{\mu_{ji}\rho_{jj}^{(0)}}{\omega + \omega_{ji}} \mu_{ij} \right) E(\omega)\end{aligned}\quad 12-52$$

In the last step, subscripts  $i$  and  $j$  were exchanged in the first summation because the sum is over all values of  $i$  and  $j$ , and in the second summation we used  $\omega_{ij} = -\omega_{ji}$ . From eq. 12-40

$$\chi^{(1)}(\omega) = P^{(1)}(\omega) / E(\omega) \quad 12-53$$

and therefore

$$\chi^{(1)}(\omega) = \frac{N}{\hbar} \sum_{i,j} \left( -\frac{|\mu_{ij}|^2}{\omega - \omega_{ji} + i\Gamma_{ji}} + \frac{|\mu_{ij}|^2}{\omega + \omega_{ji} - i\Gamma_{ji}} \right) \frac{e^{-E_i/kT}}{\sum e^{-E_i/kT}} \quad 12-54$$

where the initial Boltzmann density matrix has been explicitly written out and the damping factors  $i\Gamma_{ji}$  for each transition  $j \leftarrow i$  have been added. The expression satisfies  $\chi(\omega)^* = \chi(-\omega)$ . If  $\boldsymbol{\mu}$  and  $\mathbf{E}$  had been kept as vectors,  $|\mu_{ij}|^2$  would have become  $\mu_{ij,x} \mu_{ij,y}$  for the  $\chi_{xy} E_y$  component of  $\mathbf{P}$ , yielding  $\chi_{xy}$ , and similarly for the other eight components of the susceptibility matrix. Eq. 12-54 is our final expression for  $\chi^{(1)}(\omega)$ , and from it, all linear optical properties such as absorption coefficient  $\alpha$ , refractive index  $n$ , and dielectric constant  $\epsilon$  can be calculated.

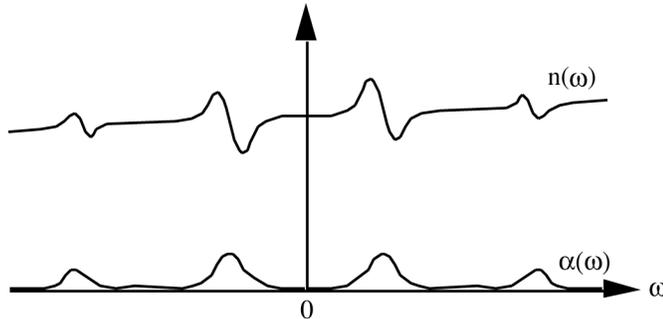


Fig. 12-6. Refractive index and absorption coefficient derived from eq. 12-54. The real part of the susceptibility is an odd function of  $\omega$ , the imaginary part an even function.

Eq. 12-54 indeed corresponds to a Lorentzian lineshape for isolated transitions. Let  $\omega \approx \omega_{ji}$  be tuned near resonance with a single molecular frequency  $\omega_{ji}$ . Then a single term from the first sum in eq. 12-54 dominates

$$-\frac{1}{(\omega - \omega_{ji}) + i\Gamma} = -\frac{(\omega - \omega_{ji}) - i\Gamma}{(\omega - \omega_{ji})^2 + \Gamma^2} \Rightarrow$$

$$\chi_r^{(1)} \approx \frac{N |\mu_{ij}|^2 e^{-E_i/kT}}{\hbar} \frac{-(\omega - \omega_{ji})}{Z (\omega - \omega_{ji})^2 + \Gamma^2} \quad 12-55$$

$$\chi_i^{(1)} = \frac{N |\mu_{ij}|^2 e^{-E_i/kT}}{\hbar} \frac{\Gamma}{Z (\Delta\omega^2 + \Gamma^2)}$$

Eq. 12-29 then yields for the absorption coefficient

$$\chi_i^{(1)} = \frac{4\pi\omega N |\mu_{ij}|^2 e^{-E_i/kT}}{\hbar c} \frac{\Gamma}{Z (\omega - \omega_{ji})^2 + \Gamma^2} \quad 12-56$$

This is identical to formula 10-40 obtained by second quantization, except for a missing factor of 1/3 because no averaging over dipole orientations with respect to the field was performed (replacing  $\boldsymbol{\mu} \rightarrow \mu$  and  $\mathbf{E} \rightarrow E$  implicitly assumes they are always oriented along the same axis). The population  $n_0$  in state  $|i\rangle$  of eq. 10-40 is given explicitly by  $N \exp[-E_i/kT]/Z$  here. The refractive index  $n_r$  and  $\alpha$  obtained from 12-70 are plotted in Fig. 12-6.

## 12.6 Time-dependent formulation of the susceptibility $\chi$ : relation to correlation function

Eq. 12-54 is the first order molecular susceptibility as a function of frequency. For a time-dependent calculation, it would be more convenient to have  $\chi^{(1)}(t)$ , which can be obtained by Fourier transformation:

$$\begin{aligned} \chi^{(1)}(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \chi^{(1)}(\omega) \\ &= \frac{N}{2\pi\hbar} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \sum_i \langle i | \{ -\sum_j \frac{\mu |j\rangle \langle j| \mu}{\omega - \omega_j + i\Gamma_j} + \sum_j \frac{\mu |j\rangle \langle j| \mu}{\omega + \omega_j - \omega_i + i\Gamma_j} \} \rho^{(0)} |i\rangle \rangle \\ &= \frac{N}{\hbar} \sum_i \langle i | \{ \sum_j \hat{\mu} |j\rangle \rangle \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\omega_j - \omega_i - i\Gamma_j - \omega} \langle j | \hat{\mu} - \\ &\quad \sum_j \hat{\mu} |j\rangle \rangle \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\omega_i - \omega_j - i\Gamma_j - \omega} \langle j | \hat{\mu} \rangle \rho^{(0)} |i\rangle \rangle \end{aligned} \quad 12-57$$

The integral in eq. 12-57 can be evaluated as follows:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\alpha - \omega} = \frac{1}{2} i e^{-i\alpha t} \quad \text{for } t > 0, \quad 12-58$$

so eq. 12-57 can be rewritten as

$$\begin{aligned} \chi^{(1)}(t) &= \frac{Ni}{2\hbar} \sum_i \langle i | \{ \sum_j \hat{\mu} |j\rangle \rangle e^{-i(\omega_j - \omega_i - \Gamma_j)t} \langle j | \hat{\mu} - \\ &\quad \sum_j \hat{\mu} |j\rangle \rangle e^{-i(\omega_i - \omega_j - \Gamma_j)t} \langle j | \hat{\mu} \rangle \rho^{(0)} |i\rangle \rangle \end{aligned} \quad 12-59$$

Letting

$$\langle i | H_i = \langle i | \hbar(\omega_i + i\Gamma_i) \text{ and } H_j |j\rangle = \hbar(\omega_j - i\Gamma_j) |j\rangle \quad 12-60$$

one can replace the complete sum

$$\sum_j |j\rangle \langle j| e^{-i\omega_j t - \Gamma_j t} = e^{-iH_j t/\hbar} \quad 12-61$$

and so

$$\begin{aligned}
\chi^{(1)}(t) &= \frac{iN}{2\hbar} \sum_i \langle i | \hat{\mu} e^{-iH_j/\hbar} \hat{\mu} \rho^{(0)} e^{iH_i/\hbar} - \hat{\mu} e^{iH_j/\hbar} \hat{\mu} \rho^{(0)} e^{-iH_i/\hbar} | i \rangle \\
&= i \frac{N}{2\hbar} \text{Tr}_i \{ \hat{\mu} e^{-iH_j/\hbar} \hat{\mu} \rho^{(0)} e^{iH_i/\hbar} \} + c.c. \\
&= -\frac{N}{\hbar} \text{Im} \{ \text{Tr}_i [ \hat{\mu} G_{ji}(t) \hat{\mu} \rho^{(0)} ] \}. \quad (t>0, \chi^{(1)}(t<0) = 0)
\end{aligned} \tag{12-62}$$

Here,  $H_j$  is the Hamiltonian for the final (excited) states, and  $H_i$  is the Hamiltonian for the initial states. The two may of course be one and the same (e.g. vibrational rather than electronic transition).  $G_{ji}(t)$  is the time domain Green function or Liouville operator. Liouville operators are "superoperators" which transform operators by 'surrounding them' with other operators. Comparing the last two lines of eq. 12-62,  $G$  is defined to act as

$$G_{ji}(t) \hat{\rho} = e^{-iH_j/\hbar} \hat{\rho} e^{iH_i/\hbar}. \tag{12-63}$$

When  $j=i$  in eq. 12-63, the familiar Liouville propagator is obtained (section 3). This would be the time propagation for the density matrix while no excitation pulse is interacting with the molecules. When  $j \neq i$ ,  $G$  propagates the ket part of  $\mu\rho^{(0)}$  with the final state Hamiltonian, and the bra part with the initial state Hamiltonian. This is what excites part of the density operator to an excited state, and creates coherence between all the populated states of the density operator. Thus, excitation by a field  $E \cos(\omega t)$  leaves the system in a coherent superposition between ground and excited state levels.

The trace in eq. 12-77 can be rewritten in terms of the Heisenberg operator  $\mu(t)$  if  $H_j = H_i = H$ , and if one uses the facts that  $\rho^{(0)} = \exp[-H/kT]$  and  $\exp[-iHt/\hbar]$  commute, and that operators in a trace can be rotated:

$$\begin{aligned}
C(t) &= \text{Tr} [ \hat{\mu} e^{-iHt/\hbar} \hat{\mu} \rho^{(0)} e^{iHt/\hbar} ] \\
&= \text{Tr} [ \rho^{(0)} e^{iHt/\hbar} \hat{\mu} e^{-iHt/\hbar} \hat{\mu} ] \\
&= \text{Tr} [ \rho^{(0)} \hat{\mu}(t) \hat{\mu}(0) ]
\end{aligned} \tag{12-64}$$

$C(t)$  is the autocorrelation function of the dipole moment operator.

One application of  $C(t)$  is that it directly relates quantities such as  $\alpha(\omega)$  or  $n(\omega)$  to the molecular dipole moment. For example,

$$\alpha(\omega) = \frac{4\pi\omega}{c} \chi_i^{(1)}(\omega) = \frac{4\pi\omega}{c} \text{Im} \int_{-\infty}^{\infty} dt e^{i\omega t} \chi^{(1)}(t) = -\frac{4\pi\omega N}{\hbar c} \int_0^{\infty} dt e^{i\omega t} \text{Tr} [ \rho^{(0)} \hat{\mu}(t) \hat{\mu}(0) ]. \tag{12-65}$$

Thus, spectral properties can be related directly to dynamical quantities. This also allows one to obtain approximate spectra from purely classical quantities, such as  $\mu(t)$ : Simply run a molecular dynamics simulation to compute  $\mu(t)$ , then calculate the autocorrelation function and Fourier-transform to get the absorption spectrum. A similar result is discussed in appendix B, where it is obtained from time-dependent perturbation theory on the wavefunction rather than the density matrix.

We conclude by noting an alternate way of writing the susceptibility 12-62. A compact notation introduces a superoperator  $\mu_{L/R}$ , defined to act either on the left or on the right of *all* that follows in the trace

$$\hat{\mu}_L \hat{\rho} = \hat{\mu} \hat{\rho} \text{ and } \hat{\mu}_R \hat{\rho} = \hat{\rho} \hat{\mu}, \tag{12-66}$$

such that eq. 12-62 can be written

$$\chi^{(1)} = -\frac{N}{\hbar} \text{Im} \{ \text{Tr}_i [ \hat{\mu}_R G_{ji}(t) \hat{\mu}_L \rho^{(0)} ] \}. \tag{12-67}$$

This notation has the advantage that it can be constructed without further derivations, to any order, from simple geometrical diagrams analogous to Feynman diagrams.

### 12.7 Feynman diagrams

Although eqs. such as 12-67 can be derived explicitly for higher orders  $\chi^{(n>1)}$ , the systematic nature of the terms as written in eq. 12-67 makes it easy to construct them from a Feynman diagram.

The sequence in eq. 12-67 can be interpreted as follows, if we assume a pure state  $|i\rangle$  with density matrix  $|i\rangle\langle i|$  as our initial state for simplicity:

- 1) start with  $\rho^{(0)} = |i\rangle\langle i|$ ;
- 2) act with the field by multiplying  $\rho$  by  $\mu$  on the left;
- 3) propagate the ket and bra sides of the resulting density matrix

$$\mu |i\rangle\langle i| = \sum_j |j\rangle\langle j| \mu |i\rangle\langle i| = \sum_j |j\rangle \mu_{ji} \langle i| \quad 12.68$$

for a time  $t$  using  $G_{ji}(t)$ ; since  $G_{ji}$  propagates with excited surface  $H_j$  on the ket side of  $\rho$ , and with initial surface  $H_i$  on the bra side of  $\rho$ , the resulting matrix is a coherence of states  $|j\rangle\langle i|$ ;

- 4) act with the field by multiplying by  $\mu$  on the right; the result is an absorption event leading to a final state of type  $|j\rangle\langle i| \mu = \sum |j\rangle \mu_{ij} \langle j|$ .

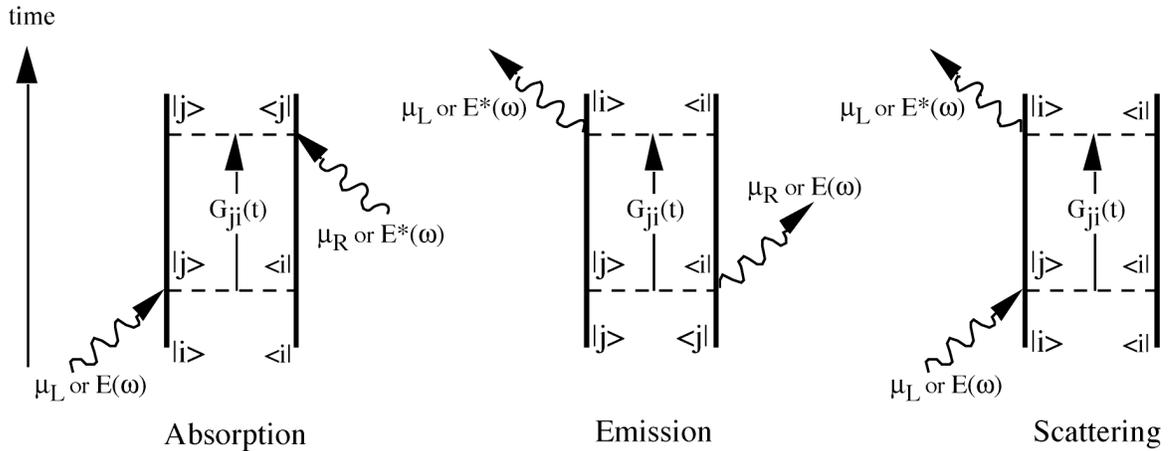


Fig. 12-7. Feynman diagrams for absorption, scattering and emission; the matter-light interaction takes place at the times indicated by dashed lines; between field interactions, the system is in a coherent state propagated by the Green function  $G$ . On the left side of the diagrams, positive frequencies (absorption) correspond to  $E(\omega)$ , while negative frequencies (emission) correspond to  $E(-\omega) = E^*(\omega)$ . On the right hand side, the conjugate nature of the bra reverses this.

Fig. 12-7 summarizes this sequence diagrammatically for absorption, emission, and resonant scattering. Absorption, emission, and scattering are all due to  $\chi^{(1)}$ , and result in the absorption coefficient  $\alpha$ , gain coefficient  $g$  ( $g = -\alpha$  for negative  $\alpha$ , when there is excess excited state population) and a refractive index  $n$  different from unity.

Let us construct the expression for scattering. To do so, one starts at the bottom of the Feynman diagram and works upward, adding pieces from right to left in the  $\{ \}$  brackets:

$$\chi^{(1)} = -\frac{N}{\hbar} \text{Im} \{ \text{Tr}_i [ \hat{\mu}_L^\dagger G_{ji}(t) \hat{\mu}_L \rho^{(0)} ] \}. \quad 12-67$$

First  $\rho^{(0)} = |i\rangle\langle i|$ , then  $\mu_L$ , then  $G_{ji}(t)$ , etc. It looks similar to the absorption expression, but  $\mu_R$  has been replaced by  $\mu_L^\dagger$  so the density matrix ends up in the ground state again. Note that in the case of  $\chi^{(1)}$  scattering the momentum conservation eq. 12-43 implies

$$\mathbf{k}_{in} = \mathbf{k}_{out}, \quad 12-69$$

so the output beam propagates in the same direction as the input beam. However, the beam is delayed in time, giving rise to the slower local speed of light associated with a refractive index greater than 1, as derived in section c).

## 12.8 Higher order susceptibilities and Feynman diagrams

Now that we have a handle on how to calculate  $\chi^{(1)}(\omega)$ ,  $\chi^{(1)}(t)$  and set up Feynman diagrams, consider higher order non-linear experiments. To calculate  $\rho^{(2)}$ , eq. 12-51 for  $\rho^{(1)}$  can be inserted into eq. 12-35. For example, consider the value of  $\rho^{(2)}$  at  $\omega = \omega_1 + \omega_2$ . This corresponds to picking all the terms with factors  $\exp[-i(\omega_1 + \omega_2)t]$  out of the Liouville equation

$$\begin{aligned} \frac{\partial}{\partial t} \rho^{(2)}(\omega = \omega_1 + \omega_2) &= \frac{i}{\hbar} (\rho^{(2)} H^{(0)} - H^{(0)} \rho^{(2)}) \\ &+ \frac{i}{\hbar} (\rho^{(1)}(\omega_2) H^{(1)}(\omega_1) - H^{(1)}(\omega_1) \rho^{(1)}(\omega_2)) + \frac{i}{\hbar} (\rho^{(1)}(\omega_1) H^{(1)}(\omega_2) - H^{(1)}(\omega_2) \rho^{(1)}(\omega_1)). \end{aligned} \quad 12-70$$

There are now two first order contributions on the right hand side, corresponding either to a field at frequency  $\omega_1$  interacting with a first-order density matrix created by a previous field at frequency  $\omega_2$ , or *vice-versa*. Computing matrix elements between states  $i$  and  $j$ ,

$$\rho_{ij}^{(2)}(\omega = \omega_1 + \omega_2) = \frac{1}{\hbar} \frac{[H^{(1)}(\omega_1), \rho^{(1)}(\omega_2)]_{ij} + [H^{(1)}(\omega_2), \rho^{(1)}(\omega_1)]_{ij}}{\omega_j - \omega + i\Gamma_j} \quad 12-71$$

follows in the same manner as eq. 12-51 (with  $i\Gamma$  already added to prevent divergence at resonance). Each order therefore adds a product term of the type

$$\frac{\mu E}{\Delta\omega} \quad 12-72$$

to the density matrix, where  $\Delta\omega$  is a resonant frequency denominator. For the third order, one likewise obtains

$$\rho_{\alpha\alpha}^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3) = \frac{1}{\hbar} \frac{[H^{(1)}(\omega_1), \rho^{(2)}(\omega_2 + \omega_3)]_{\alpha\alpha} + [H^{(1)}(\omega_2), \rho^{(2)}(\omega_1 + \omega_3)]_{\alpha\alpha} + [H^{(1)}(\omega_3), \rho^{(2)}(\omega_1 + \omega_2)]_{\alpha\alpha}}{\omega_\alpha - \omega + i\Gamma} \quad 12-73$$

As before,

$$P^{(3)} = N \text{Tr} \{ \rho^{(3)} \hat{\mu} \} \quad 12-74$$

and division by  $E(\omega_1)E(\omega_2)E(\omega_3)$  yields  $\chi^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3)$ . If we wanted the value of  $\chi^{(3)}(\omega = \omega_1 - \omega_2 + \omega_3)$ , we would collect terms multiplied by  $\exp[-i(\omega_1 - \omega_2 + \omega_3)t]$  in eq. 12-73, and divide eq. 12-74 by  $E(\omega_1)E^*(\omega_2)E(\omega_3)$  since an  $\exp[+i\omega_2 t]$  term in eq. 12-37 would be associated with  $E^*(\omega_2)$ . Clearly, since  $E^*(\omega) = E(-\omega)$ , it is sufficient to evaluate just the case in eq. 12-74, and to replace  $\omega_i \rightarrow -\omega_i$  where desired.

A typical term in the summation for  $\chi^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3)$  would be

$$\chi^{(3)} \sim \frac{N}{\hbar} \frac{\langle i|\mu|l\rangle\langle l|\mu|k\rangle\langle k|\mu|j\rangle\langle j|\mu|i\rangle}{(\omega - \omega_i + i\Gamma)(\omega_2 + \omega_3 + \omega_j + i\Gamma)(\omega_2 - \omega_j + i\Gamma)} \rho_{ii}^{(0)}. \quad 12-75$$

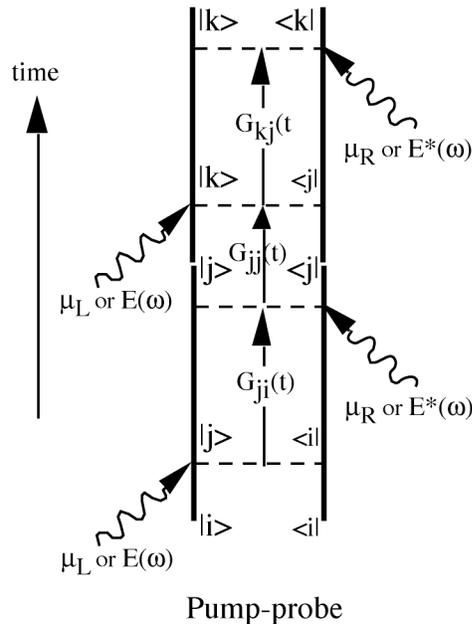
Depending on which of the diagrams in Figs. 12-9 and 12-11 one is interested in, different frequency denominators will be resonant, and usually only a few of the many terms in  $\chi^{(n)}$  contribute to a certain type of experiment.

A typical term in  $\chi^{(3)}(t_i)$  is

$$-\frac{N}{\hbar} \text{Im}\{Tr_i[\hat{\mu}_R G_{kj}(t) \hat{\mu}_L G_{jj}(t_2) \hat{\mu}_R G_{ji}(t_1) \hat{\mu}_L \rho^{(0)}]\} \quad 12-76$$

Eq. 12-76 corresponds to absorption from  $|i\rangle$  to  $|j\rangle$  via a coherent state  $|j\rangle\langle il$ , and then from  $|j\rangle$  to  $|k\rangle$  via a coherent state  $|k\rangle\langle jl$ , or the pump-probe = PP experiment in fig. 12-10. If  $G_{jj}(t_2)\mu_R$  were to be replaced by  $G_{ki}(t_2)\mu_L$ , the first two field interactions would have put the density matrix into state  $|k\rangle\langle il$  rather than  $|j\rangle\langle jl$ , corresponding to a scattering event, rather than an absorption event.

To construct expressions like eq. 12-76, Feynman diagrams for higher order processes are generated just like the first order examples, by acting with  $E(\omega_i)$  on the left and  $E^*(\omega_j)$  on the right side for absorption, and  $E^*(\omega_i)$  on the left and  $E(\omega_j)$  on the right side for stimulated emission. A process such as the pump-probe experiment in eq. 12-76 would have four field arrows instead of the two in fig. 12-7, and is shown in Fig. 12-8.



Pump-probe

Fig. 12-8. Feynman diagram for a pump-probe experiment (consecutive absorption), producing eq. 12-76

Clearly it is much easier to write down the diagram in Fig. 12-8, from that eq. 12-76, than to do the perturbation calculation explicitly. Depending on the type of experiment, only a small number of "intuitive" diagrams is usually important. Once they have been written down,  $\chi^{(n)}(t)$  can be directly written down by adding the appropriate  $\mu_{R/L}$  operators for each absorption/emission event, and the appropriate  $G(t_i)$  operators for each coherent propagation between interaction events. Any diagonal Green functions  $G_{ii}$  correspond to intermediate states populated by absorption or stimulated emission, while off-diagonal  $G_{ij}$  Green functions are associated with scattering events. The factors  $-\Gamma t$  in the excited state Hamiltonians  $H_j$  cause the coherence to decay.

The frequency domain expressions for  $\chi$  also can be generated directly from the Feynman diagrams by working backwards from  $\chi(t)$ :

- 1) Each interaction vertex on the left is associated with a term

$$\frac{1}{\hbar} \langle j | \mu E(\omega_{mj}) | i \rangle \quad 12-77$$

for absorption and a term

$$\frac{1}{\hbar} \langle j | \mu E^*(\omega_{m'}) | i \rangle \quad 12-78$$

for emission. On the right side, these equations are replaced by their Hermitian conjugates.

2) Each propagation between field interactions is associated with a frequency domain Green function (Appendix A)

$$\frac{1}{i(\sum_{m'=1}^m \omega_{m'} - \omega_j + i\Gamma_j)} \quad 12-79$$

where  $m'$  is summed over all field frequencies encountered up to that point,  $j$  and  $i$  are the subscripts on the corresponding  $G_{ji}(t)$  (i.e. the density matrix being propagated is of type  $|j\rangle\langle i|$ ), and  $\Gamma_j$  is the *ad-hoc* linewidth factor associated with state  $j$ . The frequencies  $\omega_{m'}$  are taken positive for absorption and negative for emission on the left side. If the interaction preceding propagation occurred on the right side, the Hermitian conjugate of eq. 12-94 must be used.

3) The product over all these terms is multiplied by the corresponding initial density matrix element  $\rho^{(0)}_{ii}$  and summed over all state indices  $i, j, \dots$ .

### 12.9 Detecting the value of $\chi^{(n)}$ : general scattering experiment

Once we have  $\chi$  in hand, we still need to solve the wave equation to figure out what the experimental measurement will yield. For  $\chi^{(1)}$ , we already derived how it is related to the absorption coefficient, dielectric constant, and refractive index. Values of  $\chi^{(n>1)}$  require more sophisticated nonlinear spectroscopy measurements, which in turn can yield more detailed knowledge about molecular properties. In general,  $\chi$  can be measured either by detecting scattered electric fields due to a polarization  $\mathbf{P}^{(n)}$  when it emits, or by measuring absorption due to a polarization  $\mathbf{P}^{(n)}$  when it absorbs. We consider the general formula for scattering processes first.

In scattering,  $n$  electric fields interact with the molecule to form  $\mathbf{P}^{(n)}$  (via  $\chi^{(n)}$  in eq. 12-9 or 12-14);  $\mathbf{P}^{(n)}$  then produces an output field  $E_{n+1}$ , the scattered field, as described by eq. 12-6 or 12-8. Some examples are shown in fig. 12-2. Raman scattering (RS) and stimulated Raman scattering (SRS) require an ad-hoc modification of  $\chi^{(3)}$  discussed in f) since quantum-classical theory does not describe spontaneous processes which seed SRS by providing the first emitted photon. The other processes (stimulated emission pumping SEP, coherent anti-Stokes Raman scattering CARS and laser-induced grating spectroscopy LIGS) are all fully stimulated processes and can be described essentially exactly by the quantum-classical formalism.

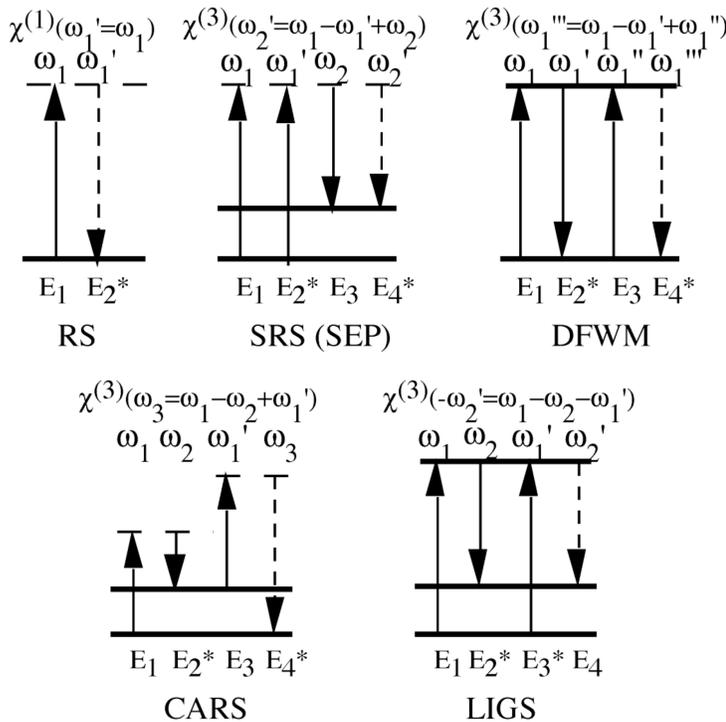


Fig. 12-9. Scattering experiments and the associated susceptibilities. RS = Raleigh scattering; SRS = stimulated Raman scattering; DFWM = degenerate four-wave mixing; CARS = coherent anti-Stokes Raman scattering; LIGS = laser-induced grating scattering. Virtual states are indicated by dashed lines, and the wave conventionally taken as the scattered wave is shown dashed. Frequencies are positive for absorption on the left side of a Feynman diagram, negative for the right side, and the reverse holds for emission (see fig. 11-7).

As discussed in a), phase matching will not be considered in detail here, and we consider the wave equation again in one dimension ( $z$ ). For a general order polarization eq. 12-8 becomes

$$\frac{\partial^2}{\partial z^2} \epsilon_{\text{osc}}(z, \omega) + \frac{\omega^2 n^2}{c^2} \epsilon_{\text{osc}}(z, \omega) = -\frac{4\pi\omega^2}{c^2} P^{(n)}(z, \omega), \quad 12-80$$

where we assume that  $P^{(n)}$  has been calculated from  $\chi^{(n)}$  in eq. 12-9 or 12-10, e.g.  $P^{(3)} = \chi^{(3)}:E_1 E_2 E_3$ . This type of differential equation is easily solved by the Green function method of Appendix A if its impulse response is known. The solution derived there is

$$E(z, \omega) = -\frac{4\pi n^2 \omega^2}{c^2} \int_{-\infty}^{\infty} dz' P(z', \omega) G(z, z') \quad 12-81$$

where the Green function is

$$G(z, z') = \frac{1}{2ik} e^{ik(z-z')}, \quad k = n\omega/c. \quad 12-82$$

Eq. 12-81 is the general formula for the scattered output field as a function of the molecular polarization; the intensity is obtained from  $E$  as in eq. 12-27.

Let us consider a specific example of this, namely degenerate four-wave mixing in a thin low-absorbance film of material. The integral 12-81 can be simplified if i) the scattering layer is thin (so  $P(z, \omega) = P(\omega)$  is approximately constant across the layer between  $z=0$  and  $z=\Delta z$

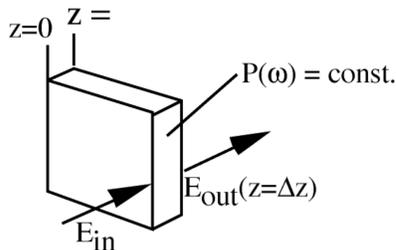


Fig. 12-10: Geometry for a scattering or absorption experiment in a thin film with constant polarization. In a thick film,  $E_{\text{in}}$  would be attenuated substantially, and  $P$  would decrease as  $z$  increases.

because the electric fields which induce it are not scattered much); and ii) if absorption is low so  $k \approx k_r \approx \omega n_r / c$ . In that case (Fig. 12-10)

$$\begin{aligned}
 E(\Delta z, \omega) &= +2\pi i k P(\omega) \int_0^{\Delta z} dz' e^{ik_r |\Delta z - z'|} \\
 &= 2\pi i k P(\omega) \frac{-1}{ik} e^{ik_r |\Delta z - z'|} \Big|_0^{\Delta z} \\
 &= -2\pi P(\omega) (1 - e^{ik_r \Delta z}) \text{ since } \frac{\partial |z - z'|}{\partial z'} = -1 \text{ if } z' < z.
 \end{aligned}
 \tag{12-83}$$

$E(\Delta z, \omega)$  is the output field at frequency  $\omega$  and position  $\Delta z$  on the output side of the thin film. The measured intensity is again evaluated using eq. 12-27

$$\begin{aligned}
 I_{out} &= 2\pi c n |P(\omega)|^2 (1 - e^{ik_r \Delta z} - e^{-ik_r \Delta z} + 1) \\
 &= 4\pi c n |P(\omega)|^2 (1 - \cos k_r \Delta z)
 \end{aligned}
 \tag{12-84}$$

In the case of DFWM, the required polarizability from Fig. 12-9 is

$$P^{(3)}(\omega) = \chi^{(3)}(\omega = \omega_1 = \omega_1 - \omega_1 + \omega_1) E_1 E_1^* E_1'' \tag{12-85}$$

and so the input field  $E_1''$  will be scattered to produce an output field at the same frequency. For a thin sample ( $k_r \Delta z \ll 1$ ) eq. 12-85 yields

$$I_{DFWM} = 2\pi c n |\chi^{(3)}|^2 k_r^2 \Delta z^2 |E_1|^2 |E_1'|^2 |E_1''|^2 \sim |\chi^{(3)}|^2 \Delta z^2 I_1 I_1' I_1'' \tag{12-86}$$

A typical geometry for such an experiment is as follows: beam  $E_1$  is vertically polarized; beam  $E_1'$  comes in at an angle and is polarized at  $45^\circ$ . These beams form a phase grating within the film substrate. Beam  $E_1''$  is collinear with beam  $E_1'$  and polarized at  $45^\circ$ ; it is scattered by this grating into an output beam collinear with  $E_1$ . It can be distinguished from  $E_1$  by inserting a polarizer which eliminates the vertical polarization component. Optical-Kerr effect spectroscopy (of which DFWM is one variant) is therefore like background-free "absorption" spectroscopy because large resonant values of  $\chi^{(3)}$  are usually paralleled by large values of  $\chi^{(1)}$ .

### 12.10 Detecting the value of $\chi^{(n)}$ : general absorption (emission) experiment

In the case of absorption (emission),  $n$  electric fields interact with the molecular sample to produce  $\mathbf{P}^{(n)}$  (via  $\chi^{(n)}$ ). The polarization  $\mathbf{P}^{(n)}$  then absorbs (emits) field  $\mathbf{E}_{n+1}$ , increasing (decreasing in stimulated emission) the molecular energy.

Some examples are shown in fig. 12-4: Linear absorption LAS has already been derived in section c). In pump-probe spectroscopy PP, an intermediate level is excited as two collinear fields at the same frequency (from the same laser beam) interact to be absorbed, and a final level is then excited by a second laser pulse at a different frequency. In stimulated emission pumping, the same sequence occurs except that the intermediate level lies above the final level, so the second process is stimulated emission instead of absorption.

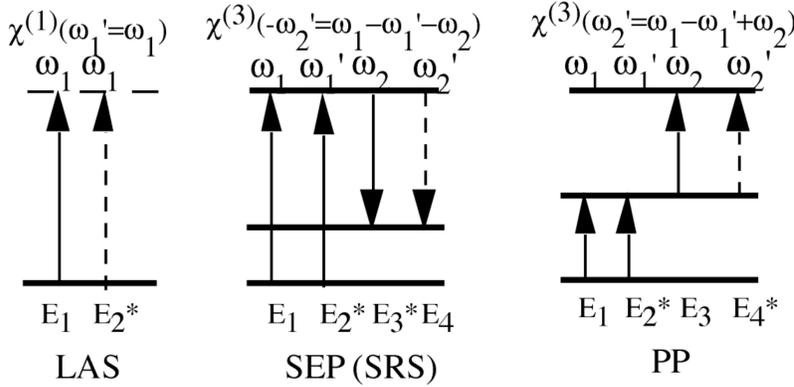


Fig. 12-11. Absorption/emission experiments and the associated susceptibilities.. LAS = Linear absorption; SEP = stimulated emission pumping; PP = pump-probe spectroscopy. The final absorbed/emitted beam is shown dashed.

Clearly the distinction between absorption and scattering experiments is somewhat arbitrary, and can be just a matter of the time sequence or the nature of the intermediate state. For example, the diagrams for SRS and SEP are identical except that in SRS the intermediate state is non-resonant. The diagrams for LIGS and SEP are also identical except that the time sequence of "up" and "down" interacting electric fields has been switched. Generally, for an experiment to be labeled as an absorption/emission experiment the following must be true: i) the states must be resonant or near-resonant; and ii) the time ordering of the fields must be such that two successive fields act as a pair in the same direction, corresponding to an actual absorption/emission event ( $I_{\text{abs}} \sim |E|^2$ ). Thus, SEP can be done with two laser pulses: one which provides the first two field interactions to pump to the intermediate state, and one which provides the second two interactions to dump to the final state. In contrast, the LIGS scattering experiment requires three input pulses: one to provide the first "up"  $\mathbf{E}$ , one for the second "down"  $\mathbf{E}$ , one for the third "up"  $\mathbf{E}$ . Then the fourth scattered field is produced. If the first and third LIGS pulses become collinear and coincident in time, LIGS and SEP become indistinguishable.

To derive the absorption intensity for any  $\mathbf{P}^{(n)}$ , we start with the relation between the induced current density in a sample volume and the electromagnetic energy density change it causes in the absorbed field. From section 2b,

$$\frac{\partial u}{\partial t} = -\mathbf{j}(t) \cdot \mathbf{E}(t) \quad 12-87$$

where  $\mathbf{j}$  is the current induced in the sample by the first set of fields ( $n$  for a  $\chi^{(n)}$  process), and  $u$  is the energy density being absorbed when this induced molecular current interacts with the last field ( $E_{n+1}$ , the one shown in eq. 12-38). In general, there could also be a  $\nabla \cdot \mathbf{S}$  term, but we will assume that all losses of energy in the sample volume are due to absorption, not to radiation leaking out of the sample.

To dipole order, the current density can be expanded as (section 2b)

$$\mathbf{j} = \mathbf{j}_0 + \frac{\partial \mathbf{P}}{\partial t} + \dots = \frac{\partial \mathbf{P}}{\partial t} \quad 12-88$$

in the absence of a dc current. For an  $n^{\text{th}}$  order induced polarization, eq. 12-38 therefore becomes

$$\frac{\partial u}{\partial t} \left( \frac{\Delta \omega}{\omega' + \omega} \right) = -\frac{\partial \mathbf{P}^{(n)}}{\partial t} \cdot \mathbf{E}(t). \quad 12-89$$

If  $\mathbf{E}(t)$  propagates along the z-axis, the absorbed power per unit area (intensity) over a length  $\Delta z$  is

$$\frac{\partial u}{\partial t} \Delta z = -\frac{\partial \mathbf{P}^{(n)}}{\partial t} \cdot \mathbf{E}(t) \Delta z = -dI_{abs} \left( \frac{W}{cm^2} \right). \quad 12-90$$

Thus, if  $\mathbf{P}^{(n)}$  can be derived from  $\chi^{(n)}$  using eqs. 12-9 or 12-14, the absorption in any experiment can be calculated. The time-integrated absorbed intensity is

$$I_{abs} \text{ (Joules/m}^2\text{)} = \Delta z \int_{-\infty}^{\infty} dt \frac{\partial \mathbf{P}^{(n)}}{\partial t} \cdot \mathbf{E}(t) \quad 12-91$$

Note that  $I_{abs} \rightarrow \infty$  unless  $\mathbf{E}(t)$  is of finite duration.

Eq. 12-91 can also be recast in the frequency domain. From the Wiener-Khinchine theorem (Appendix A),

$$I_{abs} = \int_{-\infty}^{\infty} I(t) dt = \int_{-\infty}^{\infty} I(\omega) d\omega \quad 12-92$$

the absorbed intensity is independent whether it is evaluated by frequency or time integration. Starting with eq. 12-42 and inserting the Fourier transform expressions for  $\mathbf{P}(t)$  in terms of  $\mathbf{P}(\omega)$  and  $\mathbf{E}(t)$  in terms of  $\mathbf{E}(\omega)$ ,

$$\begin{aligned} I_{abs} &= \Delta z \int_{-\infty}^{\infty} dt \frac{\partial}{\partial t} \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \mathbf{P}^{(n)}(\omega) e^{-i\omega t} \right\} \cdot \left\{ \int_{-\infty}^{\infty} d\omega' \mathbf{E}(\omega') e^{-i\omega' t} \right\} \\ &= \frac{\Delta z}{2\pi} \int_{-\infty}^{\infty} dt \left\{ \int_{-\infty}^{\infty} d\omega (-i\omega) \mathbf{P}^{(n)}(\omega) e^{-i\omega t} \right\} \cdot \left\{ \int_{-\infty}^{\infty} d\omega' \mathbf{E}(\omega') e^{-i\omega' t} \right\} \\ &= \frac{-i\Delta z}{2\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \omega \mathbf{P}^{(n)}(\omega) \cdot \mathbf{E}(\omega') \int_{-\infty}^{\infty} dt e^{-i(\omega + \omega')t} \\ &= -i\Delta z \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \omega \mathbf{P}^{(n)}(\omega) \cdot \mathbf{E}(\omega') \delta(\omega + \omega') \\ &= -i\Delta z \int_{-\infty}^{\infty} d\omega \omega \mathbf{P}^{(n)}(\omega) \cdot \mathbf{E}(-\omega) \end{aligned} \quad 12-93$$

Comparing to eq. 12-92, the intensity as a function of frequency is

$$I(\omega) = \frac{J}{m^2 Hz} = -i\omega \Delta z \mathbf{P}^{(n)}(\omega) \cdot \mathbf{E}^*(\omega) \quad 12-94$$

since  $\mathbf{E}(-\omega) = \mathbf{E}^*(\omega)$ .

As a simple example, consider linear absorption in an isotropic medium, which was already derived by different means in c):  $\mathbf{P}^{(1)}(\omega) = \mathbf{P}(\omega) = \chi^{(1)}(\omega) \mathbf{E}(\omega)$  at frequency  $\omega$ , where  $\chi$  is just a scalar. As usual, the total intensity absorbed is the sum over the positive and negative frequency components (the integral in eq. 12-44 is over negative and positive  $\omega$ ), and

$$\begin{aligned} I_{abs} &= I(\omega) + I(-\omega) = -i\omega \Delta z \chi^{(1)}(\omega) \mathbf{E}(\omega) \cdot \mathbf{E}^*(\omega) + i\omega \Delta z \chi^{(1)}(-\omega) \mathbf{E}(-\omega) \cdot \mathbf{E}^*(-\omega) \\ &= \frac{2\pi\omega}{c} I_{in} i(\chi^{(1)}(\omega) - \chi^{(1)*}(\omega)) \Delta z \\ &= \frac{4\pi\omega}{c} \chi_i^{(1)}(\omega) I_{in} \Delta z = \alpha I_{in} \Delta z. \end{aligned} \quad 12-95$$

Eq. 12-95 is again just Beer's law with absorption coefficient  $\alpha$  given in terms of the imaginary part of the molecular susceptibility. For higher-order processes,  $\mathbf{P}^{(n)}$  may depend on  $\Delta z$  and absorption is not necessarily linear in pathlength.