

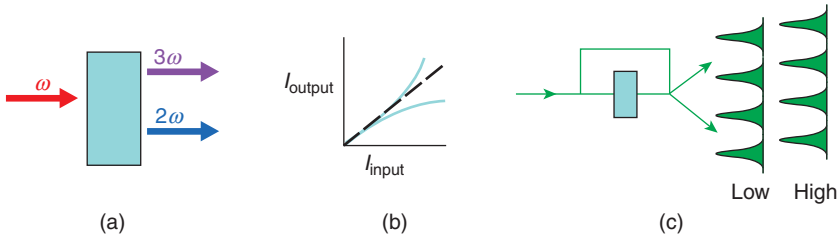
# Introduction

## 1.1 WHAT IS NONLINEAR OPTICS AND WHAT IS IT GOOD FOR?

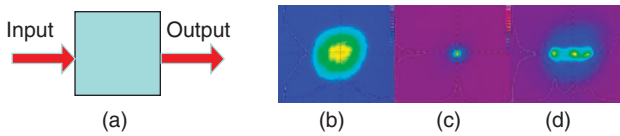
In general, nonlinear optics takes place when optical phenomena occur in materials that *change optical properties with input power or energy* and/or *generate new beams or frequencies*. Examples are power-, intensity-, or flux-dependent changes in the frequency spectrum of light, the transmission coefficient, the polarization, and/or the phase. New beams can also be generated either by a shift in frequency from the original frequency or by travelling in different directions relative to the incident beam. Although one frequently refers to the intensity or power dependence of phenomena as being signatures of nonlinear optics, there are many cases characterized by a flux dependence, i.e., changes in beam properties that are cumulative in the illumination time, usually accompanied by absorption.

A frequently asked question is: “How do I really know when nonlinear optics is occurring in my experiment?” Some examples of commonly observed phenomena are shown in Figs 1.1 and 1.2. Figure 1.1a shows harmonic generation, a second- or third-order nonlinear effect. Figure 1.1b shows nonlinear transmission, essentially a third-order nonlinear effect. In an interference experiment an increase in the input intensity can lead to a shift in fringes due to second- or third-order nonlinear optics (see Fig. 1.1c). A very common effect—self-focusing of light—is illustrated in Fig. 1.2, in which a beam narrows with an increase in the input intensity due to propagation through a sample, forming a soliton at high intensities that propagates without change in size or shape and then breaks up into “noise” filaments, i.e., multiple nondiffracting beams, at very high intensities.

The second most frequently asked question is: “What is nonlinear optics good for?” A collage of applications is shown schematically in Fig. 1.3. Probably the most frequently used nonlinear optics device is the second harmonic generator, which doubles the frequency of light, as shown in Fig. 1.1a. Along the same lines are optical parametric devices, also based on second-order nonlinearities, which include amplifiers (optical parametric amplifiers) and frequency-tunable generators (optical parametric generators and optical parametric oscillators), and the last two are commonly used as sources of tunable radiation (see Fig. 1.3a). Nonlinear absorption



**FIGURE 1.1** (a) Second and third harmonic generation. (b) Nonlinear transmission. (c) Nonlinear fringe shift between low and high intensity inputs.

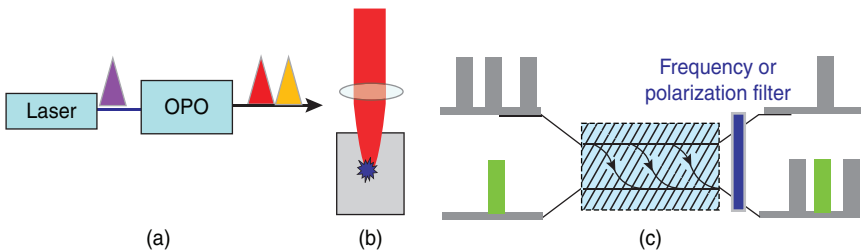


**FIGURE 1.2** (a) Beam input and output geometry. (b) Diffracted output beam at low intensity input. (c) Self-focused output beam corresponding to a spatial soliton. (d) Multiple filaments in the output beam at very high intensity.

that depends on intensity is used for the localized activation of drugs or imaging inside media (Fig. 1.3b). A third example is an all-optical control of optical signals, e.g., for communications (Fig. 1.3c).

## 1.2 NOTATION

The diversity of notations used for optical fields, nonlinear susceptibilities, and so on, is a frequently confusing aspect of this field. A perusal of the nonlinear optics literature shows that there is little consistency, especially when dealing with third-order nonlinear coefficients. Here a concentrated effort has been made to be consistent and to introduce more descriptive notations. The assumptions and notation used here are as follows:



**FIGURE 1.3** (a) An optical parametric oscillator (OPO) for producing two tunable frequencies. (b) Two-photon absorption activation of chemistry. (c) All-optical control of routing in a nonlinear coupler. A control beam (lower input arm) is used to isolate (switch out) a single pulse from the input pulse train.

1. *Plane waves* will be explicitly assumed to elucidate nonlinear phenomena in the simplest fashion. Whenever finite beams are considered, which is normally necessary to discuss devices and applications, this will be clearly stated.
2. *Continuous-wave fields* are explicitly assumed unless otherwise stated. The electromagnetic fields are written as

$$\vec{E}(\vec{r}, t) = \frac{1}{2} \vec{E}(\omega) e^{-i\omega t} + \text{c.c.} = \frac{1}{2} \vec{E}(\omega) e^{i[kz - \omega t]} + \text{c.c.} \quad (1.1)$$

3. The unit vector is written as  $\hat{e}$  and has components  $\hat{e}_i$ , where  $i = x, y, z$ .
4. The ‘‘Einstein’’ notation is used for summations over repeated indices; e.g.,  $a_i b_i c_i = a_x b_x c_x + a_y b_y c_y + a_z b_z c_z$ .
5. Quantities with a ‘‘bar’’ above, e.g.,  $\bar{\mu}$ , refer to individual molecular properties in the absence of interaction with other molecules as well as parameters in a single molecule’s frame of reference.
6. Quantities with a ‘‘tilde’’ above, e.g.,  $\tilde{\chi}_{ijk}^{(2)}$ , identify parameters and coefficients in the ‘‘zero (nonresonant) frequency’’ limit (Kleinman limit)  $\omega \ll \bar{\omega}_r$ , i.e., at frequencies much smaller than any resonant frequency  $\bar{\omega}_r$  of the material.
7. SI units are used throughout. Here intensity is used to mean power per unit area, usually in units of watts per square centimeter. It is equivalent to irradiance. In the cases of pulses of light, flux per unit area is defined as the integrated intensity of a pulse over time, typically over the duration of the pulse. Flux is defined as the energy of a pulse integrated over both time and cross section.

It is important to realize that in this textbook  $\vec{E}(\omega)$  is *not* the Fourier transform of  $\vec{E}(t)$  and its use is restricted to Eq. 1.1. For a monochromatic wave of frequency  $\omega_a$ ,  $E_i(\omega_a)$  is the notation used for the Fourier transform of the field and  $E_i(\omega_a) \neq E_i(\omega_a)$ . The relations between the two can be derived easily from the unitary Fourier transform equations:

$$\begin{aligned} E(t) &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} E(\omega) e^{-i\omega t} d\omega; & E(\omega) &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} E(t') e^{i\omega t'} dt' \\ \delta(t-t') &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega(t-t')} d\omega; & \delta(\omega-\omega_a) &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{i(\omega-\omega_a)t'} dt'. \end{aligned} \quad (1.2)$$

Substituting Eq. 1.1 for  $E(t')$  into the  $E(\omega)$  equation in Eq. 1.2 gives

$$\begin{aligned} E_i(\omega) &= \sqrt{\frac{1}{2\pi}} \frac{1}{2} \left\{ \int_{-\infty}^{\infty} E_i(\omega_a) e^{i(\omega-\omega_a)t} dt + \int_{-\infty}^{\infty} E_i^*(\omega_a) e^{i(\omega+\omega_a)t} dt \right\} \\ &= \frac{1}{2} \left\{ E_i(\omega_a) \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{i(\omega-\omega_a)t} dt + E_i^*(\omega_a) \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{i(\omega+\omega_a)t} dt \right\} \\ &\rightarrow E_i(\omega) = \frac{1}{2} [E_i(\omega_a) \delta(\omega-\omega_a) + E_i(-\omega_a) \delta(\omega+\omega_a)]. \end{aligned} \quad (1.3)$$

If fields have a distribution of frequencies, then the  $\delta$  functions are replaced by  $g(\omega - \omega_a)$  and  $g(\omega + \omega_a)$ , normalized so that their integrals over frequency are unity.

Additional notation will be introduced as needed in succeeding chapters.

### 1.3 CLASSICAL NONLINEAR OPTICS EXPANSION

The simplest and most general expansion of the nonlinear polarization induced by the mixing of optical fields is

$$\begin{aligned}
 P_i(\vec{r}, t) = \epsilon_0 & \left[ \int_{-\infty}^{\infty} \int_{-\infty}^t \hat{\chi}_{ij}^{(1)}(\vec{r}-\vec{r}'; t-t') E_j(\vec{r}', t') d\vec{r}' dt' \right. \\
 & + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^t \int_{-\infty}^t \hat{\chi}_{ijk}^{(2)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}''; t-t', t-t'') E_j(\vec{r}', t') E_k(\vec{r}'', t'') d\vec{r}' d\vec{r}'' dt' dt'' \\
 & + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t \hat{\chi}_{ijkl}^{(3)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}'', \vec{r}-\vec{r}'''; t-t', t-t'', t-t''') \\
 & \left. \times E_j(\vec{r}', t') E_k(\vec{r}'', t'') E_l(\vec{r}''', t''') d\vec{r}' d\vec{r}'' d\vec{r}''' dt' dt'' dt''' + \dots \right] \text{ with} \\
 & \int_{-\infty}^{\infty} d\vec{r}' \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx' dy' dz' \tag{1.4}
 \end{aligned}$$

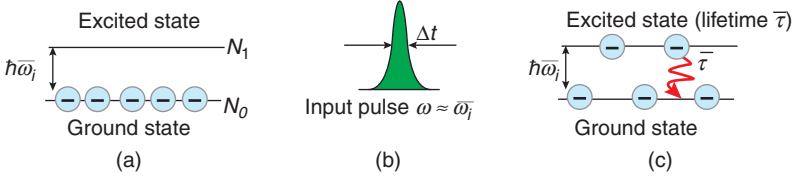
To understand the physical implications of this formula, consider the first nonlinear term due to the second-order susceptibility, i.e.,  $\hat{\chi}_{ijk}^{(2)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}''; t-t', t-t'')$ . The polarization  $P_i(\vec{r}, t)$  is created at time  $t$  and position  $\vec{r}$  by two separate interactions of the total electromagnetic field at time  $t'$  and position  $\vec{r}'$  and at time  $t''$  and position  $\vec{r}''$  in a material in which  $\chi^{(2)} \neq 0$ . This form also includes nonlocal-in-space effects, such as thermal nonlinearities, in which the refractive index changes due to absorption, e.g., diffuses. In most cases encountered on optics, the response is local in space and so

$$\hat{\chi}_{ijk}^{(2)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}''; t-t', t-t'') \rightarrow \hat{\chi}_{ijk}^{(2)}(t-t'; t-t'') \delta(\vec{r}-\vec{r}') \delta(\vec{r}-\vec{r}'') \tag{1.5}$$

and

$$P_i^{(2)}(\vec{r}, t) = \epsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{\chi}_{ijk}^{(2)}(t-t', t-t'') E_j(\vec{r}, t') E_k(\vec{r}, t'') dt' dt''. \tag{1.6}$$

Only near a “resonance” does a noninstantaneous response typically occur for Kerr-type nonlinearities. A noninstantaneous time response translates into a frequency dependence for all the susceptibilities. An example of how a noninstantaneous response occurs is shown in Fig. 1.4 for a simple two-level model.



**FIGURE 1.4** (a) Two-level model with all electrons initially in the ground state  $N_0$ . (b) Incidence of a short pulse ( $\Delta t \ll \bar{\tau}$ ) causes many electron transitions to the excited state. (c) Excited-state population after the pulse passes.

As the excited-state electrons relax back to the ground state, the induced polarization relaxes back to the ground-state polarization, leading to time evolution in both the refractive index and the absorption coefficient, as illustrated in Fig. 1.5. The Fourier transform of this time evolution gives the frequency response.

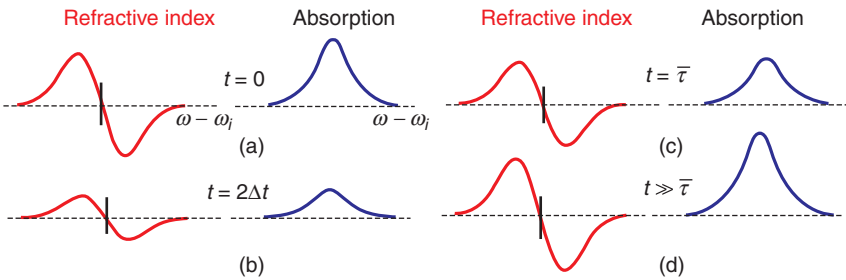
Equation 1.4 is not the one normally used because of its complexity. Assuming plane waves of the form

$$P_i(\vec{r}, t) = \frac{1}{2} P_i(\omega, z) e^{-i\omega t} + \text{c.c.}, \quad E_i(\vec{r}, t) = \frac{1}{2} \sum_m E_i^m(\omega_m, z) e^{-i\omega_m t} + \text{c.c.},$$

$$E_j^m(-\omega_m) = E_j^{*m}(\omega_m) \quad (1.7)$$

and expanding again in terms of the total field gives

$$P_i(\omega, z) e^{-i\omega t} = \varepsilon_0 \left[ \hat{\chi}_{ij}^{(1)}(-\omega; \omega_m) \sum_m E_j^m(\omega_m, z) e^{-i\omega_m t} \right. \\ + \frac{1}{2} \sum_m \sum_p \hat{\chi}_{ijk}^{(2)}(-\omega; \pm\omega_m, \pm\omega_p) E_j^m(\pm\omega_m, z) E_k^p(\pm\omega_p, z) e^{-i(\pm\omega_m \pm \omega_p)t} \\ + \frac{1}{4} \sum_m \sum_p \sum_q \hat{\chi}_{ijkl}^{(3)}(-\omega; \pm\omega_m, \pm\omega_p, \pm\omega_q) E_j^m(\pm\omega_m, z) E_k^p(\pm\omega_p, z) \\ \left. \times E_\ell^q(\pm\omega_q, z) e^{-i(\pm\omega_m \pm \omega_p \pm \omega_q)t} + \dots \right] \quad (1.8)$$



**FIGURE 1.5** (a) Spectral distribution of refractive index and absorption before the incidence of the pulse ( $t = 0$ ). (b)–(d) Time evolution of refractive index and absorption:  $t = 2\Delta t$  (b);  $t = \bar{\tau}$  (c), and  $\Delta t \gg \bar{\tau}$  (d).

In each case,  $\omega = \pm\omega_m \pm \omega_p \pm \omega_q$  is the output frequency generated by the interaction. The hat (roof) superscript is meant to emphasize that the quantity underneath is a complex number.

A key question is the order of magnitude of the nonlinear susceptibilities. The simplest atom is hydrogen. Its structure and spectrum of excited states is well known and is simple to calculate since it has only one electron, the minimum needed for the interaction of electromagnetic radiation with matter. The atomic Coulomb field binding the electron to the proton in its orbit of Bohr radius  $r_B$  is given by

$$E_{\text{atomic}} = \frac{\bar{e}}{4\pi\epsilon_0 r_B^2}, \quad r_B = \frac{4\pi\epsilon_0 \hbar^2}{\bar{m}_e \bar{e}^2}, \quad (1.9)$$

in which  $\bar{e}$  is the charge on the electron ( $-1.6 \times 10^{-19}$  C),  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F/m),  $\bar{m}_e$  ( $=9.11 \times 10^{-31}$  kg) is the electron mass, and  $h = 2\pi\hbar = 6.63 \times 10^{-34}$  J s is Planck's constant. Equation 1.9 gives the order of magnitude of  $E_{\text{atomic}} = 10^{12}$  V/m. It is reasonable to adopt this field as an approximate field at which nonlinear optics becomes important. Since  $\chi^{(1)} = n^2 - 1$  (where  $n$  is the refractive index of the order of unity) for a perturbation expansion in terms of products of electric fields to be valid,  $P^{(1)} \geq 10 \times P^{(2)}$ :

$$\frac{P^{(1)}}{P^{(2)}} = \frac{\chi^{(1)}}{\chi^{(2)}E} \approx \frac{1}{\chi^{(2)}E_{\text{atomic}}} \approx 10 \quad \rightarrow \quad \chi^{(2)} \approx 10^{-13} \text{ m/V}. \quad (1.10)$$

This is a reasonable estimate for the lower limit value of the second-order susceptibility, especially since the field was based on hydrogen, which has only a single electron and proton. Following the same approximations but now assuming that

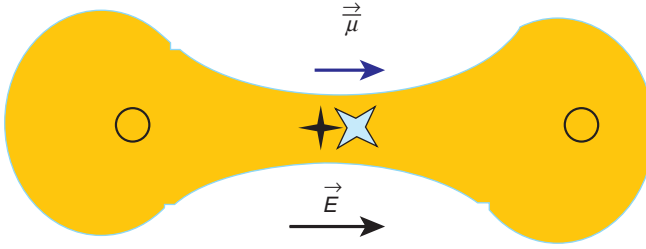
$$\frac{P^{(1)}}{P^{(3)}} = \frac{\chi^{(1)}}{\chi^{(3)}E^2} \approx \frac{\chi^{(1)}}{\chi^{(3)}E_{\text{atomic}}^2} \approx 10 \quad \rightarrow \quad \chi^{(3)} \approx 10^{-25} \text{ m}^2/\text{V}^2. \quad (1.11)$$

As will become clear later, these approximate values are close to the minimum values found for these susceptibilities.

## 1.4 SIMPLE MODEL: ELECTRON ON A SPRING AND ITS APPLICATION TO LINEAR OPTICS

There are many physical mechanisms that lead to nonlinear optical phenomena. Initially, the focus here is on transitions between the electronic states associated with atoms and molecules in matter. Although the appropriate treatment (Chapter 8) for completely describing the interaction of radiation with atoms and molecules involves quantum mechanics, initially a simpler classical approach that provides a useful description of the *linear* (and as it turns out exact) susceptibility is adopted.

As an example of this approach, consider the molecule  $\text{O}_2$  and its electron cloud, as illustrated in Fig. 1.6. This molecule has inversion symmetry (i.e., a center of



**FIGURE 1.6** The oxygen molecule  $O_2$ , its center of mass ✕, and positive and negative charges in the absence of the field. After the field is applied, + is the center of the negative charge and the electron cloud is shifted (and distorted) from its original position.

symmetry halfway between the oxygen atoms) and hence has no permanent dipole moment since the centers of positive (nuclei) and negative charges are coincident. When an electric field

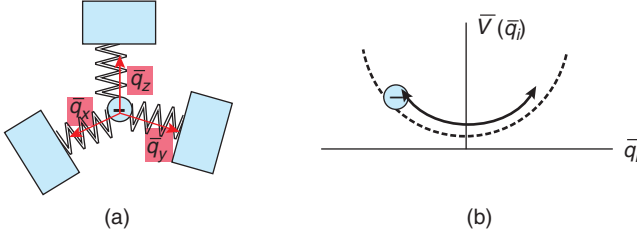
$$\vec{E}(\vec{r}, t) = \frac{1}{2} E_x(\omega_a) e^{i(kz - \omega_a t)} + \text{c.c.} \quad (1.12)$$

is applied along the molecular axis ( $+x$ -axis), the negative and positive charges and their centers of charge are displaced in opposite directions by the Coulomb forces, giving rise to the forces  $\bar{m}_{e,n}\ddot{x}_{e,n}$ , where  $\bar{m}_e$  and  $x_e$  are the electron mass and its displacement and  $\bar{m}_n$  and  $x_n$  are the nuclear mass and its displacement, respectively. Since  $\bar{m}_n \gg \bar{m}_e$ , only the displacements of the electrons are important for inducing dipoles.

The electrons are bound to the nucleus (atoms) or nuclei (molecules) by Coulomb forces and, for isolated atoms or molecules, exist in discrete states  $m$  with an energy  $\hbar(\bar{\omega}_m - \bar{\omega}_g) = \hbar\bar{\omega}_{mg}$  above the ground state and an excited-state lifetime  $\bar{\tau}_{mg}$ . They move in “orbits” around nuclei described by probability density functions  $\psi_m(\vec{r}, t)$ , with  $|\psi_m(\vec{r}, t)|^2 dx dy dz dt$  giving the probability that the electron “exists” at time  $t$  in the volume element  $dx dy dz$  at position  $\vec{r}$ . Since “optics” usually deals with the spectral region longer in wavelength (smaller in frequency) than the low frequency absorption edge of the material determined by the transitions between electronic states, the electron in the lowest lying energy level is normally the prime participant when radiation interacts with matter; i.e., it is the electron with the largest displacement. With these approximations, the dipole moment induced by an electromagnetic field is  $\bar{\mu}_x = \bar{e}_e x_e$ , as shown in Fig. 1.6. For the most general case,  $\bar{\mu}_i = \bar{\alpha}_{ij} E_j$ , where  $\bar{\alpha}_{ij}$  is the polarizability tensor, and the induced dipole and the electric field are not necessarily collinear.

In linear optics, it is possible to diagonalize the polarizability tensor. The deflections  $\vec{q} = \hat{e}_x \bar{q}_x + \hat{e}_y \bar{q}_y + \hat{e}_z \bar{q}_z$  of this representative electron are defined in terms of these axes and so  $\vec{\mu} = -\bar{e} \vec{q}$ . (Note, however, that for very anisotropic crystal classes the coordinate system may be nonorthogonal and/or frequency dependent.)

The Coulomb interaction between the net positive and negative charges provides a restoring force that oscillates at the frequency of the applied field, and so the motion of



**FIGURE 1.7** (a) Electron connected via three springs oriented along the axes that diagonalize the polarizability. (b) One-dimensional cut of the three-dimensional parabolic potential well inside which the electron oscillates at the frequency of an applied field.

the electron can be described as a simple harmonic oscillator. In three dimensions, this can be visualized as the electron attached to three orthogonal springs, as illustrated in Fig. 1.7a, and the electron motion can be described as oscillation in a harmonic potential well.

The equation of motion of an electron is described by a simple harmonic oscillator with the potential

$$\bar{V}^{(m)}(\bar{q}) = \frac{1}{2} \bar{k}_{ii}^{(m)} \bar{q}_i^{(m)} \bar{q}_i^{(m)}. \quad (1.13)$$

From classical mechanics, the restoring force is given by

$$\bar{F}_i^{(m)} = -\frac{\partial \bar{V}^{(m)}}{\partial \bar{q}_i^{(m)}} = -\frac{1}{2} \bar{k}_{ii}^{(m)} \left[ \frac{\partial \bar{q}_i^{(m)}}{\partial \bar{q}_i^{(m)}} \bar{q}_i^{(m)} + \bar{q}_i^{(m)} \frac{\partial \bar{q}_i^{(m)}}{\partial \bar{q}_i^{(m)}} \right] = -\bar{k}_{ii}^{(m)} \bar{q}_i^{(m)}, \quad (1.14)$$

in which the spring constant  $\bar{k}_{ii}^{(m)}$  is defined in terms of the excited state's energy by  $\bar{\omega}_{mg} = \sqrt{\bar{k}_{ii}^{(m)} / \bar{m}_e}$  and the restoring force is given by  $\bar{F}_i^{(m)} = \bar{m}_e \bar{\omega}_{mg}^2 \bar{q}_i^{(m)}$ . The inertial force is  $\bar{m}_e \ddot{\bar{q}}_i^{(m)}$ . Therefore, the force balance equation describing the electron motion in a simple harmonic oscillator model is

$$\begin{aligned} \bar{m}_e \left[ \ddot{\bar{q}}_i^{(m)} + 2\bar{\tau}_{mg}^{-1} \dot{\bar{q}}_i^{(m)} + \bar{\omega}_{mg}^2 \bar{q}_i^{(m)} \right] &= -\bar{e} E_i \\ \rightarrow \left[ \bar{\omega}_{mg}^2 - \omega_a^2 - 2i\omega_a \bar{\tau}_{mg}^{-1} \right] \bar{q}_i^{(m)}(t) &= -\frac{\bar{e}}{\bar{m}_e} E_i(t). \end{aligned} \quad (1.15)$$

Assuming

$$\bar{q}_i^{(m)} = \frac{1}{2} \bar{Q}_i^{(m)} e^{-i\omega_a t} + \text{c.c.} \quad \rightarrow \quad \bar{Q}_i^{(m)} = -\frac{\bar{e} E_i(\omega_a)}{\bar{m}_e D_i^{(m)}(\omega_a)}, \quad (1.16)$$

where  $D_i^{(m)}(\omega_a) = -\omega_a^2 - 2i\omega_a\bar{\tau}_{mg}^{-1} + \bar{\omega}_{mg}^2$  is the resonance denominator. When  $\omega_a \approx \bar{\omega}_{mg}$ , the amplitude of the displacement is enhanced. Note that  $\bar{e}_e = -\bar{e}$  and that in the zero-frequency limit,  $D_i^{(m)}(\omega_a) = \bar{\omega}_{mg}^2$  and  $\bar{Q}_i^{(m)} = -\bar{e}E_i(\omega_a)/\bar{m}_e\bar{\omega}_{mg}^2$  is just a net steady-state displacement of the electron.

For a dilute medium with  $N$  noninteracting atoms (molecules) per unit volume, the induced linear polarization and the first-order susceptibility  $\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)$  are given as follows:

$$\begin{aligned}
 P_i(t) &= -N\bar{e} \sum_m \left\{ \frac{1}{2} \bar{Q}_i^{(m)} e^{-i\omega_a t} + \text{c.c.} \right\} = \frac{1}{2} P_i(\omega_a) e^{-i\omega_a t} + \text{c.c.} \\
 P_i(\omega_a) &= \frac{N\bar{e}^2}{\bar{m}_e} E_i(\omega_a) \sum_m \frac{1}{D_i^{(m)}(\omega_a)} = \varepsilon_0 \hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a) E_i(\omega_a) \\
 \rightarrow \hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a) &= \frac{N\bar{e}^2}{\varepsilon_0 \bar{m}_e(\omega_a)} \sum_m \frac{1}{D_i^{(m)}(\omega_a)}.
 \end{aligned} \tag{1.17}$$

The fact that  $\hat{\chi}_{ij}^{(1)}(-\omega_a; \omega_a)$  is a diagonal tensor is a direct consequence of choosing a coordinate system in which the polarizability tensor is diagonal.

The first-order susceptibility  $\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)$  can easily be defined in terms of  $\hat{\chi}_{ii}^{(1)}(\vec{r}-\vec{r}'; t-t')$ . From Eq. 1.4,

$$P_i^{(1)}(t) = \varepsilon_0 \left[ \int \hat{\chi}_{ij}^{(1)}(t-t') E_j(t') d(t-t') \right] = \frac{1}{2} P_i^{(1)}(\omega_a) e^{-i\omega_a t} + \text{c.c.} \tag{1.18}$$

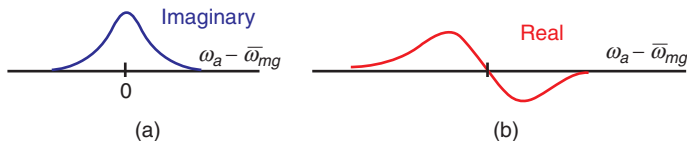
Substituting for the field  $E_j(t')$  gives

$$\begin{aligned}
 P_i^{(1)}(t) &= \frac{\varepsilon_0}{2} \left[ \int \hat{\chi}_{ij}^{(1)}(t-t') [E_j(\omega_a) e^{-i\omega_a t'} + \text{c.c.}] d(t-t') \right] \\
 &= \frac{1}{2} \varepsilon_0 E_j(\omega_a) e^{-i\omega_a t} \int_{-\infty}^{\infty} \hat{\chi}_{ij}^{(1)}(t-t') e^{i\omega_a(t-t')} d(t-t') + \text{c.c.} \\
 \rightarrow \hat{\chi}_{ij}^{(1)}(-\omega_a; \omega_a) &= \int_{-\infty}^{\infty} \hat{\chi}_{ij}^{(1)}(t-t') e^{i\omega_a(t-t')} d(t-t'),
 \end{aligned} \tag{1.19}$$

i.e.,  $\hat{\chi}_{ij}^{(1)}(-\omega_a; \omega_a)$  is the Fourier transform of  $\hat{\chi}_{ij}^{(1)}(t-t')$ .

Decomposing  $\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)$  into its real and imaginary components yields

$$\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a) = \frac{N\bar{e}^2}{\bar{m}_e \varepsilon_0} \sum_m \frac{(\bar{\omega}_{mg}^2 - \omega_a^2) + 2i\omega_a\bar{\tau}_{mg}^{-1}}{(\bar{\omega}_{mg}^2 - \omega_a^2)^2 + 4\omega_a^2\bar{\tau}_{mg}^{-2}}. \tag{1.20a}$$



**FIGURE 1.8** Spectral dispersion of the (a) imaginary and (b) real parts of  $\hat{\chi}_{ii}^{(1)}(-\omega; \omega)$ .

This equation is always valid. It can be simplified near and on resonance ( $\omega_a \approx \bar{\omega}_{mg}$ ) to give

$$\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a) = \frac{N\bar{e}^2}{2\bar{\omega}_{mg}\bar{m}_e\epsilon_0} \sum_m \frac{\bar{\omega}_{mg} - \omega_a + i\bar{\tau}_{mg}^{-1}}{(\bar{\omega}_{mg} - \omega_a)^2 + \bar{\tau}_{mg}^{-2}} \quad (1.20b)$$

and off resonance ( $|\omega_{mg} - \omega_p| \bar{\tau}_{mg} \gg 1$ ) to give

$$\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a) = \frac{N\bar{e}^2}{2\bar{\omega}_{mg}\bar{m}_e\epsilon_0} \sum_m \frac{\bar{\omega}_{mg} - \omega_a + i\bar{\tau}_{mg}^{-1}}{(\bar{\omega}_{mg} - \omega_a)^2}. \quad (1.20c)$$

Figure 1.8 shows the frequency dispersion in the imaginary and real parts of  $\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)$  for a single excited state.

The refractive index and the absorption coefficient (for the field) are defined in the usual way by  $n^2(\omega) = 1 + \Re\{\hat{\chi}_{ii}^{(1)}(-\omega; \omega)\}$  and  $\alpha(\omega) = k_{\text{vac}} \Im\{\hat{\chi}_{ii}^{(1)}(-\omega; \omega)\} / 2n(\omega)$ , respectively. Note that the absorption spectrum, i.e.,  $\alpha(\omega)$ , has contributions only from transitions from the ground state that are electric dipole allowed. For symmetric molecules in which the states are described by wave functions that are either symmetric or antisymmetric in space, the linear absorption spectrum does not contain contributions from the even-symmetry excited states because electric dipole transitions from the even-symmetry ground state are not dipole allowed.

As stated previously, optics normally refers to electromagnetic waves in the spectral region defined by frequencies below the lowest lying electronic resonance due to electric dipole transitions. Assuming that  $|\bar{\omega}_{mg} - \omega_a| \bar{\tau}_{mg}^{-1} \gg 1$ ,  $\Im\{\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)\}$  decreases faster with increasing frequency difference from the resonance  $|\bar{\omega}_{mg} - \omega_a|$  than does  $\Re\{\hat{\chi}_{ii}^{(1)}(-\omega_a; \omega_a)\}$ . This will also be the case for the real and imaginary parts of the nonlinear susceptibilities.

## 1.5 LOCAL FIELD CORRECTION

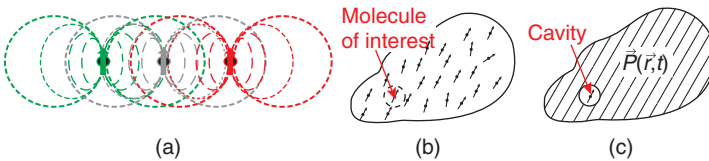
Although local field correction is discussed in most introductory textbooks on optics, it will prove useful to repeat it here since the transition to nonlinear optics is not straightforward. The preceding analysis for the linear susceptibility was for a single isolated atom or molecule and, to a good approximation, for a dilute gas. The situation is more complex in dense gases or condensed matter (liquids and solids) where the atoms and molecules interact with one another via the dipole fields induced by an applied optical field.

Experiments are usually performed with an optical field incident onto a nonlinear material from another medium, typically air. Maxwell's equations in the material and the usual boundary conditions at the interface are valid for spatial averages of the fields over volume elements small on the scale of a wavelength, but large on the scale of a molecule. The "averaged" quantities also include the refractive index, the Poynting vector, and the so-called Maxwell field, which has been written here as  $\vec{E}(\vec{r}, t)$ . It is the Maxwell field that satisfies the wave equation for a material with the averaged refractive index  $n$ .

However, at the site of a molecule the situation can be quite complex since the dipoles induced by the Maxwell electric fields on all the molecules create their own electric fields, which must be added to the "averaged" field to obtain the total ("local") field  $\vec{E}_{\text{loc}}(\vec{r}, t)$  acting on a molecule, as shown in Fig. 1.9. In the low density limit, the dipolar fields decay essentially to zero with distance from their source dipole and so  $\vec{E}_{\text{loc}}(\vec{r}, t) \cong \vec{E}(\vec{r}, t)$  and the single molecule result is converted to a macroscopic polarization by multiplying the molecular result by  $N$ , the number of molecules per unit volume.

The situation is more complex in condensed matter. It is very difficult to calculate the "local" field accurately because it depends on crystal symmetry, intermolecular interactions, and so on. Standard treatments such as Lorenz–Lorenz are only approximately valid even for isotropic and cubic crystal media. Nevertheless, they are universally used. Here the usual formulation found in standard electromagnetic textbooks will be followed. The dipole moments of the molecules induced by the Maxwell field  $\vec{E}(\vec{r}, t)$  produce a Maxwell polarization  $\vec{P}(\vec{r}, t) = \epsilon_0 \chi^{(1)} : \vec{E}(\vec{r}, t)$  in the material. Consider a spherical cavity around the molecule of interest to find the local field acting on the molecule (see Fig. 1.9c). Assuming that the effects of the induced dipoles inside the cavity average to zero, the polarization field outside the cavity induces charges on the walls of the cavity, which produce an additional electric field on the molecule in the cavity (see standard texts on electrostatics):

$$\left\langle \sum \vec{E}_{\text{dipoles}}(\vec{r}, t) \right\rangle = \frac{1}{3\epsilon_0} \vec{P}(\vec{r}, t) \quad \rightarrow \quad \vec{E}_{\text{loc}}(\vec{r}, t) = \vec{E}(\vec{r}, t) + \frac{1}{3\epsilon_0} \vec{P}^{(1)}(\vec{r}, t). \quad (1.21)$$



**FIGURE 1.9** (a) The local fields created by the induced dipoles in a medium. (b) Dipoles induced everywhere in the material. The average gives the Maxwell polarization  $\vec{P}(\vec{r}, t)$ . (c) Artificial spherical cavity assumed around the molecule of interest, embedded in a uniform medium with polarization  $\vec{P}(\vec{r}, t)$ .

The induced dipole on a molecule at the center of the cavity is now given by

$$\begin{aligned}
 \vec{p}^{(1)}(\vec{r}, t) &= \vec{\alpha} \cdot \left[ \vec{E}(\vec{r}, t) + \frac{1}{3\epsilon_0} \vec{P}^{(1)}(\vec{r}, t) \right] \\
 \rightarrow \vec{P}^{(1)}(\vec{r}, t) &= N\vec{\alpha} \cdot \left[ \vec{E}(\vec{r}, t) + \frac{1}{3\epsilon_0} \vec{P}^{(1)}(\vec{r}, t) \right] \\
 \rightarrow \left[ 1 - \frac{1}{3} N\vec{\alpha} \right] \cdot \vec{P}^{(1)}(\vec{r}, t) &= N\vec{\alpha} \cdot \vec{E}(\vec{r}, t). \tag{1.22}
 \end{aligned}$$

From the Clausius–Mossotti relation that connects the macroscopic relative dielectric constant to the molecular polarizability,

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3} \langle N\vec{\alpha} \rangle \quad \rightarrow \quad \vec{P}^{(1)}(\vec{r}, t) = \frac{\epsilon_r + 2}{3} N\vec{\alpha} \cdot \vec{E}(\vec{r}, t), \tag{1.23}$$

and so the local field and the local field correction  $f^{(1)}$  is defined as

$$\vec{E}_{\text{loc}}(\vec{r}, t) = \frac{\epsilon_r(\omega_a) + 2}{3} \vec{E}(\vec{r}, t), \quad f^{(1)} = \frac{\epsilon_r + 2}{3}, \tag{1.24}$$

respectively, where  $\epsilon_r(\omega_a) = \epsilon(\omega_a)/\epsilon_0$ . Since the field driven displacement is now

$$\bar{Q}_i^{(m)} = -f^{(1)} \frac{\bar{e}E_i(\omega_a)}{\bar{m}_e D_i^{(m)}(\omega_a)}, \tag{1.25}$$

the linear susceptibility from Eq. 1.20a, including the local field correction, becomes

$$\chi_{ii}^{(1)}(-\omega_a; \omega_a) = \frac{Ne^2 f^{(1)}(\omega_a)}{\bar{m}_e \epsilon_0} \sum_m \frac{(\bar{\omega}_{mg}^2 - \omega_a^2) + 2i\omega_a \bar{\tau}_{mg}^{-1}}{(\bar{\omega}_{mg}^2 - \omega_a^2)^2 + 4\omega_a^2 \bar{\tau}_{mg}^{-2}}. \tag{1.26}$$

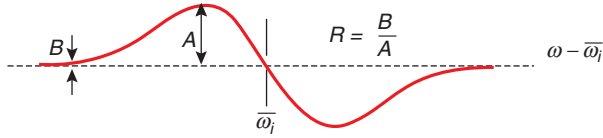
## PROBLEMS

1. The purpose of this problem is to show that absorption decreases much faster than refractive index with frequency difference from a resonance. Consider an isolated molecule with a single excited state with a transition frequency  $\bar{\omega}_i$  and a phenomenological decay constant  $\bar{\tau}_i^{-1}$ .

(a) Assuming that  $\bar{\tau}_i^{-1} \bar{\omega}_i \gg 1$  and  $\omega \approx \bar{\omega}_i$ , show that  $\chi^{(1)}$  can be written as

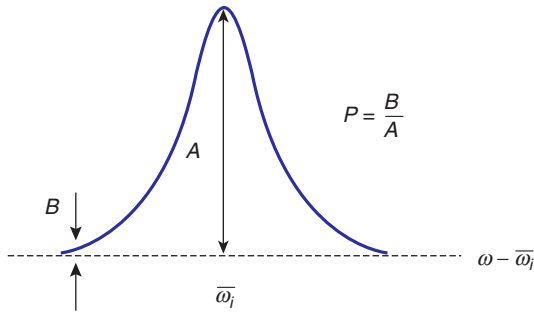
$$\begin{aligned}
 \hat{\chi}_{ii}^{(1)}(-\omega; \omega) &= \Re\{\hat{\chi}_{ii}^{(1)}\} + i \Im\{\hat{\chi}_{ii}^{(1)}\} \\
 &= \frac{Ne^2 (\bar{\omega}_i - \omega)}{2\bar{\omega}_i \bar{m}_e \epsilon_0 [(\bar{\omega}_i - \omega)^2 + \bar{\tau}_i^{-2}]} \\
 &\quad + i \frac{Ne^2 \omega \bar{\tau}_i^{-1}}{2\bar{\omega}_i^2 \bar{m}_e \epsilon_0 [(\bar{\omega}_i - \omega)^2 + \bar{\tau}_i^{-2}]}.
 \end{aligned}$$

- (b) Find the maximum change in the real part of the susceptibility and show that the ratio  $R$  of change at frequency  $\omega$  to maximum change occurs at a frequency shift given by  $\bar{\omega}_i - \omega \cong 2\bar{\tau}_i^{-1}/R$  for  $|\bar{\omega}_i - \omega| \gg 2\bar{\tau}_i^{-1}$ .



- (c) Find the maximum change in the imaginary part of the susceptibility and show that the ratio  $P$  of the change at frequency  $\omega$  to maximum change is given by

$$P = \frac{\bar{\tau}_i^{-2}}{[(\bar{\omega}_i - \omega)^2 + (\bar{\tau}_i^{-2})]}.$$



- (d) How small is  $P$  for values of  $R$  equal to 10%: 1%?

Although you have calculated this difference for the linear susceptibility, the results are also typical of what is obtained for higher order susceptibilities. A 10% or less “remnant” in the susceptibility is the upper limit for calling the value “nonresonant.”

### SUGGESTED FURTHER READING

B. I. Bleaney and B. Bleaney, *Electricity and Magnetism*, 2nd Edition (Oxford University Press, London, 1968).  
 M. Born and E. Wolf, *Principles of Optics*, 7th Edition (Cambridge University Press, Cambridge, UK, 1999).  
 R. W. Boyd, *Nonlinear Optics*, 3rd Edition (Academic Press, Burlington, MA, 2008).  
 F. A. Hopf and G. I. Stegeman, *Applied Classical Electrodynamics, Volume 1: Linear Optics* (John Wiley & Sons, New York, 1985).  
 D. L. Mills, *Nonlinear Optics: Basic Concepts*, 2nd Edition (Springer, New York, 1998).  
 Y. Ron Shen, *Principles of Nonlinear Optics* (John Wiley & Sons, New York, 1984).

