

Chapter 1

The Nonlinear Optical Susceptibility

1.1. Introduction to Nonlinear Optics

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken *et al.* (1961), shortly after the demonstration of the first working laser by Maiman in 1960.* Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. For example, second-harmonic generation occurs as a result of the part of the atomic response that scales quadratically with the strength of the applied optical field. Consequently, the intensity of the light generated at the second-harmonic frequency tends to increase as the square of the intensity of the applied laser light.

In order to describe more precisely what we mean by an optical nonlinearity, let us consider how the dipole moment per unit volume, or polarization $\tilde{P}(t)$, of a material system depends on the strength $\tilde{E}(t)$ of an applied optical

* It should be noted, however, that some nonlinear effects were discovered prior to the advent of the laser. The earliest example known to the authors is the observation of saturation effects in the luminescence of dye molecules reported by G.N. Lewis *et al.* (1941).

field.* In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in a manner that can often be described by the relationship

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t), \quad (1.1.1)$$

where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and ϵ_0 is the permittivity of free space. In nonlinear optics, the optical response can often be described by generalizing Eq. (1.1.1) by expressing the polarization $\tilde{P}(t)$ as a power series in the field strength $\tilde{E}(t)$ as

$$\begin{aligned} \tilde{P}(t) &= \epsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots] \\ &\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots \end{aligned} \quad (1.1.2)$$

The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second- and third-order nonlinear optical susceptibilities, respectively. For simplicity, we have taken the fields $\tilde{P}(t)$ and $\tilde{E}(t)$ to be scalar quantities in writing Eqs. (1.1.1) and (1.1.2). In Section 1.3 we show how to treat the vector nature of the fields; in such a case $\chi^{(1)}$ becomes a second-rank tensor, $\chi^{(2)}$ becomes a third-rank tensor, and so on. In writing Eqs. (1.1.1) and (1.1.2) in the forms shown, we have also assumed that the polarization at time t depends only on the instantaneous value of the electric field strength. The assumption that the medium responds instantaneously also implies (through the Kramers–Kronig relations[†]) that the medium must be lossless and dispersionless. We shall see in Section 1.3 how to generalize these equations for the case of a medium with dispersion and loss. In general, the nonlinear susceptibilities depend on the frequencies of the applied fields, but under our present assumption of instantaneous response, we take them to be constants.

We shall refer to $\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$ as the second-order nonlinear polarization and to $\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}^3(t)$ as the third-order nonlinear polarization. We shall see later in this section that physical processes that occur as a result of the second-order polarization $\tilde{P}^{(2)}$ tend to be distinct from those that occur as a result of the third-order polarization $\tilde{P}^{(3)}$. In addition, we shall show in Section 1.5 that second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals—that is, in crystals that do not display inversion symmetry. Since liquids, gases, amorphous solids (such as glass),

* Throughout the text, we use the tilde (\sim) to denote a quantity that varies rapidly in time. Constant quantities, slowly varying quantities, and Fourier amplitudes are written without the tilde. See, for example, Eq. (1.2.1).

[†] See, for example, Loudon (1973, Chapter 4) or the discussion in Section 1.7 of this book for a discussion of the Kramers–Kronig relations.

and even many crystals display inversion symmetry, $\chi^{(2)}$ vanishes identically for such media, and consequently such materials cannot produce second-order nonlinear optical interactions. On the other hand, third-order nonlinear optical interactions (i.e., those described by a $\chi^{(3)}$ susceptibility) can occur for both centrosymmetric and noncentrosymmetric media.

We shall see in later sections of this book how to calculate the values of the nonlinear susceptibilities for various physical mechanisms that lead to optical nonlinearities. For the present, we shall make a simple order-of-magnitude estimate of the size of these quantities for the common case in which the nonlinearity is electronic in origin (see, for instance, Armstrong *et al.*, 1962). One might expect that the lowest-order correction term $\tilde{P}^{(2)}$ would be comparable to the linear response $\tilde{P}^{(1)}$ when the amplitude of the applied field \tilde{E} is of the order of the characteristic atomic electric field strength $E_{\text{at}} = e/(4\pi\epsilon_0 a_0^2)$, where $-e$ is the charge of the electron and $a_0 = 4\pi\epsilon_0\hbar^2/me^2$ is the Bohr radius of the hydrogen atom (here \hbar is Planck's constant divided by 2π , and m is the mass of the electron). Numerically, we find that $E_{\text{at}} = 5.14 \times 10^{11}$ V/m.* We thus expect that under conditions of nonresonant excitation the second-order susceptibility $\chi^{(2)}$ will be of the order of $\chi^{(1)}/E_{\text{at}}$. For condensed matter $\chi^{(1)}$ is of the order of unity, and we hence expect that $\chi^{(2)}$ will be of the order of $1/E_{\text{at}}$, or that

$$\chi^{(2)} \simeq 1.94 \times 10^{-12} \text{ m/V}. \quad (1.1.3)$$

Similarly, we expect $\chi^{(3)}$ to be of the order of $\chi^{(1)}/E_{\text{at}}^2$, which for condensed matter is of the order of

$$\chi^{(3)} \simeq 3.78 \times 10^{-24} \text{ m}^2/\text{V}^2. \quad (1.1.4)$$

These predictions are in fact quite accurate, as one can see by comparing these values with actual measured values of $\chi^{(2)}$ (see, for instance, Table 1.5.3) and $\chi^{(3)}$ (see, for instance, Table 4.3.1).

For certain purposes, it is useful to express the second- and third-order susceptibilities in terms of fundamental physical constants. As just noted, for condensed matter $\chi^{(1)}$ is of the order of unity. This result can be justified either as an empirical fact or can be justified more rigorously by noting that $\chi^{(1)}$ is the product of atomic number density and atomic polarizability. The number density N of condensed matter is of the order of $(a_0)^{-3}$, and the nonresonant polarizability is of the order of $(a_0)^3$. We thus deduce that $\chi^{(1)}$ is of the order of unity. We then find that $\chi^{(2)} \simeq (4\pi\epsilon_0)^3 \hbar^4/m^2 e^5$ and $\chi^{(3)} \simeq (4\pi\epsilon_0)^6 \hbar^8/m^4 e^{10}$. See Boyd (1999) for further details.

* Except where otherwise noted, we use the SI (MKS) system of units throughout this book. The appendix to this book presents a prescription for converting among systems of units.

The most usual procedure for describing nonlinear optical phenomena is based on expressing the polarization $\tilde{P}(t)$ in terms of the applied electric field strength $\tilde{E}(t)$, as we have done in Eq. (1.1.2). The reason why the polarization plays a key role in the description of nonlinear optical phenomena is that a time-varying polarization can act as the source of new components of the electromagnetic field. For example, we shall see in Section 2.1 that the wave equation in nonlinear optical media often has the form

$$\nabla^2 \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{P}^{\text{NL}}}{\partial t^2}, \quad (1.1.5)$$

where n is the usual linear refractive index and c is the speed of light in vacuum. We can interpret this expression as an inhomogeneous wave equation in which the polarization \tilde{P}^{NL} associated with the nonlinear response drives the electric field \tilde{E} . Since $\partial^2 \tilde{P}^{\text{NL}} / \partial t^2$ is a measure of the acceleration of the charges that constitute the medium, this equation is consistent with Larmor's theorem of electromagnetism which states that accelerated charges generate electromagnetic radiation.

It should be noted that the power series expansion expressed by Eq. (1.1.2) need not necessarily converge. In such circumstances the relationship between the material response and the applied electric field amplitude must be expressed using different procedures. One such circumstance is that of resonant excitation of an atomic system, in which case an appreciable fraction of the atoms can be removed from the ground state. Saturation effects of this sort can be described by procedures developed in Chapter 6. Even under nonresonant conditions, Eq. (1.1.2) loses its validity if the applied laser field strength becomes comparable to the characteristic atomic field strength E_{at} , because of strong photoionization that can occur under these conditions. For future reference, we note that the laser intensity associated with a peak field strength of E_{at} is given by

$$I_{\text{at}} = \frac{1}{2} \epsilon_0 c E_{\text{at}}^2 = 3.5 \times 10^{20} \text{ W/m}^2 = 3.5 \times 10^{16} \text{ W/cm}^2. \quad (1.1.6)$$

We shall see later in this book (see especially Chapter 13) how nonlinear optical processes display qualitatively distinct features when excited by such super-intense fields.

1.2. Descriptions of Nonlinear Optical Processes

In the present section, we present brief qualitative descriptions of a number of nonlinear optical processes. In addition, for those processes that can oc-

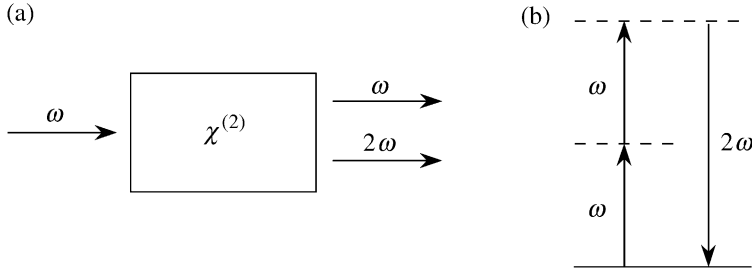


FIGURE 1.2.1 (a) Geometry of second-harmonic generation. (b) Energy-level diagram describing second-harmonic generation.

cur in a lossless medium, we indicate how they can be described in terms of the nonlinear contributions to the polarization described by Eq. (1.1.2).^{*} Our motivation is to provide an indication of the variety of nonlinear optical phenomena that can occur. These interactions are described in greater detail in later sections of this book. In this section we also introduce some notational conventions and some of the basic concepts of nonlinear optics.

1.2.1. Second-Harmonic Generation

As an example of a nonlinear optical interaction, let us consider the process of second-harmonic generation, which is illustrated schematically in Fig. 1.2.1. Here a laser beam whose electric field strength is represented as

$$\tilde{E}(t) = E e^{-i\omega t} + \text{c.c.} \quad (1.2.1)$$

is incident upon a crystal for which the second-order susceptibility $\chi^{(2)}$ is nonzero. The nonlinear polarization that is created in such a crystal is given according to Eq. (1.1.2) as $\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$ or explicitly as

$$\tilde{P}^{(2)}(t) = 2\epsilon_0 \chi^{(2)} E E^* + (\epsilon_0 \chi^{(2)} E^2 e^{-i2\omega t} + \text{c.c.}). \quad (1.2.2)$$

We see that the second-order polarization consists of a contribution at zero frequency (the first term) and a contribution at frequency 2ω (the second term). According to the driven wave equation (1.1.5), this latter contribution can lead to the generation of radiation at the second-harmonic frequency. Note that the first contribution in Eq. (1.2.2) does not lead to the generation of electromagnetic radiation (because its second time derivative vanishes); it leads to a process known as optical rectification, in which a static electric field is created across the nonlinear crystal.

^{*} Recall that Eq. (1.1.2) is valid only for a medium that is lossless and dispersionless.

Under proper experimental conditions, the process of second-harmonic generation can be so efficient that nearly all of the power in the incident beam at frequency ω is converted to radiation at the second-harmonic frequency 2ω . One common use of second-harmonic generation is to convert the output of a fixed-frequency laser to a different spectral region. For example, the Nd:YAG laser operates in the near infrared at a wavelength of $1.06 \mu\text{m}$. Second-harmonic generation is routinely used to convert the wavelength of the radiation to $0.53 \mu\text{m}$, in the middle of the visible spectrum.

Second-harmonic generation can be visualized by considering the interaction in terms of the exchange of photons between the various frequency components of the field. According to this picture, which is illustrated in part (b) of Fig. 1.2.1, two photons of frequency ω are destroyed, and a photon of frequency 2ω is simultaneously created in a single quantum-mechanical process. The solid line in the figure represents the atomic ground state, and the dashed lines represent what are known as virtual levels. These levels are not energy eigenlevels of the free atom but rather represent the combined energy of one of the energy eigenstates of the atom and of one or more photons of the radiation field.

The theory of second-harmonic generation is developed more fully in Section 2.6.

1.2.2. Sum- and Difference-Frequency Generation

Let us next consider the circumstance in which the optical field incident upon a second-order nonlinear optical medium consists of two distinct frequency components, which we represent in the form

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + \text{c.c.} \quad (1.2.3)$$

Then, assuming as in Eq. (1.1.2) that the second-order contribution to the nonlinear polarization is of the form

$$\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}(t)^2, \quad (1.2.4)$$

we find that the nonlinear polarization is given by

$$\begin{aligned} \tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} [& E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2)t} \\ & + 2E_1 E_2^* e^{-i(\omega_1 - \omega_2)t} + \text{c.c.}] + 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*]. \end{aligned} \quad (1.2.5)$$

It is convenient to express this result using the notation

$$\tilde{P}^{(2)}(t) = \sum_n P(\omega_n) e^{-i\omega_n t}, \quad (1.2.6)$$

where the summation extends over positive and negative frequencies ω_n . The complex amplitudes of the various frequency components of the nonlinear polarization are hence given by

$$\begin{aligned} P(2\omega_1) &= \epsilon_0 \chi^{(2)} E_1^2 \quad (\text{SHG}), \\ P(2\omega_2) &= \epsilon_0 \chi^{(2)} E_2^2 \quad (\text{SHG}), \\ P(\omega_1 + \omega_2) &= 2\epsilon_0 \chi^{(2)} E_1 E_2 \quad (\text{SFG}), \\ P(\omega_1 - \omega_2) &= 2\epsilon_0 \chi^{(2)} E_1 E_2^* \quad (\text{DFG}), \\ P(0) &= 2\epsilon_0 \chi^{(2)} (E_1 E_1^* + E_2 E_2^*) \quad (\text{OR}). \end{aligned} \quad (1.2.7)$$

Here we have labeled each expression by the name of the physical process that it describes, such as second-harmonic generation (SHG), sum-frequency generation (SFG), difference-frequency generation (DFG), and optical rectification (OR). Note that, in accordance with our complex notation, there is also a response at the negative of each of the nonzero frequencies just given:

$$\begin{aligned} P(-2\omega_1) &= \epsilon_0 \chi^{(2)} E_1^{*2}, & P(-2\omega_2) &= \epsilon_0 \chi^{(2)} E_2^{*2}, \\ P(-\omega_1 - \omega_2) &= 2\epsilon_0 \chi^{(2)} E_1^* E_2^*, & P(\omega_2 - \omega_1) &= 2\epsilon_0 \chi^{(2)} E_2 E_1^*. \end{aligned} \quad (1.2.8)$$

However, since each of these quantities is simply the complex conjugate of one of the quantities given in Eq. (1.2.7), it is not necessary to take explicit account of both the positive and negative frequency components.*

* Not all workers in nonlinear optics use our convention that the fields and polarizations are given by Eqs. (1.2.3) and (1.2.6). Another common convention is to define the field amplitudes according to

$$\begin{aligned} \tilde{E}(t) &= \frac{1}{2} (E'_1 e^{-i\omega_1 t} + E'_2 e^{-i\omega_2 t} + \text{c.c.}), \\ \tilde{P}(t) &= \frac{1}{2} \sum_n P'(\omega_n) e^{i\omega_n t}, \end{aligned}$$

where in the second expression the summation extends over all positive and negative frequencies. Using this convention, one finds that

$$\begin{aligned} P'(2\omega_1) &= \frac{1}{2} \epsilon_0 \chi^{(2)} E_1'^2, & P'(2\omega_2) &= \frac{1}{2} \epsilon_0 \chi^{(2)} E_2'^2, \\ P'(\omega_1 + \omega_2) &= \epsilon_0 \chi^{(2)} E'_1 E'_2, & P'(\omega_1 - \omega_2) &= \epsilon_0 \chi^{(2)} E'_1 E_2'^*, \\ P'(0) &= \epsilon_0 \chi^{(2)} (E'_1 E_1'^* + E_2' E_2'^*). \end{aligned}$$

Note that these expressions differ from Eqs. (1.2.7) by factors of $\frac{1}{2}$.

We see from Eq. (1.2.7) that four different nonzero frequency components are present in the nonlinear polarization. However, typically no more than one of these frequency components will be present with any appreciable intensity in the radiation generated by the nonlinear optical interaction. The reason for this behavior is that the nonlinear polarization can efficiently produce an output signal only if a certain phase-matching condition (which is discussed in detail in Section 2.7) is satisfied, and usually this condition cannot be satisfied for more than one frequency component of the nonlinear polarization. Operationally, one often chooses which frequency component will be radiated by properly selecting the polarization of the input radiation and the orientation of the nonlinear crystal.

1.2.3. Sum-Frequency Generation

Let us now consider the process of sum-frequency generation, which is illustrated in Fig. 1.2.2. According to Eq. (1.2.7), the complex amplitude of the nonlinear polarization describing this process is given by the expression

$$P(\omega_1 + \omega_2) = 2\epsilon_0\chi^{(2)} E_1 E_2. \quad (1.2.9)$$

In many ways the process of sum-frequency generation is analogous to that of second-harmonic generation, except that in sum-frequency generation the two input waves are at different frequencies. One application of sum-frequency generation is to produce tunable radiation in the ultraviolet spectral region by choosing one of the input waves to be the output of a fixed-frequency visible laser and the other to be the output of a frequency-tunable visible laser. The theory of sum-frequency generation is developed more fully in Sections 2.2 and 2.4.

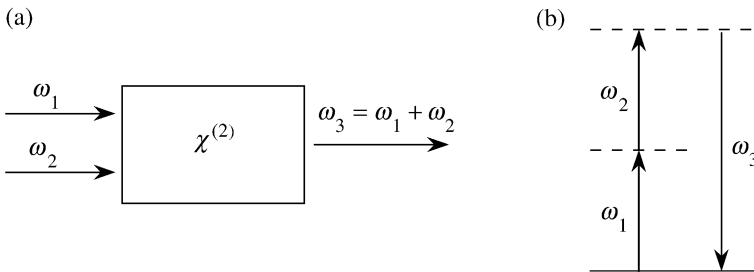


FIGURE 1.2.2 Sum-frequency generation. (a) Geometry of the interaction. (b) Energy-level description.

1.2.4. Difference-Frequency Generation

The process of difference-frequency generation is described by a nonlinear polarization of the form

$$P(\omega_1 - \omega_2) = 2\epsilon_0\chi^{(2)}E_1E_2^* \quad (1.2.10)$$

and is illustrated in Fig. 1.2.3. Here the frequency of the generated wave is the difference of those of the applied fields. Difference-frequency generation can be used to produce tunable infrared radiation by mixing the output of a frequency-tunable visible laser with that of a fixed-frequency visible laser.

Superficially, difference-frequency generation and sum-frequency generation appear to be very similar processes. However, an important difference between the two processes can be deduced from the description of difference-frequency generation in terms of a photon energy-level diagram (part (b) of Fig. 1.2.3). We see that conservation of energy requires that for every photon that is created at the difference frequency $\omega_3 = \omega_1 - \omega_2$, a photon at the higher input frequency (ω_1) must be destroyed and a photon at the lower input frequency (ω_2) must be created. Thus, the lower-frequency input field is amplified by the process of difference-frequency generation. For this reason, the process of difference-frequency generation is also known as optical parametric amplification. According to the photon energy-level description of difference-frequency generation, the atom first absorbs a photon of frequency ω_1 and jumps to the highest virtual level. This level decays by a two-photon emission process that is stimulated by the presence of the ω_2 field, which is already present. Two-photon emission can occur even if the ω_2 field is not applied. The generated fields in such a case are very much weaker, since they are created by *spontaneous* two-photon emission from a virtual level. This process is known as parametric

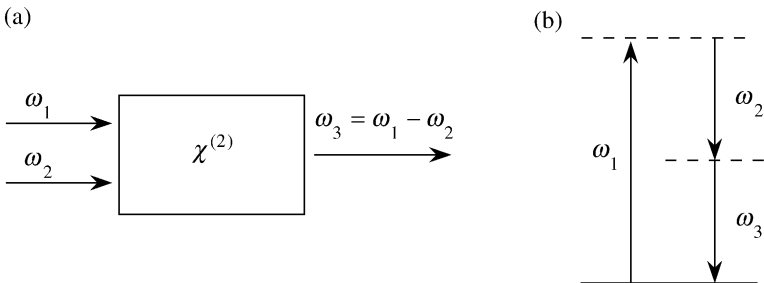


FIGURE 1.2.3 Difference-frequency generation. (a) Geometry of the interaction. (b) Energy-level description.

fluorescence and has been observed experimentally (Byer and Harris, 1968; Harris *et al.*, 1967).

The theory of difference-frequency generation is developed more fully in Section 2.5.

1.2.5. Optical Parametric Oscillation

We have just seen that in the process of difference-frequency generation the presence of radiation at frequency ω_2 or ω_3 can stimulate the emission of additional photons at these frequencies. If the nonlinear crystal used in this process is placed inside an optical resonator, as shown in Fig. 1.2.4, the ω_2 and/or ω_3 fields can build up to large values. Such a device is known as an optical parametric oscillator. Optical parametric oscillators are frequently used at infrared wavelengths, where other sources of tunable radiation are not readily available. Such a device is tunable because any frequency ω_2 that is smaller than ω_1 can satisfy the condition $\omega_2 + \omega_3 = \omega_1$ for some frequency ω_3 . In practice, one controls the output frequency of an optical parametric oscillator by adjusting the phase-matching condition, as discussed in Section 2.7. The applied field frequency ω_1 is often called the pump frequency, the desired output frequency is called the signal frequency, and the other, unwanted, output frequency is called the idler frequency.

1.2.6. Third-Order Nonlinear Optical Processes

We next consider the third-order contribution to the nonlinear polarization

$$\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}(t)^3. \quad (1.2.11)$$

For the general case in which the field $\tilde{E}(t)$ is made up of several different frequency components, the expression for $\tilde{P}^{(3)}(t)$ is very complicated. For this reason, we first consider the simple case in which the applied field is

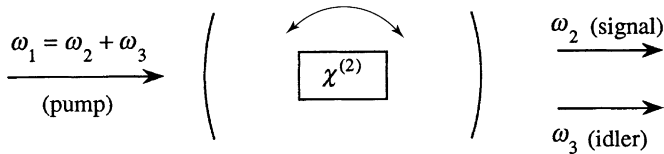


FIGURE 1.2.4 The optical parametric oscillator. The cavity end mirrors have high reflectivities at frequencies ω_2 and/or ω_3 . The output frequencies can be tuned by means of the orientation of the crystal.

monochromatic and is given by

$$\tilde{E}(t) = \mathcal{E} \cos \omega t. \quad (1.2.12)$$

Then, through use of the identity $\cos^3 \omega t = \frac{1}{4} \cos 3\omega t + \frac{3}{4} \cos \omega t$, we can express the nonlinear polarization as

$$\tilde{P}^{(3)}(t) = \frac{1}{4} \epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos 3\omega t + \frac{3}{4} \epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos \omega t. \quad (1.2.13)$$

The significance of each of the two terms in this expression is described briefly below.

1.2.7. Third-Harmonic Generation

The first term in Eq. (1.2.13) describes a response at frequency 3ω that is created by an applied field at frequency ω . This term leads to the process of third-harmonic generation, which is illustrated in Fig. 1.2.5. According to the photon description of this process, shown in part (b) of the figure, three photons of frequency ω are destroyed and one photon of frequency 3ω is created in the microscopic description of this process.

1.2.8. Intensity-Dependent Refractive Index

The second term in Eq. (1.2.13) describes a nonlinear contribution to the polarization at the frequency of the incident field; this term hence leads to a nonlinear contribution to the refractive index experienced by a wave at frequency ω . We shall see in Section 4.1 that the refractive index in the presence of this type of nonlinearity can be represented as

$$n = n_0 + n_2 I, \quad (1.2.14a)$$

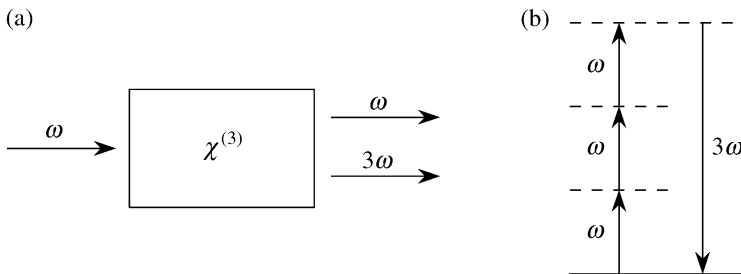


FIGURE 1.2.5 Third-harmonic generation. (a) Geometry of the interaction. (b) Energy-level description.

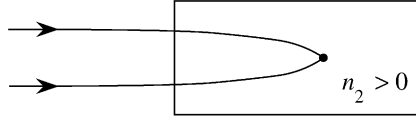


FIGURE 1.2.6 Self-focusing of light.

where n_0 is the usual (i.e., linear or low-intensity) refractive index, where

$$n_2 = \frac{3}{2n_0^2\epsilon_0 c} \chi^{(3)} \quad (1.2.14b)$$

is an optical constant that characterizes the strength of the optical nonlinearity, and where $I = \frac{1}{2}n_0\epsilon_0 c \mathcal{E}^2$ is the intensity of the incident wave.

Self-Focusing One of the processes that can occur as a result of the intensity-dependent refractive index is self-focusing, which is illustrated in Fig. 1.2.6. This process can occur when a beam of light having a nonuniform transverse intensity distribution propagates through a material for which n_2 is positive. Under these conditions, the material effectively acts as a positive lens, which causes the rays to curve toward each other. This process is of great practical importance because the intensity at the focal spot of the self-focused beam is usually sufficiently large to lead to optical damage of the material. The process of self-focusing is described in greater detail in Section 7.1.

1.2.9. Third-Order Interactions (General Case)

Let us next examine the form of the nonlinear polarization

$$\tilde{\mathbf{P}}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{\mathbf{E}}^3(t) \quad (1.2.15a)$$

induced by an applied field that consists of three frequency components:

$$\tilde{\mathbf{E}}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + \text{c.c.} \quad (1.2.15b)$$

When we calculate $\tilde{\mathbf{E}}^3(t)$, we find that the resulting expression contains 44 different frequency components, if we consider positive and negative frequencies to be distinct. Explicitly, these frequencies are

$$\begin{aligned} &\omega_1, \omega_2, \omega_3, 3\omega_1, 3\omega_2, 3\omega_3, (\omega_1 + \omega_2 + \omega_3), (\omega_1 + \omega_2 - \omega_3), \\ &(\omega_1 + \omega_3 - \omega_2), (\omega_2 + \omega_3 - \omega_1), (2\omega_1 \pm \omega_2), (2\omega_1 \pm \omega_3), (2\omega_2 \pm \omega_1), \\ &(2\omega_2 \pm \omega_3), (2\omega_3 \pm \omega_1), (2\omega_3 \pm \omega_2), \end{aligned}$$

and the negative of each. Again representing the nonlinear polarization as

$$\tilde{P}^{(3)}(t) = \sum_n P(\omega_n) e^{-i\omega_n t}, \quad (1.2.16)$$

we can write the complex amplitudes of the nonlinear polarization for each of the positive frequencies as

$$\begin{aligned} P(\omega_1) &= \epsilon_0 \chi^{(3)} (3E_1 E_1^* + 6E_2 E_2^* + 6E_3 E_3^*) E_1, \\ P(\omega_2) &= \epsilon_0 \chi^{(3)} (6E_1 E_1^* + 3E_2 E_2^* + 6E_3 E_3^*) E_2, \\ P(\omega_3) &= \epsilon_0 \chi^{(3)} (6E_1 E_1^* + 6E_2 E_2^* + 3E_3 E_3^*) E_3, \\ P(3\omega_1) &= \epsilon_0 \chi^{(3)} E_1^3, \quad P(3\omega_2) = \epsilon_0 \chi^{(3)} E_2^3, \quad P(3\omega_3) = \epsilon_0 \chi^{(3)} E_3^3, \\ P(\omega_1 + \omega_2 + \omega_3) &= 6\epsilon_0 \chi^{(3)} E_1 E_2 E_3, \\ P(\omega_1 + \omega_2 - \omega_3) &= 6\epsilon_0 \chi^{(3)} E_1 E_2 E_3^*, \\ P(\omega_1 + \omega_3 - \omega_2) &= 6\epsilon_0 \chi^{(3)} E_1 E_3 E_2^*, \\ P(\omega_2 + \omega_3 - \omega_1) &= 6\epsilon_0 \chi^{(3)} E_2 E_3 E_1^*, \\ P(2\omega_1 + \omega_2) &= 3\epsilon_0 \chi^{(3)} E_1^2 E_2, \quad P(2\omega_1 + \omega_3) = 3\epsilon_0 \chi^{(3)} E_1^2 E_3, \\ P(2\omega_2 + \omega_1) &= 3\epsilon_0 \chi^{(3)} E_2^2 E_1, \quad P(2\omega_2 + \omega_3) = 3\epsilon_0 \chi^{(3)} E_2^2 E_3, \\ P(2\omega_3 + \omega_1) &= 3\epsilon_0 \chi^{(3)} E_3^2 E_1, \quad P(2\omega_3 + \omega_2) = 3\epsilon_0 \chi^{(3)} E_3^2 E_2, \\ P(2\omega_1 - \omega_2) &= 3\epsilon_0 \chi^{(3)} E_1^2 E_2^*, \quad P(2\omega_1 - \omega_3) = 3\epsilon_0 \chi^{(3)} E_1^2 E_3^*, \\ P(2\omega_2 - \omega_1) &= 3\epsilon_0 \chi^{(3)} E_2^2 E_1^*, \quad P(2\omega_2 - \omega_3) = 3\epsilon_0 \chi^{(3)} E_2^2 E_3^*, \\ P(2\omega_3 - \omega_1) &= 3\epsilon_0 \chi^{(3)} E_3^2 E_1^*, \quad P(2\omega_3 - \omega_2) = 3\epsilon_0 \chi^{(3)} E_3^2 E_2^* \end{aligned} \quad (1.2.17)$$

We have displayed these expressions in complete detail because it is very instructive to study their form. In each case the frequency argument of P is equal to the sum of the frequencies associated with the field amplitudes appearing on the right-hand side of the equation, if we adopt the convention that a negative frequency is to be associated with a field amplitude that appears as a complex conjugate. Also, the numerical factor (1, 3, or 6) that appears in each term on the right-hand side of each equation is equal to the number of distinct permutations of the field frequencies that contribute to that term.

Some of the nonlinear optical mixing processes described by Eq. (1.2.17) are illustrated in Fig. 1.2.7.

1.2.10. Parametric versus Nonparametric Processes

All of the processes described thus far in this chapter are examples of what are known as parametric processes. The origin of this terminology is obscure,

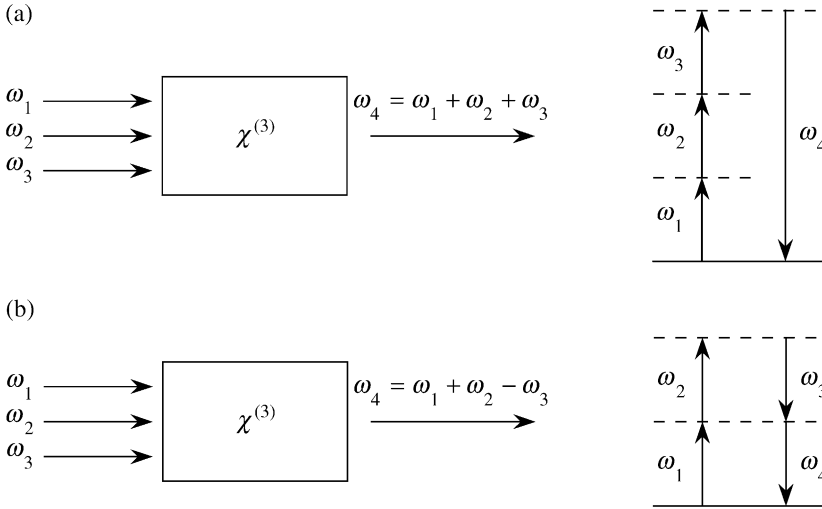


FIGURE 1.2.7 Two of the possible mixing processes described by Eq. (1.2.17) that can occur when three input waves interact in a medium characterized by a $\chi^{(3)}$ susceptibility.

but the word parametric has come to denote a process in which the initial and final quantum-mechanical states of the system are identical. Consequently, in a parametric process population can be removed from the ground state only for those brief intervals of time when it resides in a virtual level. According to the uncertainty principle, population can reside in a virtual level for a time interval of the order of $\hbar/\delta E$, where δE is the energy difference between the virtual level and the nearest real level. Conversely, processes that do involve the transfer of population from one real level to another are known as nonparametric processes. The processes that we describe in the remainder of the present section are all examples of nonparametric processes.

One difference between parametric and nonparametric processes is that parametric processes can always be described by a real susceptibility; conversely, nonparametric processes are described by a complex susceptibility by means of a procedure described in the following section. Another difference is that photon energy is always conserved in a parametric process; photon energy need not be conserved in a nonparametric process, because energy can be transferred to or from the material medium. For this reason, photon energy level diagrams of the sort shown in Figs. 1.2.1, 1.2.2, 1.2.3, 1.2.5, and 1.2.7 to describe parametric processes play a less definitive role in describing nonparametric processes.

As a simple example of the distinction between parametric and nonparametric processes, we consider the case of the usual (linear) index of refraction. The real part of the refractive index describes a response that occurs as a consequence of parametric processes, whereas the imaginary part occurs as a consequence of nonparametric processes. This conclusion holds because the imaginary part of the refractive index describes the absorption of radiation, which results from the transfer of population from the atomic ground state to an excited state.

1.2.11. Saturable Absorption

One example of a nonparametric nonlinear optical process is saturable absorption. Many material systems have the property that their absorption coefficient decreases when measured using high laser intensity. Often the dependence of the measured absorption coefficient α on the intensity I of the incident laser radiation is given by the expression*

$$\alpha = \frac{\alpha_0}{1 + I/I_s}, \quad (1.2.18)$$

where α_0 is the low-intensity absorption coefficient, and I_s is a parameter known as the saturation intensity.

Optical Bistability One consequence of saturable absorption is optical bistability. One way of constructing a bistable optical device is to place a saturable absorber inside a Fabry–Perot resonator, as illustrated in Fig. 1.2.8. As the input intensity is increased, the field inside the cavity also increases, lowering the absorption that the field experiences and thus increasing the field intensity still further. If the intensity of the incident field is subsequently lowered, the field inside the cavity tends to remain large because the absorption of the material system has already been reduced. A plot of the input-versus-output characteristics thus looks qualitatively like that shown in Fig. 1.2.9. Note that

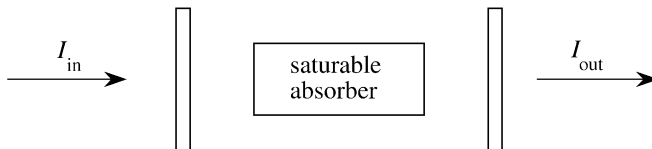


FIGURE 1.2.8 Bistable optical device.

* This form is valid, for instance, for the case of homogeneous broadening of a simple atomic transition.

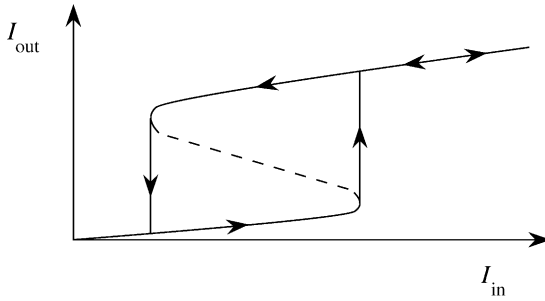


FIGURE 1.2.9 Typical input-versus-output characteristics of a bistable optical device.

over some range of input intensities more than one output intensity is possible. The process of optical bistability is described in greater detail in Section 7.3.

1.2.12. Two-Photon Absorption

In the process of two-photon absorption, which is illustrated in Fig. 1.2.10, an atom makes a transition from its ground state to an excited state by the simultaneous absorption of two laser photons. The absorption cross section σ describing this process increases linearly with laser intensity according to the relation

$$\sigma = \sigma^{(2)} I, \quad (1.2.19)$$

where $\sigma^{(2)}$ is a coefficient that describes strength of the two-photon-absorption process. (Recall that in conventional, linear optics the absorption cross section σ is a constant.) Consequently, the atomic transition rate R due to two-photon absorption scales as the square of the laser intensity. To justify this conclusion, we note that $R = \sigma I / \hbar \omega$, and consequently that

$$R = \frac{\sigma^{(2)} I^2}{\hbar \omega}. \quad (1.2.20)$$

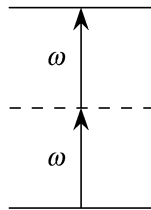


FIGURE 1.2.10 Two-photon absorption.

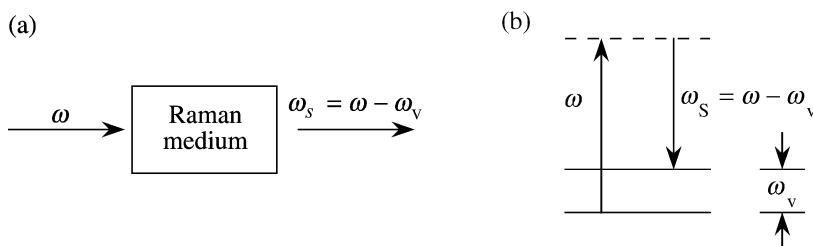


FIGURE 1.2.11 Stimulated Raman scattering.

Two-photon absorption is a useful spectroscopic tool for determining the positions of energy levels that are not connected to the atomic ground state by a one-photon transition. Two-photon absorption was first observed experimentally by Kaiser and Garrett (1961).

1.2.13. Stimulated Raman Scattering

In stimulated Raman scattering, which is illustrated in Fig. 1.2.11, a photon of frequency ω is annihilated and a photon at the Stokes shifted frequency $\omega_s = \omega - \omega_v$ is created, leaving the molecule (or atom) in an excited state with energy $\hbar\omega_v$. The excitation energy is referred to as ω_v because stimulated Raman scattering was first studied in molecular systems, where $\hbar\omega_v$ corresponds to a vibrational energy. The efficiency of this process can be quite large, with often 10% or more of the power of the incident light being converted to the Stokes frequency. In contrast, the efficiency of normal or spontaneous Raman scattering is typically many orders of magnitude smaller. Stimulated Raman scattering is described more fully in Chapter 10.

Other stimulated scattering processes such as stimulated Brillouin scattering and stimulated Rayleigh scattering also occur and are described more fully in Chapter 9.

1.3. Formal Definition of the Nonlinear Susceptibility

Nonlinear optical interactions can be described in terms of a nonlinear polarization given by Eq. (1.1.2) only for a material system that is lossless and dispersionless. In the present section, we consider the more general case of a material with dispersion and/or loss. In this more general case the nonlinear susceptibility becomes a complex quantity relating the complex amplitudes of the electric field and polarization.

We assume that we can represent the electric field vector of the optical wave as the discrete sum of a number of frequency components as

$$\tilde{\mathbf{E}}(\mathbf{r}, t) = \sum_n' \tilde{\mathbf{E}}_n(\mathbf{r}, t), \quad (1.3.1)$$

where

$$\tilde{\mathbf{E}}_n(\mathbf{r}, t) = \mathbf{E}_n(\mathbf{r})e^{-i\omega_n t} + \text{c.c.} \quad (1.3.2)$$

The prime on the summation sign of Eq. (1.3.1) indicates that the summation is to be taken over positive frequencies only. It is also convenient to define the spatially slowly varying field amplitude \mathbf{A}_n by means of the relation

$$\mathbf{E}_n(\mathbf{r}) = \mathbf{A}_n e^{i\mathbf{k}_n \cdot \mathbf{r}}, \quad (1.3.3)$$

so that

$$\tilde{\mathbf{E}}(\mathbf{r}, t) = \sum_n' \mathbf{A}_n e^{i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} + \text{c.c.} \quad (1.3.4)$$

On occasion, we shall express these field amplitudes using the alternative notation

$$\mathbf{E}_n = \mathbf{E}(\omega_n) \quad \text{and} \quad \mathbf{A}_n = \mathbf{A}(\omega_n), \quad (1.3.5)$$

where

$$\mathbf{E}(-\omega_n) = \mathbf{E}(\omega_n)^* \quad \text{and} \quad \mathbf{A}(-\omega_n) = \mathbf{A}(\omega_n)^*. \quad (1.3.6)$$

Using this new notation, we can write the total field in the more compact form

$$\begin{aligned} \tilde{\mathbf{E}}(\mathbf{r}, t) &= \sum_n \mathbf{E}(\omega_n) e^{-i\omega_n t} \\ &= \sum_n \mathbf{A}(\omega_n) e^{i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)}, \end{aligned} \quad (1.3.7)$$

where the unprimed summation symbol denotes a summation over all frequencies, both positive and negative.

Note that according to our definition of field amplitude, the field given by

$$\tilde{\mathbf{E}}(\mathbf{r}, t) = \mathcal{E} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (1.3.8)$$

is represented by the complex field amplitudes

$$\mathbf{E}(\omega) = \frac{1}{2} \mathcal{E} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \mathbf{E}(-\omega) = \frac{1}{2} \mathcal{E} e^{-i\mathbf{k} \cdot \mathbf{r}}, \quad (1.3.9)$$

or alternatively, by the slowly varying amplitudes

$$\mathbf{A}(\omega) = \frac{1}{2}\mathcal{E}, \quad \mathbf{A}(-\omega) = \frac{1}{2}\mathcal{E}. \quad (1.3.10)$$

In either representation, factors of $\frac{1}{2}$ appear because the physical field amplitude \mathcal{E} has been divided equally between the positive- and negative-frequency field components.

Using a notation similar to that of Eq. (1.3.7), we can express the nonlinear polarization as

$$\tilde{\mathbf{P}}(\mathbf{r}, t) = \sum_n \mathbf{P}(\omega_n) e^{-i\omega_n t}, \quad (1.3.11)$$

where, as before, the summation extends over all positive- and negative-frequency field components.

We now define the components of the second-order susceptibility tensor $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$ as the constants of proportionality relating the amplitude of the nonlinear polarization to the product of field amplitudes according to

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m). \quad (1.3.12)$$

Here the indices ijk refer to the Cartesian components of the fields. The notation (nm) indicates that, in performing the summation over n and m , the sum $\omega_n + \omega_m$ is to be held fixed, although ω_n and ω_m are each allowed to vary. Since the amplitude $E(\omega_n)$ is associated with the time dependence $\exp(-i\omega_n t)$, and the amplitude $E(\omega_m)$ is associated with the time dependence $\exp(-i\omega_m t)$, their product $E(\omega_n)E(\omega_m)$ is associated with the time dependence $\exp[-i(\omega_n + \omega_m)t]$. Hence the product $E(\omega_n)E(\omega_m)$ does in fact lead to a contribution to the nonlinear polarization oscillating at frequency $\omega_n + \omega_m$, as the notation of Eq. (1.3.12) suggests. Following convention, we have written $\chi^{(2)}$ as a function of three frequency arguments. This is technically unnecessary in that the first argument is always the sum of the other two. To emphasize this fact, the susceptibility $\chi^{(2)}(\omega_3, \omega_2, \omega_1)$ is sometimes written as $\chi^{(2)}(\omega_3; \omega_2, \omega_1)$ as a reminder that the first argument is different from the other two, or it may be written symbolically as $\chi^{(2)}(\omega_3 = \omega_2 + \omega_1)$.

Let us examine some of the consequences of the definition of the nonlinear susceptibility as given by Eq. (1.3.12) by considering two simple examples.

1. *Sum-frequency generation.* We let the input field frequencies be ω_1 and ω_2 and the sum frequency be ω_3 , so that $\omega_3 = \omega_1 + \omega_2$. Then, by carrying

out the summation over ω_n and ω_m in Eq. (1.3.12), we find that

$$P_i(\omega_3) = \epsilon_0 \sum_{jk} [\chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) + \chi_{ikj}^{(2)}(\omega_3, \omega_2, \omega_1) E_j(\omega_2) E_k(\omega_1)]. \quad (1.3.13)$$

We now note that j and k are dummy indices and thus can be interchanged in the second term. We next assume that the nonlinear susceptibility possesses intrinsic permutation symmetry (this symmetry is discussed in more detail in Eq. (1.5.6) below), which states that

$$\chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) = \chi_{ikj}^{(2)}(\omega_m + \omega_n, \omega_n, \omega_m). \quad (1.3.14)$$

Through use of this relation, the expression for the nonlinear polarization becomes

$$P_i(\omega_3) = 2\epsilon_0 \sum_{jk} \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2), \quad (1.3.15)$$

and for the special case in which both input fields are polarized in the x direction the polarization becomes

$$P_i(\omega_3) = 2\epsilon_0 \chi_{ixx}^{(2)}(\omega_3, \omega_1, \omega_2) E_x(\omega_1) E_x(\omega_2). \quad (1.3.16)$$

2. *Second-harmonic generation.* We take the input frequency as ω_1 and the generated frequency as $\omega_3 = 2\omega_1$. If we again perform the summation over field frequencies in Eq. (1.3.12), we obtain

$$P_i(\omega_3) = \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_1) E_j(\omega_1) E_k(\omega_1). \quad (1.3.17)$$

Again assuming the special case of an input field polarization along the x direction, this result becomes

$$P_i(\omega_3) = \epsilon_0 \chi_{ixx}^{(2)}(\omega_3, \omega_1, \omega_1) E_x(\omega_1)^2. \quad (1.3.18)$$

Note that a factor of two appears in Eqs. (1.3.15) and (1.3.16), which describe sum-frequency generation, but not in Eqs. (1.3.17) and (1.3.18), which describe second-harmonic generation. The fact that these expressions remain different even as ω_2 approaches ω_1 is perhaps at first sight surprising, but is a consequence of our convention that $\chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2)$ must approach $\chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_1)$ as ω_1 approaches ω_2 . Note that the expressions for $P(2\omega_2)$ and $P(\omega_1 + \omega_2)$ that apply for the case of a dispersionless nonlinear susceptibility (Eq. (1.2.7)) also differ by a factor of two. Moreover, one should expect the nonlinear polarization produced by two distinct fields to be larger than that

produced by a single field (both of the same amplitude, say), because the total light intensity is larger in the former case.

In general, the summation over field frequencies ($\sum_{(nm)}$) in Eq. (1.3.12) can be performed formally to obtain the result

$$P_i(\omega_n + \omega_m) = \epsilon_0 D \sum_{jk} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m), \quad (1.3.19)$$

where D is known as the degeneracy factor and is equal to the number of distinct permutations of the applied field frequencies ω_n and ω_m .

The expression (1.3.12) defining the second-order susceptibility can readily be generalized to higher-order interactions. In particular, the components of the third-order susceptibility are defined as the coefficients relating the amplitudes according to the expression

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 \sum_{jkl} \sum_{(mno)} \chi_{ijkl}^{(3)}(\omega_o + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) \times E_j(\omega_o) E_k(\omega_n) E_l(\omega_m). \quad (1.3.20)$$

We can again perform the summation over m , n , and o to obtain the result

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 D \sum_{jkl} \chi_{ijkl}^{(3)}(\omega_o + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) \times E_j(\omega_o) E_k(\omega_n) E_l(\omega_m), \quad (1.3.21)$$

where the degeneracy factor D represents the number of distinct permutations of the frequencies ω_m , ω_n , and ω_o .

1.4. Nonlinear Susceptibility of a Classical Anharmonic Oscillator

The Lorentz model of the atom, which treats the atom as a harmonic oscillator, is known to provide a very good description of the linear optical properties of atomic vapors and of nonmetallic solids. In the present section, we extend the Lorentz model by allowing the possibility of a nonlinearity in the restoring force exerted on the electron. The details of the analysis differ depending upon whether or not the medium possesses inversion symmetry.* We first treat the case of a noncentrosymmetric medium, and we find that such a medium

* The role of symmetry in determining the nature of the nonlinear susceptibility is discussed from a more fundamental point of view in Section 1.5. See especially the treatment leading from Eq. (1.5.31) to (1.5.35).

can give rise to a second-order optical nonlinearity. We then treat the case of a medium that possesses a center of symmetry and find that the lowest-order nonlinearity that can occur in this case is a third-order nonlinear susceptibility. Our treatment is similar to that of Owyong (1971).

The primary shortcoming of the classical model of optical nonlinearities presented here is that this model ascribes a single resonance frequency (ω_0) to each atom. In contrast, the quantum-mechanical theory of the nonlinear optical susceptibility, to be developed in Chapter 3, allows each atom to possess many energy eigenvalues and hence more than one resonance frequency. Since the present model allows for only one resonance frequency, it cannot properly describe the complete resonance nature of the nonlinear susceptibility (such as, for example, the possibility of simultaneous one- and two-photon resonances). However, it provides a good description for those cases in which all of the optical frequencies are considerably smaller than the lowest electronic resonance frequency of the material system.

1.4.1. *Noncentrosymmetric Media*

For the case of noncentrosymmetric media, we take the equation of motion of the electron position \tilde{x} to be of the form

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -e\tilde{E}(t)/m. \quad (1.4.1)$$

In this equation we have assumed that the applied electric field is given by $\tilde{E}(t)$, that the charge of the electron is $-e$, that there is a damping force of the form* $-2m\gamma\dot{\tilde{x}}$, and that the restoring force is given by

$$\tilde{F}_{\text{restoring}} = -m\omega_0^2\tilde{x} - ma\tilde{x}^2, \quad (1.4.2)$$

where a is a parameter that characterizes the strength of the nonlinearity. We obtain this form by assuming that the restoring force is a nonlinear function of the displacement of the electron from its equilibrium position and retaining the linear and quadratic terms in the Taylor series expansion of the restoring force in the displacement \tilde{x} . We can understand the nature of this form of the restoring force by noting that it corresponds to a potential energy function of the form

$$U(\tilde{x}) = - \int \tilde{F}_{\text{restoring}} d\tilde{x} = \frac{1}{2}m\omega_0^2\tilde{x}^2 + \frac{1}{3}ma\tilde{x}^3. \quad (1.4.3)$$

* The factor of two is introduced to make γ the dipole damping rate. 2γ is therefore the full width at half maximum in angular frequency units of the atomic absorption profile in the limit of linear response.

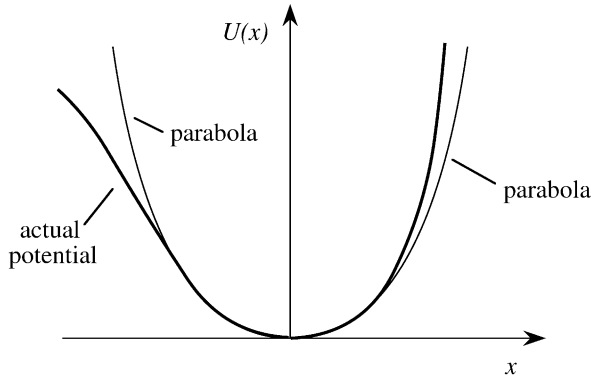


FIGURE 1.4.1 Potential energy function for a noncentrosymmetric medium.

Here the first term corresponds to a harmonic potential and the second term corresponds to an anharmonic correction term, as illustrated in Fig. 1.4.1. This model corresponds to the physical situation of electrons in real materials, because the actual potential well that the atomic electron feels is not perfectly parabolic. The present model can describe only noncentrosymmetric media because we have assumed that the potential energy function $U(\tilde{x})$ of Eq. (1.4.3) contains both even and odd powers of \tilde{x} ; for a centrosymmetric medium only even powers of \tilde{x} could appear, because the potential function $U(\tilde{x})$ must possess the symmetry $U(\tilde{x}) = U(-\tilde{x})$. For simplicity, we have written Eq. (1.4.1) in the scalar-field approximation; note that we cannot treat the tensor nature of the nonlinear susceptibility without making explicit assumptions regarding the symmetry properties of the material.

We assume that the applied optical field is of the form

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + \text{c.c.} \quad (1.4.4)$$

No general solution to Eq. (1.4.1) for an applied field of the form (1.4.4) is known. However, if the applied field is sufficiently weak, the nonlinear term $a\tilde{x}^2$ will be much smaller than the linear term $\omega_0^2 \tilde{x}$ for any displacement \tilde{x} that can be induced by the field. Under this circumstance, Eq. (1.4.1) can be solved by means of a perturbation expansion. We use a procedure analogous to that of Rayleigh–Schrödinger perturbation theory in quantum mechanics. We replace $\tilde{E}(t)$ in Eq. (1.4.1) by $\lambda \tilde{E}(t)$, where λ is a parameter that ranges continuously between zero and one and that will be set equal to one at the end of the calculation. The expansion parameter λ thus characterizes the strength of the perturbation. Equation (1.4.1) then becomes

$$\ddot{\tilde{x}} + 2\gamma \dot{\tilde{x}} + \omega_0^2 \tilde{x} + a\tilde{x}^2 = -\lambda e \tilde{E}(t)/m. \quad (1.4.5)$$

We now seek a solution to Eq. (1.4.5) in the form of a power series expansion in the strength λ of the perturbation, that is, a solution of the form

$$\tilde{x} = \lambda \tilde{x}^{(1)} + \lambda^2 \tilde{x}^{(2)} + \lambda^3 \tilde{x}^{(3)} + \dots \quad (1.4.6)$$

In order for Eq. (1.4.6) to be a solution to Eq. (1.4.5) for any value of the coupling strength λ , we require that the terms in Eq. (1.4.5) proportional to λ , λ^2 , λ^3 , etc., each satisfy the equation separately. We find that these terms lead respectively to the equations

$$\ddot{\tilde{x}}^{(1)} + 2\gamma \dot{\tilde{x}}^{(1)} + \omega_0^2 \tilde{x}^{(1)} = -e\tilde{E}(t)/m, \quad (1.4.7a)$$

$$\ddot{\tilde{x}}^{(2)} + 2\gamma \dot{\tilde{x}}^{(2)} + \omega_0^2 \tilde{x}^{(2)} + a[\tilde{x}^{(1)}]^2 = 0, \quad (1.4.7b)$$

$$\ddot{\tilde{x}}^{(3)} + 2\gamma \dot{\tilde{x}}^{(3)} + \omega_0^2 \tilde{x}^{(3)} + 2a\tilde{x}^{(1)}\tilde{x}^{(2)} = 0, \quad \text{etc.} \quad (1.4.7c)$$

We see from Eq. (1.4.7a) that the lowest-order contribution $\tilde{x}^{(1)}$ is governed by the same equation as that of the conventional (i.e., linear) Lorentz model. Its steady-state solution is thus given by

$$\tilde{x}^{(1)}(t) = x^{(1)}(\omega_1)e^{-i\omega_1 t} + x^{(1)}(\omega_2)e^{-i\omega_2 t} + \text{c.c.}, \quad (1.4.8)$$

where the amplitudes $x^{(1)}(\omega_j)$ have the form

$$x^{(1)}(\omega_j) = -\frac{e}{m} \frac{E_j}{D(\omega_j)}, \quad (1.4.9)$$

where we have introduced the complex denominator function

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma. \quad (1.4.10)$$

This expression for $\tilde{x}^{(1)}(t)$ is now squared and substituted into Eq. (1.4.7b), which is solved to obtain the lowest-order correction term $\tilde{x}^{(2)}$. The square of $\tilde{x}^{(1)}(t)$ contains the frequencies $\pm 2\omega_1$, $\pm 2\omega_2$, $\pm(\omega_1 + \omega_2)$, $\pm(\omega_1 - \omega_2)$, and 0. To determine the response at frequency $2\omega_1$, for instance, we must solve the equation

$$\ddot{\tilde{x}}^{(2)} + 2\gamma \dot{\tilde{x}}^{(2)} + \omega_0^2 \tilde{x}^{(2)} = \frac{-a(eE_1/m)^2 e^{-2i\omega_1 t}}{D^2(\omega_1)}. \quad (1.4.11)$$

We seek a steady-state solution of the form

$$\tilde{x}^{(2)}(t) = x^{(2)}(2\omega_1)e^{-2i\omega_1 t}. \quad (1.4.12)$$

Substitution of Eq. (1.4.12) into Eq. (1.4.11) leads to the result

$$x^{(2)}(2\omega_1) = \frac{-a(e/m)^2 E_1^2}{D(2\omega_1)D^2(\omega_1)}, \quad (1.4.13)$$

where we have made use of the definition (1.4.10) of the function $D(\omega_j)$. Analogously, the amplitudes of the responses at the other frequencies are found to be

$$x^{(2)}(2\omega_2) = \frac{-a(e/m)^2 E_2^2}{D(2\omega_2)D^2(\omega_2)}, \quad (1.4.14a)$$

$$x^{(2)}(\omega_1 + \omega_2) = \frac{-2a(e/m)^2 E_1 E_2}{D(\omega_1 + \omega_2)D(\omega_1)D(\omega_2)}, \quad (1.4.14b)$$

$$x^{(2)}(\omega_1 - \omega_2) = \frac{-2a(e/m)^2 E_1 E_2^*}{D(\omega_1 - \omega_2)D(\omega_1)D(-\omega_2)}, \quad (1.4.14c)$$

$$x^{(2)}(0) = \frac{-2a(e/m)^2 E_1 E_1^*}{D(0)D(\omega_1)D(-\omega_1)} + \frac{-2a(e/m)^2 E_2 E_2^*}{D(0)D(\omega_2)D(-\omega_2)}. \quad (1.4.14d)$$

We next express these results in terms of the linear ($\chi^{(1)}$) and nonlinear ($\chi^{(2)}$) susceptibilities. The linear susceptibility is defined through the relation

$$P^{(1)}(\omega_j) = \epsilon_0 \chi^{(1)}(\omega_j) E(\omega_j). \quad (1.4.15)$$

Since the linear contribution to the polarization is given by

$$P^{(1)}(\omega_j) = -Nex^{(1)}(\omega_j), \quad (1.4.16)$$

where N is the number density of atoms, we find using Eqs. (1.4.8) and (1.4.9) that the linear susceptibility is given by

$$\chi^{(1)}(\omega_j) = \frac{N(e^2/m)}{\epsilon_0 D(\omega_j)}. \quad (1.4.17)$$

The nonlinear susceptibilities are calculated in an analogous manner. The nonlinear susceptibility describing second-harmonic generation is defined by the relation

$$P^{(2)}(2\omega_1) = \epsilon_0 \chi^{(2)}(2\omega_1, \omega_1, \omega_1) E(\omega_1)^2, \quad (1.4.18)$$

where $P^{(2)}(2\omega_1)$ is the amplitude of the component of the nonlinear polarization oscillating at frequency $2\omega_1$ and is defined by the relation

$$P^{(2)}(2\omega_1) = -Nex^{(2)}(2\omega_1). \quad (1.4.19)$$

Comparison of these equations with Eq. (1.4.13) gives

$$\chi^{(2)}(2\omega_1, \omega_1, \omega_1) = \frac{N(e^3/m^2)a}{\epsilon_0 D(2\omega_1)D^2(\omega_1)}. \quad (1.4.20)$$

Through use of Eq. (1.4.17), this result can be written instead in terms of the product of linear susceptibilities as

$$\chi^{(2)}(2\omega_1, \omega_1, \omega_1) = \frac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(2\omega_1) [\chi^{(1)}(\omega_1)]^2. \quad (1.4.21)$$

The nonlinear susceptibility for second-harmonic generation of the ω_2 field is obtained trivially from Eqs. (1.4.20) and (1.4.21) through the substitution $\omega_1 \rightarrow \omega_2$.

The nonlinear susceptibility describing sum-frequency generation is obtained from the relations

$$P^{(2)}(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) E(\omega_1) E(\omega_2) \quad (1.4.22)$$

and

$$P^{(2)}(\omega_1 + \omega_2) = -N e x^{(2)}(\omega_1 + \omega_2). \quad (1.4.23)$$

Note that in this case the relation defining the nonlinear susceptibility contains a factor of two because the two input fields are distinct, as discussed in relation to Eq. (1.3.19). By comparison of these equations with (1.4.14b), the nonlinear susceptibility is seen to be given by

$$\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{N(e^3/m^2)a}{\epsilon_0 D(\omega_1 + \omega_2) D(\omega_1) D(\omega_2)}, \quad (1.4.24)$$

which can be expressed in terms of the product of linear susceptibilities as

$$\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2). \quad (1.4.25)$$

It can be seen by comparison of Eqs. (1.4.20) and (1.4.24) that, as ω_2 approaches ω_1 , $\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2)$ approaches $\chi^{(2)}(2\omega_1, \omega_1, \omega_1)$.

The nonlinear susceptibilities describing the other second-order processes are obtained in an analogous manner. For difference-frequency generation we find that

$$\begin{aligned} \chi^{(2)}(\omega_1 - \omega_2, \omega_1, -\omega_2) &= \frac{N(e^3/\epsilon_0 m^2)a}{D(\omega_1 - \omega_2) D(\omega_1) D(-\omega_2)} \\ &= \frac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1 - \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_2), \end{aligned} \quad (1.4.26)$$

and for optical rectification we find that

$$\begin{aligned}\chi^{(2)}(0, \omega_1, -\omega_1) &= \frac{N(e^3/m^2)a}{\epsilon_0 D(0)D(\omega_1)D(-\omega_1)} \\ &= \frac{\epsilon_0^2 m a}{N^2 e^3} \chi^{(1)}(0) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_1).\end{aligned}\quad (1.4.27)$$

The analysis just presented shows that the lowest-order nonlinear contribution to the polarization of a noncentrosymmetric material is second order in the applied field strength. This analysis can readily be extended to include higher-order effects. The solution to Eq. (1.4.7c), for example, leads to a third-order or $\chi^{(3)}$ susceptibility, and more generally terms proportional to λ^n in the expansion described by Eq. (1.4.6) lead to a $\chi^{(n)}$ susceptibility.

1.4.2. Miller's Rule

An empirical rule due to Miller (Miller, 1964; see also Garrett and Robinson, 1966) can be understood in terms of the calculation just presented. Miller noted that the quantity

$$\frac{\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2)}{\chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2)} \quad (1.4.28)$$

is nearly constant for all noncentrosymmetric crystals. By comparison with Eq. (1.4.25), we see this quantity will be constant only if the combination

$$\frac{m a \epsilon_0^2}{N^2 e^3} \quad (1.4.29)$$

is nearly constant. In fact, the atomic number density N is nearly the same ($\sim 10^{22} \text{ cm}^{-3}$) for all condensed matter, and the parameters m and e are fundamental constants. We can estimate the size of the nonlinear coefficient a by noting that the linear and nonlinear contributions to the restoring force given by Eq. (1.4.2) would be expected to become comparable when the displacement \tilde{x} of the electron from its equilibrium position is approximately equal to the size of the atom. This distance is of the order of the separation between atoms—that is, of the lattice constant d . This reasoning leads to the order-of-magnitude estimate that $m\omega_0^2 d = m a d^2$ or that

$$a = \frac{\omega_0^2}{d}. \quad (1.4.30)$$

Since ω_0 and d are roughly the same for most solids, the quantity a would also be expected to be roughly the same for all materials where it does not vanish by reasons of symmetry.

We can also make use of the estimate of the nonlinear coefficient a given by Eq. (1.4.30) to estimate of the size of the second-order susceptibility under highly nonresonant conditions. If we replace $D(\omega)$ by ω_0^2 in the denominator of Eq. (1.4.24), set N equal to $1/d^3$, and set a equal to ω_0^2/d , we find that $\chi^{(2)}$ is given approximately by

$$\chi^{(2)} = \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4}. \quad (1.4.31)$$

Using the values $\omega_0 = 1 \times 10^{16}$ rad/s, $d = 3$ Å, $e = 1.6 \times 10^{-19}$ C, and $m = 9.1 \times 10^{-31}$ kg, we find that

$$\chi^{(2)} \simeq 6.9 \times 10^{-12} \text{ m/V}, \quad (1.4.32)$$

which is in good agreement with the measured values presented in Table 1.5.3 (see p. 50).

1.4.3. Centrosymmetric Media

For the case of a centrosymmetric medium, we assume that the electronic restoring force is given not by Eq. (1.4.2) but rather by

$$\tilde{F}_{\text{restoring}} = -m\omega_0^2 \tilde{x} + mb\tilde{x}^3, \quad (1.4.33)$$

where b is a parameter that characterizes the strength of the nonlinearity. This restoring force corresponds to the potential energy function

$$U(\tilde{x}) = - \int \tilde{F}_{\text{restoring}} d\tilde{x} = \frac{1}{2} m\omega_0^2 \tilde{x}^2 - \frac{1}{4} mb\tilde{x}^4. \quad (1.4.34)$$

This potential function is illustrated in the Fig. 1.4.2 (for the usual case in which b is positive) and is seen to be symmetric under the operation $\tilde{x} \rightarrow -\tilde{x}$, which it must be for a medium that possesses a center of inversion symmetry. Note that $-mb\tilde{x}^4/4$ is simply the lowest-order correction term to the parabolic potential well described by the term $\frac{1}{2}m\omega_0^2\tilde{x}^2$. We assume that the electronic displacement \tilde{x} never becomes so large that it is necessary to include higher-order terms in the potential function.

We shall see below that the lowest-order nonlinear response resulting from the restoring force of Eq. (1.4.33) is a third-order contribution to the polarization, which can be described by a $\chi^{(3)}$ susceptibility. As in the case of non-centrosymmetric media, the tensor properties of this susceptibility cannot be specified unless the internal symmetries of the medium are completely known. One of the most important cases is that of a material that is isotropic

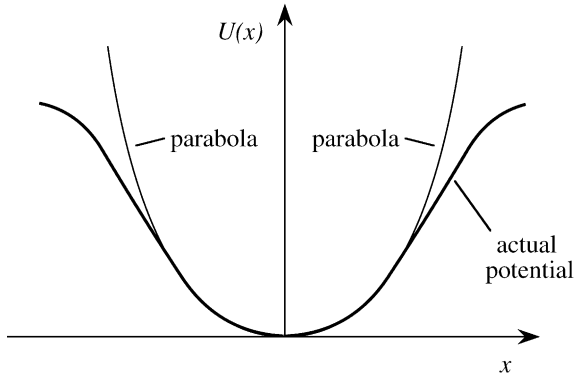


FIGURE 1.4.2 Potential energy function for a centrosymmetric medium.

(as well as being centrosymmetric). Examples of such materials are glasses and liquids. In such a case, we can take the restoring force to have the form

$$\tilde{\mathbf{F}}_{\text{restoring}} = -m\omega_0^2\tilde{\mathbf{r}} + mb(\tilde{\mathbf{r}} \cdot \tilde{\mathbf{r}})\tilde{\mathbf{r}}. \quad (1.4.35)$$

The second contribution to the restoring force must have the form shown because it is the only form that is third-order in the displacement $\tilde{\mathbf{r}}$ and is directed in the $\tilde{\mathbf{r}}$ direction, which is the only possible direction for an isotropic medium.

The equation of motion for the electron displacement from equilibrium is thus

$$\ddot{\tilde{\mathbf{r}}} + 2\gamma\dot{\tilde{\mathbf{r}}} + \omega_0^2\tilde{\mathbf{r}} - b(\tilde{\mathbf{r}} \cdot \tilde{\mathbf{r}})\tilde{\mathbf{r}} = -e\tilde{\mathbf{E}}(t)/m. \quad (1.4.36)$$

We assume that the applied field is given by

$$\tilde{\mathbf{E}}(t) = \mathbf{E}_1 e^{-i\omega_1 t} + \mathbf{E}_2 e^{-i\omega_2 t} + \mathbf{E}_3 e^{-i\omega_3 t} + \text{c.c.}; \quad (1.4.37)$$

we allow the field to have three distinct frequency components because this is the most general possibility for a third-order interaction. However, the algebra becomes very tedious if all three terms are written explicitly, and hence we express the applied field as

$$\tilde{\mathbf{E}}(t) = \sum_n \mathbf{E}(\omega_n) e^{-i\omega_n t}. \quad (1.4.38)$$

The method of solution is analogous to that used above for a noncentrosymmetric medium. We replace $\tilde{\mathbf{E}}(t)$ in Eq. (1.4.36) by $\lambda\tilde{\mathbf{E}}(t)$, where λ is a parameter that characterizes the strength of the perturbation and that is set equal to unity at the end of the calculation. We seek a solution to Eq. (1.4.36) having

the form of a power series in the parameter λ :

$$\tilde{\mathbf{r}}(t) = \lambda \tilde{\mathbf{r}}^{(1)}(t) + \lambda^2 \tilde{\mathbf{r}}^{(2)}(t) + \lambda^3 \tilde{\mathbf{r}}^{(3)}(t) + \dots \quad (1.4.39)$$

We insert Eq. (1.4.39) into Eq. (1.4.36) and require that the terms proportional to λ^n vanish separately for each value of n . We thereby find that

$$\ddot{\mathbf{r}}^{(1)} + 2\gamma \dot{\mathbf{r}}^{(1)} + \omega_0^2 \tilde{\mathbf{r}}^{(1)} = -e\tilde{\mathbf{E}}(t)/m, \quad (1.4.40a)$$

$$\ddot{\mathbf{r}}^{(2)} + 2\gamma \dot{\mathbf{r}}^{(2)} + \omega_0^2 \tilde{\mathbf{r}}^{(2)} = 0, \quad (1.4.40b)$$

$$\ddot{\mathbf{r}}^{(3)} + 2\gamma \dot{\mathbf{r}}^{(3)} + \omega_0^2 \tilde{\mathbf{r}}^{(3)} - b(\tilde{\mathbf{r}}^{(1)} \cdot \tilde{\mathbf{r}}^{(1)})\tilde{\mathbf{r}}^{(1)} = 0 \quad (1.4.40c)$$

for $n = 1, 2$, and 3 , respectively. Equation (1.4.40a) is simply the vector version of Eq. (1.4.7a), encountered above. Its steady-state solution is

$$\tilde{\mathbf{r}}^{(1)}(t) = \sum_n \mathbf{r}^{(1)}(\omega_n) e^{-i\omega_n t}, \quad (1.4.41a)$$

where

$$\mathbf{r}^{(1)}(\omega_n) = \frac{-e\mathbf{E}(\omega_n)/m}{D(\omega_n)} \quad (1.4.41b)$$

with $D(\omega_n)$ given as above by $D(\omega_n) = \omega_0^2 - \omega_n^2 - 2i\omega_n\gamma$. Since the polarization at frequency ω_n is given by

$$\mathbf{P}^{(1)}(\omega_n) = -Ne\mathbf{r}^{(1)}(\omega_n), \quad (1.4.42)$$

we can describe the Cartesian components of the polarization through the relation

$$P_i^{(1)}(\omega_n) = \epsilon_0 \sum_j \chi_{ij}^{(1)}(\omega_n) E_j(\omega_n). \quad (1.4.43a)$$

Here the linear susceptibility is given by

$$\chi_{ij}^{(1)}(\omega_n) = \chi^{(1)}(\omega_n) \delta_{ij} \quad (1.4.43b)$$

with $\chi^{(1)}(\omega_n)$ given as in Eq. (1.4.17) by

$$\chi^{(1)}(\omega_n) = \frac{Ne^2/m}{\epsilon_0 D(\omega_n)} \quad (1.4.43c)$$

and where δ_{ij} is the Kronecker delta, which is defined such that $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$.

The second-order response of the system is described by Eq. (1.4.40b). Since this equation is damped but not driven, its steady-state solution vanishes, that is,

$$\tilde{\mathbf{r}}^{(2)} = 0. \quad (1.4.44)$$

To calculate the third-order response, we substitute the expression for $\tilde{\mathbf{r}}^{(1)}(t)$ given by Eq. (1.4.41a) into Eq. (1.4.40c), which becomes

$$\ddot{\tilde{\mathbf{r}}}^{(3)} + 2\gamma\dot{\tilde{\mathbf{r}}}^{(3)} + \omega_0^2\tilde{\mathbf{r}}^{(3)} = - \sum_{mnp} \frac{be^3[\mathbf{E}(\omega_m) \cdot \mathbf{E}(\omega_n)]\mathbf{E}(\omega_p)}{m^3 D(\omega_m)D(\omega_n)D(\omega_p)} \times e^{-i(\omega_m+\omega_n+\omega_p)t}. \quad (1.4.45)$$

Because of the summation over m , n , and p , the right-hand side of this equation contains many different frequencies. We denote one of these frequencies by $\omega_q = \omega_m + \omega_n + \omega_p$. The solution to Eq. (1.4.45) can then be written in the form

$$\tilde{\mathbf{r}}^{(3)}(t) = \sum_q \mathbf{r}^{(3)}(\omega_q) e^{-i\omega_q t}. \quad (1.4.46)$$

We substitute Eq. (1.4.46) into Eq. (1.4.45) and find that $\mathbf{r}^{(3)}(\omega_q)$ is given by

$$(-\omega_q^2 - i\omega_q 2\gamma + \omega_0^2)\mathbf{r}^{(3)}(\omega_q) = - \sum_{(mnp)} \frac{be^3[\mathbf{E}(\omega_m) \cdot \mathbf{E}(\omega_n)]\mathbf{E}(\omega_p)}{m^3 D(\omega_m)D(\omega_n)D(\omega_p)}, \quad (1.4.47)$$

where the summation is to be carried out over frequencies ω_m , ω_n , and ω_p with the restriction that $\omega_m + \omega_n + \omega_p$ must equal ω_q . Since the coefficient of $\mathbf{r}^{(3)}(\omega_q)$ on the left-hand side is just $D(\omega_q)$, we obtain

$$\mathbf{r}^{(3)}(\omega_q) = - \sum_{(mnp)} \frac{be^3[\mathbf{E}(\omega_m) \cdot \mathbf{E}(\omega_n)]\mathbf{E}(\omega_p)}{m^3 D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}. \quad (1.4.48)$$

The amplitude of the polarization component oscillating at frequency ω_q then is given in terms of this amplitude by

$$\mathbf{P}^{(3)}(\omega_q) = -Ne\mathbf{r}^{(3)}(\omega_q). \quad (1.4.49)$$

We next recall the definition of the third-order nonlinear susceptibility Eq. (1.3.20),

$$P_i^{(3)}(\omega_q) = \epsilon_0 \sum_{jkl} \sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p). \quad (1.4.50)$$

Since this equation contains a summation over the dummy variables m , n , and p , there is more than one possible choice for the expression for the nonlinear susceptibility. An obvious choice for this expression for the susceptibility,

based on the way in which Eqs. (1.4.48) and (1.4.49) are written, is

$$\chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) = \frac{Nbe^4\delta_{jk}\delta_{il}}{\epsilon_0 m^3 D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}. \quad (1.4.51)$$

While Eq. (1.4.51) is a perfectly adequate expression for the nonlinear susceptibility, it does not explicitly show the full symmetry of the interaction in terms of the arbitrariness of which field we call $E_j(\omega_m)$, which we call $E_k(\omega_n)$, and which we call $E_l(\omega_p)$. It is conventional to define nonlinear susceptibilities in a manner that displays this symmetry, which is known as intrinsic permutation symmetry. Since there are six possible permutations of the orders in which $E_j(\omega_m)$, $E_k(\omega_n)$, and $E_l(\omega_p)$ may be taken, we define the third-order susceptibility to be one-sixth of the sum of the six expressions analogous to Eq. (1.4.51) with the input fields taken in all possible orders. When we carry out this prescription, we find that only three distinct contributions occur and that the resulting form for the nonlinear susceptibility is given by

$$\chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) = \frac{Nbe^4[\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]}{3\epsilon_0 m^3 D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}. \quad (1.4.52)$$

This expression can be rewritten in terms of the linear susceptibilities at the four different frequencies $\omega_q, \omega_m, \omega_n$, and ω_p by using Eq. (1.4.43c) to eliminate the resonance denominator factors $D(\omega)$. We thereby obtain

$$\begin{aligned} \chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) &= \frac{bm\epsilon_0^3}{3N^3e^4} [\chi^{(1)}(\omega_q)\chi^{(1)}(\omega_m)\chi^{(1)}(\omega_n)\chi^{(1)}(\omega_p)] \\ &\quad \times [\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]. \end{aligned} \quad (1.4.53)$$

We can estimate the value of the phenomenological constant b that appears in this result by means of an argument analogous to that used above (see Eq. (1.4.30)) to estimate the value of the constant a that appears in the expression for $\chi^{(2)}$. We assume that the linear and nonlinear contributions to the restoring force given by Eq. (1.4.33) will become comparable in magnitude when the displacement \tilde{x} becomes comparable to the atomic dimension d , that is, when $m\omega_0^2 d = mbd^3$, which implies that

$$b = \frac{\omega_0^2}{d^2}. \quad (1.4.54)$$

Using this expression for b , we can now estimate the value of the nonlinear susceptibility. For the case of nonresonant excitation, $D(\omega)$ is approximately

equal to ω_0^2 , and hence from Eq. (1.4.52) we obtain

$$\chi^{(3)} \simeq \frac{Nbe^4}{\epsilon_0 m^3 \omega_0^8} = \frac{e^4}{\epsilon_0 m^3 \omega_0^6 d^5}. \quad (1.4.55)$$

Taking $d = 3 \text{ \AA}$ and $\omega_0 = 7 \times 10^{15} \text{ rad/sec}$, we obtain

$$\chi^{(3)} \simeq 344 \text{ pm}^2/\text{V}^2 \quad (1.4.56)$$

We shall see in Chapter 4 that this value is typical of the nonlinear susceptibility of many materials.

1.5. Properties of the Nonlinear Susceptibility

In this section we study some of the formal symmetry properties of the nonlinear susceptibility. Let us first see why it is important that we understand these symmetry properties. We consider the mutual interaction of three waves of frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$, as illustrated in Fig. 1.5.1. A complete description of the interaction of these waves requires that we know the nonlinear polarizations $\mathbf{P}(\omega_i)$ influencing each of them. Since these quantities are given in general (see also Eq. (1.3.12)) by the expression

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m), \quad (1.5.1)$$

we therefore need to determine the six tensors

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega_1, \omega_3, -\omega_2), \quad \chi_{ijk}^{(2)}(\omega_1, -\omega_2, \omega_3), \quad \chi_{ijk}^{(2)}(\omega_2, \omega_3, -\omega_1), \\ \chi_{ijk}^{(2)}(\omega_2, -\omega_1, \omega_3), \quad \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2), \quad \text{and} \quad \chi_{ijk}^{(2)}(\omega_3, \omega_2, \omega_1) \end{aligned}$$

and six additional tensors in which each frequency is replaced by its negative. In these expressions, the indices i , j , and k can independently take on the values x , y , and z . Since each of these 12 tensors thus consists of 27 Cartesian components, as many as 324 different (complex) numbers need to be specified in order to describe the interaction.

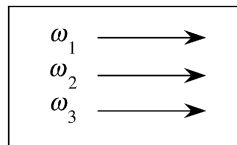


FIGURE 1.5.1 Optical waves of frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$ interact in a lossless second-order nonlinear optical medium.

Fortunately, there are a number of restrictions resulting from symmetries that relate the various components of $\chi^{(2)}$, and hence far fewer than 324 numbers are usually needed to describe the nonlinear coupling. In this section, we study some of these formal properties of the nonlinear susceptibility. The discussion will deal primarily with the second-order $\chi^{(2)}$ susceptibility, but can readily be extended to $\chi^{(3)}$ and higher-order susceptibilities.

1.5.1. Reality of the Fields

Recall that the nonlinear polarization describing the sum-frequency response to input fields at frequencies ω_n and ω_m has been represented as

$$\tilde{P}_i(\mathbf{r}, t) = P_i(\omega_n + \omega_m)e^{-i(\omega_n + \omega_m)t} + P_i(-\omega_n - \omega_m)e^{i(\omega_n + \omega_m)t}. \quad (1.5.2)$$

Since $\tilde{P}_i(\mathbf{r}, t)$ is a physically measurable quantity, it must be purely real, and hence its positive- and negative-frequency components must be related by

$$P_i(-\omega_n - \omega_m) = P_i(\omega_n + \omega_m)^*. \quad (1.5.3)$$

The electric field must also be a real quantity, and its complex frequency components must obey the analogous conditions:

$$E_j(-\omega_n) = E_j(\omega_n)^*, \quad (1.5.4a)$$

$$E_k(-\omega_m) = E_k(\omega_m)^*. \quad (1.5.4b)$$

Since the fields and polarization are related to each other through the second-order susceptibility of Eq. (1.5.1), we conclude that the positive- and negative-frequency components of the susceptibility must be related according to

$$\chi_{ijk}^{(2)}(-\omega_n - \omega_m, -\omega_n, -\omega_m) = \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)^*. \quad (1.5.5)$$

1.5.2. Intrinsic Permutation Symmetry

Earlier we introduced the concept of intrinsic permutation symmetry when we rewrote the expression (1.4.51) for the nonlinear susceptibility of a classical, anharmonic oscillator in the conventional form of Eq. (1.4.52). In the present section, we treat the concept of intrinsic permutation symmetry from a more general point of view.

According to Eq. (1.5.1), one of the contributions to the nonlinear polarization $P_i(\omega_n + \omega_m)$ is the product $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)E_j(\omega_n)E_k(\omega_m)$. However, since j, k, n , and m are dummy indices, we could just as well have written this contribution with n interchanged with m and with j interchanged

with k , that is, as $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n)E_k(\omega_m)E_j(\omega_n)$. These two expressions are numerically equal if we require that the nonlinear susceptibility be unchanged by the simultaneous interchange of its last two frequency arguments and its last two Cartesian indices:

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) = \chi_{ikj}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n). \quad (1.5.6)$$

This property is known as intrinsic permutation symmetry. More physically, this condition is simply a statement that it cannot matter which is the first field and which is the second field in products such as $E_j(\omega_n)E_k(\omega_m)$.

Note that this symmetry condition is introduced purely as a matter of convenience. For example, we could set one member of the pair of elements shown in Eq. (1.5.6) equal to zero and double the value of the other member. Then, when the double summation of Eq. (1.5.1) was carried out, the result for the physically meaningful quantity $P_j(\omega_n + \omega_m)$ would be left unchanged.

This symmetry condition can also be derived from a more general point of view using the concept of the nonlinear response function (Butcher, 1965; Flytzanis, 1975).

1.5.3. Symmetries for Lossless Media

Two additional symmetries of the nonlinear susceptibility tensor occur for the case of a lossless nonlinear medium.

The first of these conditions states that for a lossless medium all of the components of $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$ are real. This result is obeyed for the classical anharmonic oscillator described in Section 1.4, as can be verified by evaluating the expression for $\chi^{(2)}$ in the limit in which all of the applied frequencies and their sums and differences are significantly different from the resonance frequency. The general proof that $\chi^{(2)}$ is real for a lossless medium is obtained by verifying that the quantum-mechanical expression for $\chi^{(2)}$ (which is derived in Chapter 3) is also purely real in this limit.

The second of these new symmetries is *full* permutation symmetry. This condition states that *all* of the frequency arguments of the nonlinear susceptibility can be freely interchanged, as long as the corresponding Cartesian indices are interchanged simultaneously. In permuting the frequency arguments, it must be recalled that the first argument is always the sum of the latter two, and thus that the signs of the frequencies must be inverted when the first frequency is interchanged with either of the latter two. Full permutation symmetry implies, for instance, that

$$\chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jki}^{(2)}(-\omega_1 = \omega_2 - \omega_3). \quad (1.5.7)$$

However, according to Eq. (1.5.5), the right-hand side of this equation is equal to $\chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3)^*$, which, due to the reality of $\chi^{(2)}$ for a lossless medium, is equal to $\chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3)$. We hence conclude that

$$\chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3). \quad (1.5.8)$$

By an analogous procedure, one can show that

$$\chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{kij}^{(2)}(\omega_2 = \omega_3 - \omega_1). \quad (1.5.9)$$

A general proof of the validity of the condition of full permutation symmetry entails verifying that the quantum-mechanical expression for $\chi^{(2)}$ (which is derived in Chapter 3) obeys this condition when all of the optical frequencies are detuned many linewidths from the resonance frequencies of the optical medium. Full permutation symmetry can also be deduced from a consideration of the field energy density within a nonlinear medium, as shown below.

1.5.4. Field Energy Density for a Nonlinear Medium

The condition that the nonlinear susceptibility must possess full permutation symmetry for a lossless medium can be deduced from a consideration of the form of the electromagnetic field energy within a nonlinear medium. For the case of a linear medium, the energy density associated with the electric field

$$\tilde{E}_i(t) = \sum_n E_i(\omega_n) e^{-i\omega_n t} \quad (1.5.10)$$

is given according to Poynting's theorem as

$$U = \frac{1}{2} \langle \tilde{\mathbf{D}} \cdot \tilde{\mathbf{E}} \rangle = \frac{1}{2} \sum_i \langle \tilde{D}_i \tilde{E}_i \rangle, \quad (1.5.11)$$

where the angular brackets denote a time average. Since the displacement vector is given by

$$\tilde{D}_i(t) = \epsilon_0 \sum_j \epsilon_{ij} \tilde{E}_j(t) = \epsilon_0 \sum_j \sum_n \epsilon_{ij}(\omega_n) E_j(\omega_n) e^{-i\omega_n t}, \quad (1.5.12)$$

where the dielectric tensor is given by

$$\epsilon_{ij}(\omega_n) = \delta_{ij} + \chi_{ij}^{(1)}(\omega_n), \quad (1.5.13)$$

we can write the energy density as

$$U = \frac{\epsilon_0}{2} \sum_i \sum_n E_i^*(\omega_n) E_i(\omega_n) + \frac{\epsilon_0}{2} \sum_{ij} \sum_n E_i^*(\omega_n) \chi_{ij}^{(1)}(\omega_n) E_j(\omega_n). \quad (1.5.14)$$

Here the first term represents the energy density associated with the electric field in vacuum and the second term represents the energy stored in the polarization of the medium.

For the case of a nonlinear medium, the expression for the electric field energy density (Armstrong *et al.*, 1962; Kleinman, 1962; Pershan, 1963) associated with the polarization of the medium takes the more general form

$$\begin{aligned} U = & \frac{\epsilon_0}{2} \sum_{ij} \sum_n \chi_{ij}^{(1)}(\omega_n) E_i^*(\omega_n) E_j(\omega_n) \\ & + \frac{\epsilon_0}{3} \sum_{ijk} \sum_{mn} \chi_{ijk}^{(2')}(-\omega_n - \omega_m, \omega_m, \omega_n) E_i^*(\omega_m + \omega_n) E_j(\omega_m) E_k(\omega_n) \\ & + \frac{\epsilon_0}{4} \sum_{ijkl} \sum_{mno} \chi_{ijkl}^{(3')}(-\omega_o - \omega_n - \omega_m, \omega_m, \omega_n, \omega_o) \\ & \times E_i^*(\omega_m + \omega_n + \omega_o) E_j(\omega_m) E_k(\omega_n) E_l(\omega_o) + \dots \end{aligned} \quad (1.5.15)$$

For the present, the quantities $\chi^{(2)'}$, $\chi^{(3)'}$, ... are to be thought of simply as coefficients in the power series expansion of U in the amplitudes of the applied field; later these quantities will be related to the nonlinear susceptibilities. Since the order in which the fields are multiplied together in determining U is immaterial, the quantities $\chi^{(n)'}$ clearly possess full permutation symmetry, that is, their frequency arguments can be freely permuted as long as the corresponding indices are also permuted.

In order to relate the expression (1.5.15) for the energy density to the nonlinear polarization, and subsequently to the nonlinear susceptibility, we use the result that the polarization of a medium is given (Landau and Lifshitz, 1960; Pershan, 1963) by the expression

$$P_i(\omega_n) = \frac{\partial U}{\partial E_i^*(\omega_n)}. \quad (1.5.16)$$

Thus, by differentiation of Eq. (1.5.15), we obtain an expression for the linear polarization as

$$P_i^{(1)}(\omega_m) = \epsilon_0 \sum_j \chi_{ij}^{(1)}(\omega_m) E_j(\omega_m), \quad (1.5.17a)$$

and for the nonlinear polarization as*

$$P_i^{(2)}(\omega_m + \omega_n) = \epsilon_0 \sum_{jk} \sum_{(mn)} \chi_{ijk}^{(2)'}(-\omega_m - \omega_n, \omega_m, \omega_n) E_j(\omega_m) E_k(\omega_n) \quad (1.5.17b)$$

$$P_i^{(3)}(\omega_m + \omega_n + \omega_o) = \epsilon_0 \sum_{jkl} \sum_{(mno)} \chi_{ijkl}^{(3)'}(-\omega_m - \omega_n - \omega_o, \omega_m, \omega_n, \omega_o) \\ \times E_j(\omega_m) E_k(\omega_n) E_l(\omega_o). \quad (1.5.17c)$$

We note that these last two expressions are identical to Eqs. (1.3.12) and (1.3.20), which define the nonlinear susceptibilities (except for the unimportant fact that the quantities $\chi^{(n)}$ and $\chi^{(n)'}$ use opposite conventions regarding the sign of the first frequency argument). Since the quantities $\chi^{(n)'}$ possess full permutation symmetry, we conclude that the susceptibilities $\chi^{(n)}$ do also. Note that this demonstration is valid only for the case of a lossless medium, because only in this case is the internal energy a function of state.

1.5.5. Kleinman's Symmetry

Quite often nonlinear optical interactions involve optical waves whose frequencies ω_i are much smaller than the lowest resonance frequency of the material system. Under these conditions, the nonlinear susceptibility is essentially independent of frequency. For example, the expression (1.4.24) for the second-order susceptibility of an anharmonic oscillator predicts a value of the susceptibility that is essentially independent of the frequencies of the applied waves whenever these frequencies are much smaller than the resonance frequency ω_0 . Furthermore, under conditions of low-frequency excitation the system responds essentially instantaneously to the applied field, and we have seen in Section 1.2 that under such conditions the nonlinear polarization can be described in the time domain by the relation

$$\tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t), \quad (1.5.18)$$

where $\chi^{(2)}$ can be taken to be a constant.

Since the medium is necessarily lossless whenever the applied field frequencies ω_i are very much smaller than the resonance frequency ω_0 , the condition of full permutation symmetry (1.5.7) must be valid under these circumstances. This condition states that the indices can be permuted as long as the

* In performing the differentiation, the prefactors $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$ of Eq. (1.5.15) disappear because 2, 3, 4, ... equivalent terms appear as the result of the summations over the frequency arguments.

frequencies are permuted simultaneously, and it leads to the conclusion that

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) &= \chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3) = \chi_{kij}^{(2)}(\omega_2 = \omega_3 - \omega_1) \\
 &= \chi_{ikj}^{(2)}(\omega_3 = \omega_2 + \omega_1) = \chi_{kji}^{(2)}(\omega_2 = -\omega_1 + \omega_3) \\
 &= \chi_{jik}^{(2)}(\omega_1 = \omega_3 - \omega_2).
 \end{aligned}$$

However, under the present conditions $\chi^{(2)}$ does not actually depend on the frequencies, and we can therefore permute the indices without permuting the frequencies, leading to the result

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) &= \chi_{jki}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{kij}^{(2)}(\omega_3 = \omega_1 + \omega_2) \\
 &= \chi_{ikj}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jik}^{(2)}(\omega_3 = \omega_1 + \omega_2) \\
 &= \chi_{kji}^{(2)}(\omega_3 = \omega_1 + \omega_2). \tag{1.5.19}
 \end{aligned}$$

This result is known as the Kleinman symmetry condition. It is valid whenever dispersion of the susceptibility can be neglected.

1.5.6. Contracted Notation

We now introduce a notational device that is often used when the Kleinman symmetry condition is valid. We introduce the tensor

$$d_{ijk} = \frac{1}{2} \chi_{ijk}^{(2)} \tag{1.5.20}$$

and for simplicity suppress the frequency arguments. The factor of $\frac{1}{2}$ is a consequence of historical convention. The nonlinear polarization can then be written as

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} 2d_{ijk} E_j(\omega_n) E_k(\omega_m). \tag{1.5.21}$$

We now assume that d_{ijk} is symmetric in its last two indices. This assumption is valid whenever Kleinman's symmetry condition is valid and in addition is valid in general for second-harmonic generation, since in this case ω_n and ω_m are equal. We then simplify the notation by introducing a contracted matrix d_{il} according to the prescription

$$\begin{array}{llllll}
 jk: & 11 & 22 & 33 & 23, 32 & 31, 13 & 12, 21 \\
 l: & 1 & 2 & 3 & 4 & 5 & 6
 \end{array} \tag{1.5.22}$$

The nonlinear susceptibility tensor can then be represented as the 3×6 matrix

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}. \quad (1.5.23)$$

If we now *explicitly* introduce the Kleinman symmetry condition—that is, we assert that the indices d_{ijk} can be freely permuted, we find that not all of the 18 elements of d_{il} are independent. For instance, we see that

$$d_{12} \equiv d_{122} = d_{212} \equiv d_{26} \quad (1.5.24a)$$

and that

$$d_{14} \equiv d_{123} = d_{213} \equiv d_{25}. \quad (1.5.24b)$$

By applying this type of argument systematically, we find that d_{il} has only 10 independent elements when the Kleinman symmetry condition is valid; the form of d_{il} under these conditions is

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{bmatrix}. \quad (1.5.25)$$

We can describe the nonlinear polarization leading to second-harmonic generation in terms of d_{il} by the matrix equation

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = 2\epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix}. \quad (1.5.26)$$

When the Kleinman symmetry condition is valid, we can describe the nonlinear polarization leading to sum-frequency generation (with $\omega_3 = \omega_1 + \omega_2$) by

the equation

$$\begin{bmatrix} P_x(\omega_3) \\ P_y(\omega_3) \\ P_z(\omega_3) \end{bmatrix} = 4\epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \times \begin{bmatrix} E_x(\omega_1)E_x(\omega_2) \\ E_y(\omega_1)E_y(\omega_2) \\ E_z(\omega_1)E_z(\omega_2) \\ E_y(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_y(\omega_2) \\ E_x(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_x(\omega_2) \\ E_x(\omega_1)E_y(\omega_2) + E_y(\omega_1)E_x(\omega_2) \end{bmatrix}. \quad (1.5.27)$$

As described above in relation to Eq. (1.3.16), the extra factor of 2 comes from the summation over n and m in Eq. (1.5.21).

1.5.7. Effective Value of d (d_{eff})

For a fixed geometry (i.e., for fixed propagation and polarization directions) it is possible to express the nonlinear polarization giving rise to sum-frequency generation by means of the scalar relationship

$$P(\omega_3) = 4\epsilon_0 d_{\text{eff}} E(\omega_1)E(\omega_2), \quad (1.5.28)$$

and analogously for second-harmonic generation by

$$P(2\omega) = 2\epsilon_0 d_{\text{eff}} E(\omega)^2, \quad (1.5.29)$$

where

$$E(\omega) = |\mathbf{E}(\omega)| \quad \text{and} \quad P(\omega) = |\mathbf{P}(\omega)|.$$

In each case, d_{eff} is obtained by first determining \mathbf{P} explicitly through use of Eq. (1.5.26) or (1.5.27).

A general prescription for calculating d_{eff} for each of the crystal classes has been presented by Midwinter and Warner (1965); see also Table 3.1 of Zernike and Midwinter (1973). They show, for example, that for a negative uniaxial crystal of crystal class $3m$ the effective value of d is given by the expression

$$d_{\text{eff}} = d_{31} \sin \theta - d_{22} \cos \theta \sin 3\phi \quad (1.5.30a)$$

under conditions (known as type I conditions) such that the two lower-frequency waves have the same polarization, and by

$$d_{\text{eff}} = d_{22} \cos^2 \theta \cos 3\phi \quad (1.5.30b)$$

under conditions (known as type II conditions) such that the polarizations are orthogonal. In these equations, θ is the angle between the propagation vector and the crystalline z axis (the optic axis), and ϕ is the azimuthal angle between the propagation vector and the xz crystalline plane.

1.5.8. *Spatial Symmetry of the Nonlinear Medium*

The forms of the linear and nonlinear susceptibility tensors are constrained by the symmetry properties of the optical medium. To see why this should be so, let us consider a crystal for which the x and y directions are equivalent but for which the z direction is different. By saying that the x and y directions are equivalent, we mean that if the crystal were rotated by 90 degrees about the z axis, the crystal structure would look identical after the rotation. The z axis is then said to be a fourfold axis of symmetry. For such a crystal, we would expect that the optical response would be the same for an applied optical field polarized in either the x or the y direction, and thus, for example, that the second-order susceptibility components $\chi_{zxx}^{(2)}$ and $\chi_{zyy}^{(2)}$ would be equal.

For any particular crystal, the form of the linear and nonlinear optical susceptibilities can be determined by considering the consequences of all of the symmetry properties for that particular crystal. For this reason, it is necessary to determine what types of symmetry properties can occur in a crystalline medium. By means of the mathematical method known as group theory, crystallographers have found that all crystals can be classified as belonging to one of 32 possible crystal classes depending on what is called the point group symmetry of the crystal. The details of this classification scheme lie outside of the subject matter of the present text.* However, by way of examples, a crystal is said to belong to point group 4 if it possesses only a fourfold axis of symmetry, to point group 3 if it possesses only a threefold axis of symmetry, and to belong to point group $3m$ if it possesses a threefold axis of symmetry and in addition a plane of mirror symmetry perpendicular to this axis.

1.5.9. *Influence of Spatial Symmetry on the Linear Optical Properties of a Material Medium*

As an illustration of the consequences of spatial symmetry on the optical properties of a material system, let us first consider the restrictions that this

* The reader who is interested in the details should consult Buerger (1963) or any of the other books on group theory and crystal symmetry listed in the bibliography at the end of this chapter.

symmetry imposes on the form of the linear susceptibility tensor $\chi^{(1)}$. The results of a group theoretical analysis shows that five different cases are possible depending on the symmetry properties of the material system. These possibilities are summarized in Table 1.5.1. Each entry is labeled by the crystal system to which the material belongs. By convention, crystals are categorized in terms of seven possible crystal systems on the basis of the form of the crystal lattice. (Table 1.5.2 on p. 47 gives the correspondence between crystal system and each of the 32 point groups.) For completeness, isotropic materials (such as liquids and gases) are also included in Table 1.5.1. We see from this table that cubic and isotropic materials are isotropic in their linear optical properties, because $\chi^{(1)}$ is diagonal with equal diagonal components. All of the other crystal systems are anisotropic in their linear optical properties (in the sense that the polarization \mathbf{P} need not be parallel to the applied electric field \mathbf{E}) and consequently display the property of birefringence. Tetragonal, trigonal, and hexagonal crystals are said to be uniaxial crystals because there is one particular direction (the z axis) for which the linear optical properties display rotational symmetry. Crystals of the triclinic, monoclinic, and orthorhombic systems are said to be biaxial.

TABLE 1.5.1 Form of the linear susceptibility tensor $\chi^{(1)}$ as determined by the symmetry properties of the optical medium, for each of the seven crystal classes and for isotropic materials. Each nonvanishing element is denoted by its cartesian indices

| | |
|--------------|--|
| Triclinic | $\begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix}$ |
| Monoclinic | $\begin{bmatrix} xx & 0 & xz \\ 0 & yy & 0 \\ zx & 0 & zz \end{bmatrix}$ |
| Orthorhombic | $\begin{bmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & zz \end{bmatrix}$ |
| Tetragonal | $\begin{bmatrix} xx & 0 & 0 \\ 0 & xx & 0 \\ 0 & 0 & zz \end{bmatrix}$ |
| Trigonal | |
| Hexagonal | |
| Cubic | $\begin{bmatrix} xx & 0 & 0 \\ 0 & xx & 0 \\ 0 & 0 & xx \end{bmatrix}$ |
| Isotropic | |

1.5.10. *Influence of Inversion Symmetry on the Second-Order Nonlinear Response*

One of the symmetry properties that some but not all crystals possess is centrosymmetry, also known as inversion symmetry. For a material system that is centrosymmetric (i.e., possesses a center of inversion) the $\chi^{(2)}$ nonlinear susceptibility must vanish identically. Since 11 of the 32 crystal classes possess inversion symmetry, this rule is very powerful, as it immediately eliminates all crystals belonging to these classes from consideration for second-order nonlinear optical interactions.

Although the result that $\chi^{(2)}$ vanishes for a centrosymmetric medium is general in nature, we shall demonstrate this fact only for the special case of second-harmonic generation in a medium that responds instantaneously to the applied optical field. We assume that the nonlinear polarization is given by

$$\tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t), \quad (1.5.31)$$

where the applied field is given by

$$\tilde{E}(t) = \mathcal{E} \cos \omega t. \quad (1.5.32)$$

If we now change the sign of the applied electric field $\tilde{E}(t)$, the sign of the induced polarization $\tilde{P}(t)$ must also change, because we have assumed that the medium possesses inversion symmetry. Hence the relation (1.5.31) must be replaced by

$$-\tilde{P}(t) = \epsilon_0 \chi^{(2)} [-\tilde{E}(t)]^2, \quad (1.5.33)$$

which shows that

$$-\tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t). \quad (1.5.34)$$

By comparison of this result with Eq. (1.5.31), we see that $\tilde{P}(t)$ must equal $-\tilde{P}(t)$, which can occur only if $\tilde{P}(t)$ vanishes identically. This result shows that

$$\chi^{(2)} = 0. \quad (1.5.35)$$

This result can be understood intuitively by considering the motion of an electron in a nonparabolic potential well. Because of the nonlinearity of the associated restoring force, the atomic response will show significant harmonic distortion. Part (a) of Fig. 1.5.2 shows the waveform of the incident monochromatic electromagnetic wave of frequency ω . For the case of a medium with linear response (part (b)), there is no distortion of the waveform associated with the polarization of the medium. Part (c) shows the induced po-

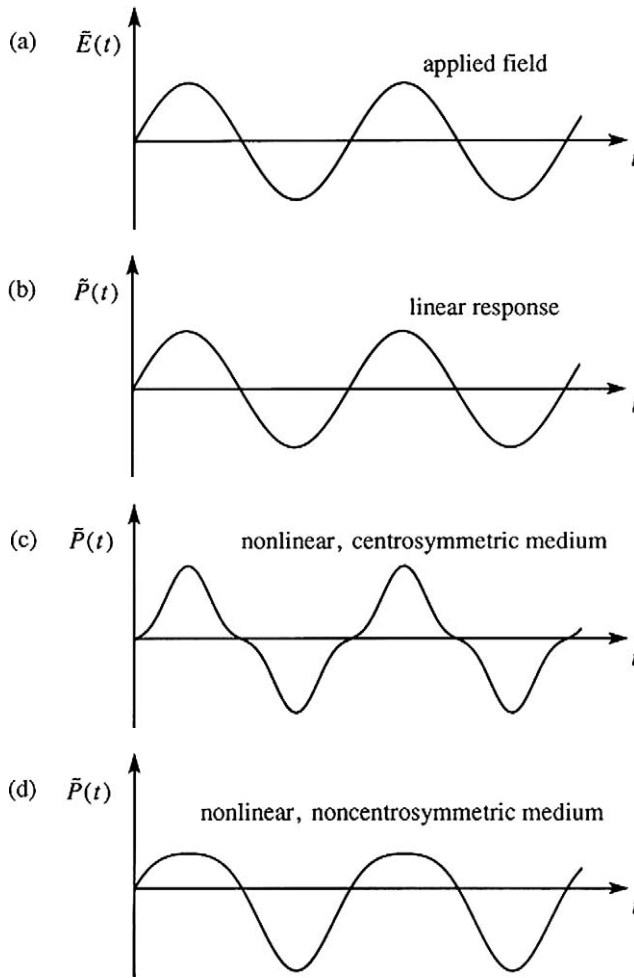


FIGURE 1.5.2 Waveforms associated with the atomic response.

larization for the case of a nonlinear medium that possesses a center of symmetry and whose potential energy function has the form shown in Fig. 1.4.2. Although significant waveform distortion is evident, only odd harmonics of the fundamental frequency are present. For the case (part (d)) of a nonlinear, noncentrosymmetric medium having a potential energy function of the form shown in Fig. 1.4.1, both even and odd harmonics are present in the waveform associated with the atomic response. Note also the qualitative difference between the waveforms shown in parts (c) and (d). For the centrosymmetric medium (part (c)), the time-averaged response is zero, whereas for the

noncentrosymmetric medium (part (d)) the time-average response is nonzero, because the medium responds differently to an electric field pointing, say, in the upward direction than to one pointing downward.*

1.5.11. *Influence of Spatial Symmetry on the Second-Order Susceptibility*

We have just seen how inversion symmetry when present requires that the second-order vanish identically. Any additional symmetry property of a nonlinear optical medium can impose additional restrictions on the form of the nonlinear susceptibility tensor. By explicit consideration of the symmetries of each of the 32 crystal classes, one can determine the allowed form of the susceptibility tensor for crystals of that class. The results of such a calculation for the second-order nonlinear optical response, which was performed originally by Butcher (1965), are presented in Table 1.5.2. Under those conditions (described following Eq. (1.5.21)) where the second-order susceptibility can be described using contracted notation, the results presented in Table 1.5.2 can usefully be displayed graphically. These results, as adapted from Zernike and Midwinter (1973), are presented in Fig. 1.5.3. Note that the influence of Kleinman symmetry is also described in the figure. As an example of how to use the table, the diagram for a crystal of class $3m$ is meant to imply that the form of the d_{il} matrix is

$$d_{il} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

The second-order nonlinear optical susceptibilities of a number of crystals are summarized in Table 1.5.3. This table should be used only with some caution. There is considerable spread in the values of the nonlinear coefficients quoted in the literature, both because of the wavelength dependence of the nonlinear susceptibility and because of measurement inaccuracies. A detailed analysis of the measurement of nonlinear coefficients has been presented by Shoji *et al.* (1997). The references cited in the footnote to the table provide more detailed tabulations of nonlinear coefficients.

* Parts (a) and (b) of Fig. 1.5.2 are plots of the function $\sin \omega t$, part (c) is a plot of the function $\sin \omega t - 0.25 \sin 3\omega t$, and part (d) is a plot of $-0.2 + \sin \omega t + 0.2 \cos 2\omega t$.

TABLE 1.5.2 Form of the second-order susceptibility tensor for each of the 32 crystal classes. Each element is denoted by its Cartesian indices

| Crystal System | Crystal Class | Nonvanishing Tensor Elements |
|----------------|------------------------------------|--|
| Triclinic | $1 = C_1$ | All elements are independent and nonzero |
| | $\bar{1} = S_2$ | Each element vanishes |
| Monoclinic | $2 = C_2$ | $xyz, xzy, xxy, xyx, yxx, yyy, yzz, yzx, yxz, zyz,$ zzy, zxy, zyx (twofold axis parallel to \hat{y}) |
| | $m = C_{1h}$ | $xxx, xyy, xzz, xzx, xxz, yyz, yzy, yxy, yyx, zxx,$ zyy, zzz, zzx, zxz (mirror plane perpendicular to \hat{y}) |
| | $2/m = C_{2h}$ | Each element vanishes |
| Orthorhombic | $222 = D_2$ | $xyz, xzy, yzx, yxz, zxy, zyx$ |
| | $mm2 = C_{2v}$ | $xzx, xxz, yyz, yzy, zxx, zyy, zzz$ |
| | $mmm = D_{2h}$ | Each element vanishes |
| Tetragonal | $4 = C_4$ | $xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz,$ $zxx = zyy, zzz, zxy = -zyx$ |
| | $\bar{4} = S_4$ | $xyz = yxz, xzy = yzx, xzx = -yzy, xxz = -yyz,$ $zxx = -zyy, zxy = zyx$ |
| | $422 = D_4$ | $xyz = -yxz, xzy = -yzx, zxy = -zyx$ |
| | $4mm = C_{4v}$ | $xzx = yzy, xxz = yyz, zxx = zyy, zzz$ |
| | $\bar{4}2m = D_{2d}$ | $xyz = yxz, xzy = yzx, zxy = zyx$ |
| | $4/m = C_{4h}$ | Each element vanishes |
| | $4/mmm = D_{4h}$ | Each element vanishes |
| | | |
| Cubic | $432 = O$ | $xyz = -xzy = yzx = -yxz = zxy = -zyx$ |
| | $\bar{4}3m = T_d$ | $xyz = xzy = yzx = yxz = zxy = zyx$ |
| | $23 = T$ | $xyz = yzx = zxy, xzy = yxz = zyx$ |
| | $m\bar{3} = T_h, m\bar{3}m = O_h$ | Each element vanishes |
| Trigonal | $3 = C_3$ | $xxx = -xyy = -yyz = -yxy, xyz = -yxz, xzy = -yzx,$ $xzx = yzy, xxz = yyz, yyy = -yxx = -xxy = -xyx,$ $zxx = zyy, zzz, zxy = -zyx$ |
| | $32 = D_3$ | $xxx = -xyy = -yyx = -yxy, xyz = -yxz,$ $xzy = -yzx, zxy = -zyx$ |
| | $3m = C_{3v}$ | $xzx = yzy, xxz = yyz, zxx = zyy, zzz, yyy = -yxx =$ $-xxy = -xyx$ (mirror plane perpendicular to \hat{x}) |
| | $\bar{3} = S_6, \bar{3}m = D_{3d}$ | Each element vanishes |
| | | |
| Hexagonal | $6 = C_6$ | $xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz,$ $zxx = zyy, zzz, zxy = -zyx$ |
| | $\bar{6} = C_{3h}$ | $xxx = -xyy = -yxy = -yyx,$ $yyy = -yxx = -xyx = -xxxy$ |
| | $622 = D_6$ | $xyz = -yxz, xzy = -yzx, zxy = -zyx$ |
| | $6mm = C_{6v}$ | $xzx = yzy, xxz = yyz, zxx = zyy, zzz$ |
| | $\bar{6}m2 = D_{3h}$ | $yyy = -yxx = -xxy = -xyx$ |
| | $6/m = C_{6h}$ | Each element vanishes |
| | $6/mmm = D_{6h}$ | Each element vanishes |

1.5.12. Number of Independent Elements of $\chi_{ijk}^{(2)}(\omega_3, \omega_2, \omega_1)$

We remarked in relation to Eq. (1.5.1) that as many as 324 complex numbers must be specified in order to describe the general interaction of three optical waves. In practice, this number is often greatly reduced.

Because of the reality of the physical fields, only half of these numbers are independent (see Eq. (1.5.5)). Furthermore, the intrinsic permutation symmetry of $\chi^{(2)}$ (Eq. (1.5.6)) shows that there are only 81 independent parameters.

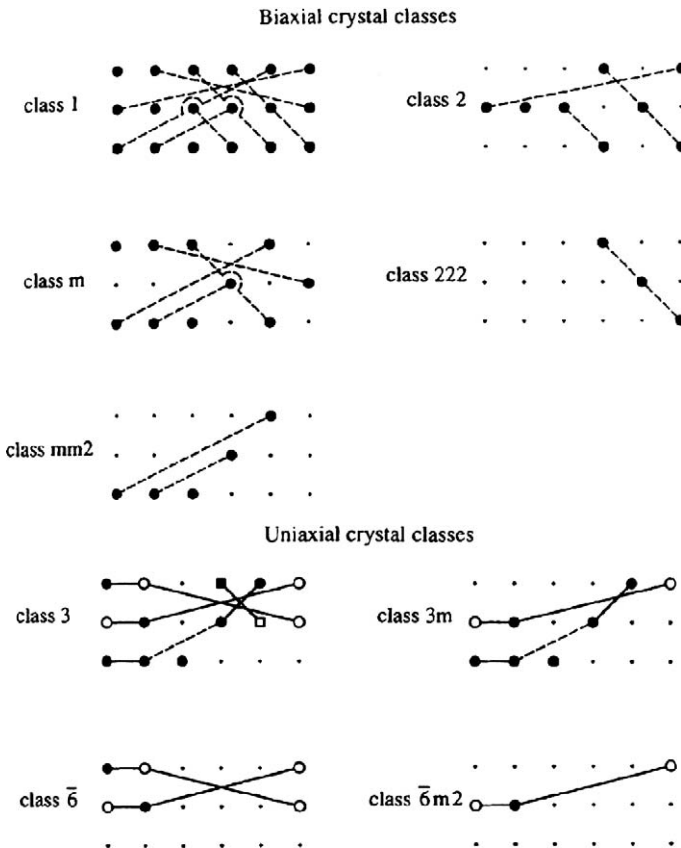


FIGURE 1.5.3 Form of the d_{il} matrix for the 21 crystal classes that lack inversion symmetry. Small dot: zero coefficient; large dot: nonzero coefficient; square: coefficient that is zero when Kleinman's symmetry condition is valid; connected symbols: numerically equal coefficients, but the open-symbol coefficient is opposite in sign to the closed symbol to which it is joined. Dashed connections are valid only under Kleinman's symmetry conditions. (After Zernike and Midwinter, 1973.)

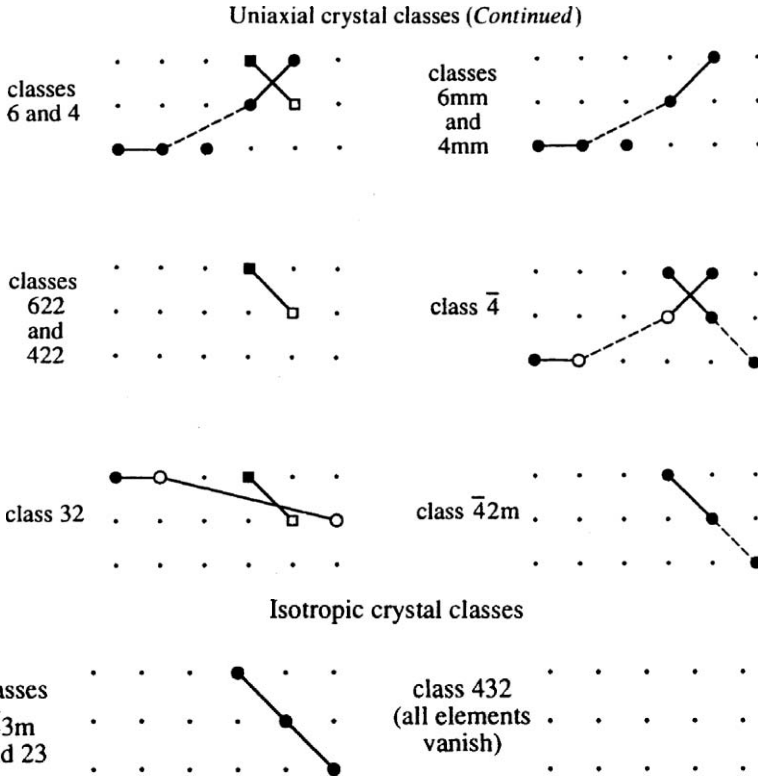


FIGURE 1.5.3 (continued)

For a lossless medium, all elements of $\chi^{(2)}$ are real and the condition of full permutation symmetry is valid, implying that only 27 of these numbers are independent. For second-harmonic generation, contracted notation can be used, and only 18 independent elements exist. When Kleinman's symmetry is valid, only 10 of these elements are independent. Furthermore, any crystalline symmetries of the nonlinear material can reduce this number further.

1.5.13. Distinction between Noncentrosymmetric and Cubic Crystal Classes

It is worth noting that a material can possess a cubic lattice and yet be non-centrosymmetric. In fact, gallium arsenide is an example of a material with just these properties. Gallium arsenide crystallizes in what is known as the zincblende structure (named after the well-known mineral form of zinc sulfide), which has crystal point group $\bar{4}3m$. As can be seen from Table 1.5.2

TABLE 1.5.3 Second-order nonlinear optical susceptibilities for several crystals

| Material | Point Group | d_{il} (pm/V) |
|--|----------------------|------------------------------------|
| Ag ₃ AsS ₃ (proustite) | $3m = C_{3v}$ | $d_{22} = 18$ $d_{15} = 11$ |
| AgGaSe ₂ | $\bar{4}2m = D_{2d}$ | $d_{36} = 33$ |
| AgSbS ₃ (pyrargyrite) | $3m = C_{3v}$ | $d_{15} = 8$ $d_{22} = 9$ |
| beta-BaB ₂ O ₄ (BBO) (beta barium borate) | $3m = C_{3v}$ | $d_{22} = 2.2$ |
| CdGeAs ₂ | $\bar{4}2m = D_{2d}$ | $d_{36} = 235$ |
| CdS | $6mm = C_{6v}$ | $d_{33} = 78$ $d_{31} = -40$ |
| GaAs | $\bar{4}3m$ | $d_{36} = 370$ |
| KH ₂ PO ₄ (KDP) | $2m$ | $d_{36} = 0.43$ |
| KD ₂ PO ₄ (KD*P) | $2m$ | $d_{36} = 0.42$ |
| LiIO ₃ | $6 = C_6$ | $d_{15} = -5.5$ $d_{31} = -7$ |
| LiNbO ₃ | $3m = C_{3v}$ | $d_{32} = -30$ $d_{31} = -5.9$ |
| Quartz | $32 = D_3$ | $d_{11} = 0.3$ $d_{14} = 0.008$ |

Notes: Values are obtained from a variety of sources. Some of the more complete tabulations are those of R.L. Sutherland (1996), that of A.V. Smith, and the data sheets of Cleveland Crystals, Inc.

To convert to the gaussian system, multiply each entry by $(3 \times 10^{-8})/4\pi = 2.386 \times 10^{-9}$ to obtain d in esu units of cm/statvolt.

In any system of units, $\chi^{(2)} = 2d$ by convention.

or from Fig. 1.5.3, materials of the $\bar{4}3m$ crystal class possess a nonvanishing second-order nonlinear optical response. In fact, as can be seen from Table 1.5.3, gallium arsenide has an unusually large second-order nonlinear susceptibility. However, as the zincblende crystal structure possesses a cubic lattice, gallium arsenide does not display birefringence. We shall see in Chapter 2 that it is necessary that a material possess adequate birefringence in order that the phase matching condition of nonlinear optics be satisfied. Because gallium arsenide does not possess birefringence, it cannot normally participate in phase-matched second-order interactions.

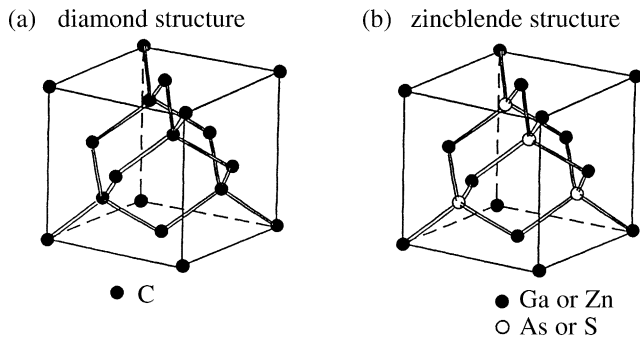


FIGURE 1.5.4 Illustration of (a) the diamond structure and (b) the zincblende structure. Both possess a cubic lattice and thus cannot display birefringence, but the carbon structure is centrosymmetric, whereas the zincblende structure is noncentrosymmetric.

It is perhaps surprising that a material can possess the highly regular spatial arrangement of atoms characteristic of the cubic lattice and yet be noncentrosymmetric. This distinction can be appreciated by examination of Fig. 1.5.4, which shows both the diamond structure (point group $m\bar{3}m$) and the zincblende structure (point group $\bar{4}3m$). One sees that the crystal lattice is the same in the two cases, but that the arrangement of atoms within the lattice allows carbon but not zincblende to possess a center of inversion symmetry. In detail, a point of inversion symmetry for the diamond structure is located midway between any two nearest-neighbor carbon atoms. This symmetry does not occur in the zincblende structure because the nearest neighbors are of different species.

1.5.14. Distinction between Noncentrosymmetric and Polar Crystal Classes

As noted above, of the 32 crystal point groups, only 21 are noncentrosymmetric and consequently can possess a nonzero second-order susceptibility $\chi^{(2)}$. A more restrictive condition is that certain crystal possess a permanent dipole moment. Crystals of this sort are known as *polar* crystals, or as *ferroelectric* crystals.* This property has important technological consequences, because crystals of this sort can display the pyroelectric effect (a change of permanent dipole moment with temperature, which can be used to construct optical

* The subtle distinctions among polar, pyroelectric, piezoelectric, and ferroelectric crystals are described by Nye (1985, pp. 78–81).

detectors)* or the photorefractive effect, which is described in greater detail in Chapter 11. Group theoretical arguments (see, for instance, Nye, 1985) demonstrate that the polar crystal classes are

| | | | | |
|----------|------------|-----------|------------|------------|
| 1 | 2 | 3 | 4 | 6 |
| <i>m</i> | <i>mm2</i> | <i>3m</i> | <i>4mm</i> | <i>6mm</i> |

Clearly, all polar crystal classes are noncentrosymmetric, but not all noncentrosymmetric crystal classes are polar. This distinction can be seen straightforwardly by means of an example from molecular physics. Consider a molecule with tetrahedral symmetry such as CCl_4 . In this molecule the four chlorine ions are arranged on the vertices of a regular tetrahedron, which is centered on the carbon ion. Clearly this arrangement cannot possess a permanent dipole moment, but this structure is nonetheless noncentrosymmetric.

1.5.15. *Influence of Spatial Symmetry on the Third-Order Nonlinear Response*

The spatial symmetry of the nonlinear optical medium also restricts the form of the third-order nonlinear optical susceptibility. The allowed form of the susceptibility has been calculated by Butcher (1965) and has been summarized by Hellwarth (1977); a minor correction to these results was later pointed out by Shang and Hsu (1987). These results are presented in Table 1.5.4. Note that for the important special case of an isotropic optical material, the results presented in Table 1.5.4 agree with the result derived explicitly in the discussion of the nonlinear refractive index in Section 4.2.

1.6. Time-Domain Description of Optical Nonlinearities

In the preceding sections, we described optical nonlinearities in terms of the response of an optical material to one or more essentially monochromatic applied fields. We found that the induced nonlinear polarization consists of a discrete summation of frequency components at the harmonics of and the sums and differences of the frequencies present in the applied field. In particular, we described the nonlinear response in the frequency domain by relating the frequency components $P(\omega)$ of the nonlinear polarization to those of the applied optical field, $E(\omega')$.

It is also possible to describe optical nonlinearities directly in the time domain by considering the polarization $\tilde{P}(t)$ that is produced by some arbitrary

* The operation of pyroelectric detectors is described, for instance, in Section 13.3 of Boyd (1983).

TABLE 1.5.4 Form of the third-order susceptibility tensor $\chi^{(3)}$ for each of the crystal classes and for isotropic materials. Each element is denoted by its Cartesian indices

Isotropic

There are 21 nonzero elements, of which only 3 are independent. They are:

$$\begin{aligned} y y z z &= z z y y = z z x x = x x z z = x x y y = y y x x, \\ y z y z &= z y z y = z x z x = x z x z = x y x y = y x y x, \\ y z z y &= z y y z = z x x z = x z z x = x y y x = y x x y; \end{aligned}$$

and

$$x x x x = y y y y = z z z z = x x y y + x y x y + x y y x.$$

Cubic

For the two classes 23 and $m\bar{3}$, there are 21 nonzero elements, of which only 7 are independent. They are:

$$\begin{aligned} x x x x &= y y y y = z z z z, \\ y y z z &= z z x x = x x y y, \\ z z y y &= x x z z = y y x x, \\ y z y z &= z x z x = x y x y, \\ z y z y &= x z x z = y x y x, \\ y z z y &= z x x z = x y y x, \\ z y y z &= x z z x = y x x y. \end{aligned}$$

For the three classes 432, $\bar{4}3m$, and $m\bar{3}m$, there are 21 nonzero elements, of which only 4 are independent. They are:

$$\begin{aligned} x x x x &= y y y y = z z z z, \\ y y z z &= z z y y = z z x x = x x z z = x x y y = y y x x, \\ y z y z &= z y z y = z x z x = x z x z = x y x y = y x y x, \\ y z z y &= z y y z = z x x z = x z z x = x y y x = y x x y. \end{aligned}$$

Hexagonal

For the three classes 6, $\bar{6}$, and $6/m$, there are 41 nonzero elements, of which only 19 are independent. They are:

$$\begin{aligned} & z z z z, \\ x x x x &= y y y y = x x y y + x y y x + x y x y, & \begin{cases} x x y y = y y x x, \\ x y y x = y x x y, \\ x y x y = y x y x, \end{cases} \\ y y z z &= x x z z, & x y z z &= -y x z z, \\ z z y y &= z z x x, & z z x y &= -z z y x, \\ z y y z &= z x x z, & z x y z &= -z y x z, \\ y z z y &= x z z x, & x z z y &= -y z z x, \\ y z y z &= x z x z, & x z y z &= -y z x z, \\ z y z y &= z x z x, & z x z y &= -z y z x, \\ x x x y &= -y y y x = y y x y + y x y y + x y y y, & \begin{cases} y y x y = -x x y x, \\ y x y y = -x y x x, \\ x y y y = -y x x x. \end{cases} \end{aligned}$$

(continued)

TABLE 1.5.4 (continued)

For the four classes 622 , $6mm$, $6/mmm$, and $\bar{6}m2$, there are 21 nonzero elements, of which only 10 are independent. They are:

$$\begin{aligned}
 & \begin{aligned} & zzzz, \\ & xxx = yyy = xxy + xyx + yxy, \end{aligned} & \begin{cases} xxy = yxx, \\ xyx = yxy, \\ xxy = yxy, \end{cases} \\
 & yyz = xzx, \\
 & zzy = zxz, \\
 & zyz = zxz, \\
 & yzy = xzx, \\
 & yzy = xzx, \\
 & zzy = zxz.
 \end{aligned}$$

Trigonal

For the two classes 3 and $\bar{3}$, there are 73 nonzero elements, of which only 27 are independent. They are:

$$\begin{aligned}
 & \begin{aligned} & zzzz, \\ & xxx = yyy = xxy + xyx + yxy, \end{aligned} & \begin{cases} xxy = yxx, \\ xyx = yxy, \\ xxy = yxy, \end{cases} \\
 & yyz = xzx, \quad xyz = -yxz, \\
 & zzy = zxz, \quad zzy = -zyx, \\
 & zyz = zxz, \quad zyz = -zyx, \\
 & yzy = xzx, \quad xzy = -yzx, \\
 & yzy = xzx, \quad xzy = -yzx, \\
 & zzy = zxz, \quad zzy = -zyx, \\
 & xxy = -yyy = yxy + yxy + xyy, & \begin{cases} yxy = -xxy, \\ yxy = -xxy, \\ xyy = -yxx. \end{cases} \\
 & yyy = -yxz = -xyx = -xxy, \\
 & yzy = -yxz = -xyz = -xzy, \\
 & yzy = -yzx = -xzy = -xzy, \\
 & zyy = -zyx = -xzy = -xzy, \\
 & zyy = -zyx = -xzy = -xzy, \\
 & xxx = -xyy = -xyx = -yxx, \\
 & xxx = -xyy = -xyx = -yxx, \\
 & xxx = -xyy = -xyx = -yxx, \\
 & xxx = -xyy = -xyx = -yxx.
 \end{aligned}$$

For the three classes $3m$, $\bar{3}m$, and 32 , there are 37 nonzero elements, of which only 14 are independent. They are:

$$\begin{aligned}
 & \begin{aligned} & zzzz, \\ & xxx = yyy = xxy + xyx + yxy, \end{aligned} & \begin{cases} xxy = yxx, \\ xyx = yxy, \\ xxy = yxy, \end{cases}
 \end{aligned}$$

TABLE 1.5.4 (*continued*)

$$\begin{aligned}
yyzz &= xxzz, & xxxz &= -xyyz = -yxzy = -yyxz, \\
zzyy &= zzxx, & xxzx &= -xyzx = -yxzy = -yyzx, \\
zyyz &= zxzx, & xzxz &= -xzyy = -yzxy = -zyyx, \\
yzzy &= xzzx, & zxxx &= -zxyy = -zyxy = -zyyx, \\
& & yzyz &= xzxz, \\
& & zzyy &= zxzx.
\end{aligned}$$

Tetragonal

For the three classes 4, $\bar{4}$, and $4/m$, there are 41 nonzero elements, of which only 21 are independent. They are:

$$\begin{aligned}
& xxxx = yyyy, \quad zzzz, \\
zzxx &= zzyy, & xyzx &= -yxzz, & xxyy &= yyxx, & xxyx &= -yyyx, \\
xxzz &= zzyy, & zzxxy &= -zzyx, & xyxy &= yxyx, & xxyx &= -yyxy, \\
zxzx &= zyzzy, & xzyz &= -yzxz, & xyyx &= yxxy, & xyxx &= -xyyy, \\
xzxz &= yzyz, & zxzy &= -zyzx, & & & yxxx &= -xyyy, \\
zxzx &= zyyz, & zxyz &= -zyxz, & & & & \\
xxzx &= yzzy, & xzzy &= -yzzx.
\end{aligned}$$

For the four classes 422 , $4mm$, $4/mmm$, and $\bar{4}2m$, there are 21 nonzero elements, of which only 11 are independent. They are:

$$\begin{aligned}
& xxxx = yyyy, \quad zzzz, \\
yyzz &= xxzz, & yzzy &= xzzx & xxyy &= yyxx, \\
zzyy &= zzxx, & yzyz &= xzxz & xyxy &= yxyx, \\
zyyz &= zxzx, & zyzzy &= zxzx & xyyx &= yxxy.
\end{aligned}$$

Monoclinic

For the three classes 2, m , and $2/m$, there are 41 independent nonzero elements, consisting of:

- 3 elements with indices all equal,
- 18 elements with indices equal in pairs,
- 12 elements with indices having two y's one x, and one z,
- 4 elements with indices having three x's and one z,
- 4 elements with indices having three z's and one x.

Orthorhombic

For all three classes, 222 , $mm2$, and mmm , there are 21 independent nonzero elements, consisting of:

- 3 elements with indices all equal,
- 18 elements with indices equal in pairs.

Triclinic

For both classes, 1 and $\bar{1}$, there are 81 independent nonzero elements.

applied field $\tilde{E}(t)$. These two methods of description are entirely equivalent, although description in the time domain is more convenient for certain types of problems, such as those involving applied fields in the form of short pulses;

conversely, description in the frequency domain is more convenient when each input field is nearly monochromatic.

Let us first consider the special case of a material that displays a purely linear response. We can describe the polarization induced in such a material by

$$\tilde{P}^{(1)}(t) = \epsilon_0 \int_0^\infty R^{(1)}(\tau) \tilde{E}(t - \tau) d\tau. \quad (1.6.1)$$

Here $R^{(1)}(\tau)$ is the linear response function, which gives the contribution to the polarization produced at time t by an electric field applied at the earlier time $t - \tau$. The total polarization is obtained by integrating these contributions over all previous times τ . In writing Eq. (1.6.1) as shown, with the lower limit of integration set equal to zero and not to $-\infty$, we have assumed that $R^{(1)}(\tau)$ obeys the causality condition $R^{(1)}(\tau) = 0$ for $\tau < 0$. This condition expresses the fact that $\tilde{P}^{(1)}(t)$ depends only on past and not on future values of $\tilde{E}(t)$.

Equation (1.6.1) can be transformed to the frequency domain by introducing the Fourier transforms of the various quantities that appear in this equation. We adopt the following definition of the Fourier transform:

$$E(\omega) = \int_{-\infty}^\infty \tilde{E}(t) e^{i\omega t} dt \quad (1.6.2a)$$

$$\tilde{E}(t) = \frac{1}{2\pi} \int_{-\infty}^\infty E(\omega) e^{-i\omega t} d\omega \quad (1.6.2b)$$

with analogous definitions for other quantities. By introducing Eq. (1.6.2b) into Eq. (1.6.1), we obtain

$$\begin{aligned} \tilde{P}^{(1)}(t) &= \epsilon_0 \int_0^\infty d\tau \int_{-\infty}^\infty \frac{d\omega}{2\pi} R^{(1)}(\tau) E(\omega) e^{-i\omega(t-\tau)} \\ &= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega}{2\pi} \int_0^\infty d\tau R^{(1)}(\tau) e^{i\omega\tau} E(\omega) e^{-i\omega t} \end{aligned} \quad (1.6.3)$$

or

$$\tilde{P}^{(1)}(t) = \epsilon_0 \int_{-\infty}^\infty \frac{d\omega}{2\pi} \chi^{(1)}(\omega; \omega) E(\omega) e^{-i\omega t}, \quad (1.6.4)$$

where we have introduced an explicit expression for the linear susceptibility

$$\chi^{(1)}(\omega; \omega) = \int_0^\infty d\tau R^{(1)}(\tau) e^{i\omega\tau}. \quad (1.6.5)$$

Equation (1.6.4) gives the time-varying polarization in terms of the frequency components of the applied field and the frequency dependent susceptibility.

By replacing the left-hand side of this equation with $\int P^{(1)}(\omega) \exp(-i\omega t) d\omega / 2\pi$ and noting that the equality must be maintained for each frequency ω , we recover the usual frequency domain description of linear response:

$$P^{(1)}(\omega) = \epsilon_0 \chi^{(1)}(\omega; \omega) E(\omega). \quad (1.6.6)$$

The nonlinear response can be described by analogous procedures. The contribution to the polarization second-order in the applied field strength is represented as

$$\tilde{P}^{(2)}(t) = \epsilon_0 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) E(t - \tau_1) E(t - \tau_2), \quad (1.6.7)$$

where the causality condition requires that $R^{(2)}(\tau_1, \tau_2) = 0$ if either τ_1 or τ_2 is negative. As above, we write $E(t - \tau_1)$ and $E(t - \tau_2)$ in terms of their Fourier transforms using Eq. (1.6.2b) so that the expression for the second-order polarization becomes

$$\begin{aligned} \tilde{P}^{(2)}(t) &= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) \\ &\quad \times E(\omega_1) e^{-i\omega_1(t-\tau_1)} E(\omega_2) e^{-i\omega_2(t-\tau_2)} \\ &= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \chi^{(2)}(\omega_\sigma; \omega_1, \omega_2) E(\omega_1) E(\omega_2) e^{-i\omega_\sigma t}, \end{aligned} \quad (1.6.8)$$

where we have defined $\omega_\sigma = \omega_1 + \omega_2$ and have introduced the second-order susceptibility

$$\chi^{(2)}(\omega_\sigma; \omega_1, \omega_2) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) e^{i(\omega_1 \tau_1 + \omega_2 \tau_2)}. \quad (1.6.9)$$

This procedure can readily be generalized to higher-order susceptibilities. In particular, we can express the third-order polarization as

$$\begin{aligned} \tilde{P}^{(3)}(t) &= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \int_{-\infty}^\infty \frac{d\omega_3}{2\pi} \chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) \\ &\quad \times E(\omega_1) E(\omega_2) E(\omega_3) e^{-i\omega_\sigma t}, \end{aligned} \quad (1.6.10)$$

where $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ and where

$$\begin{aligned} \chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = & \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times R^{(3)}(\tau_1, \tau_2, \tau_3) e^{i(\omega_1 \tau_1 + \omega_2 \tau_2 + \omega_3 \tau_3)}. \end{aligned} \quad (1.6.11)$$

1.7. Kramers–Kronig Relations in Linear and Nonlinear Optics

Kramers–Kronig relations are often encountered in linear optics. These conditions relate the real and imaginary parts of frequency-dependent quantities such as the linear susceptibility. They are useful because, for instance, they allow one to determine the real part of the susceptibility at some particular frequency from a knowledge of the frequency dependence of the imaginary part of the susceptibility. Since it is often easier to measure an absorption spectrum than to measure the frequency dependence of the refractive index, this result is of considerable practical importance. In this section, we review the derivation of the Kramers–Kronig relations as they are usually formulated for a system with linear response, and then show how Kramers–Kronig relations can be formulated to apply to some (but not all) nonlinear optical interactions.

1.7.1. Kramers–Kronig Relations in Linear Optics

We saw in the previous section that the linear susceptibility can be represented as

$$\chi^{(1)}(\omega) \equiv \chi^{(1)}(\omega; \omega) = \int_0^\infty R^{(1)}(\tau) e^{i\omega\tau} d\tau, \quad (1.7.1)$$

where the lower limit of integration has been set equal to zero to reflect the fact that $R^{(1)}(\tau)$ obeys the causality condition $R^{(1)}(\tau) = 0$ for $\tau < 0$. Note also (e.g., from Eq. (1.6.1)) that $R^{(1)}(\tau)$ is necessarily real, since it relates two inherently real quantities $\tilde{P}(t)$ and $\tilde{E}(t)$. We thus deduce immediately from Eq. (1.7.1) that

$$\chi^{(1)}(-\omega) = \chi^{(1)}(\omega)^*. \quad (1.7.2)$$

Let us examine some of the other mathematical properties of the linear susceptibility. In doing so, it is useful, as a purely mathematical artifact, to treat the frequency ω as a complex quantity $\omega = \text{Re } \omega + i \text{Im } \omega$. An important mathematical property of $\chi(\omega)$ is the fact that it is analytic (i.e., single-valued

and possessing continuous derivatives) in the upper half of the complex plane, that is, for $\text{Im } \omega \geq 0$. In order to demonstrate that $\chi(\omega)$ is analytic in the upper half plane, it is adequate to show that the integral in Eq. (1.7.1) converges everywhere in that region. We first note that the integrand in Eq. (1.7.1) is of the form $R^{(1)}(\tau) \exp[i(\text{Re } \omega)\tau] \exp[-(\text{Im } \omega)\tau]$, and since $R^{(1)}(\tau)$ is everywhere finite, the presence of the factor $\exp[-(\text{Im } \omega)\tau]$ is adequate to ensure convergence of the integral for $\text{Im } \omega > 0$. For $\text{Im } \omega = 0$ (that is, along the real axis) the integral can be shown to converge, either from a mathematical argument based on the fact the $R^{(1)}(\tau)$ must be square integrable or from the physical statement that $\chi(\omega)$ for ω real is a physically measurable quantity and hence must be finite.

To establish the Kramers–Kronig relations, we next consider the integral

$$\text{Int} = \int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega') d\omega'}{\omega' - \omega}. \quad (1.7.3)$$

We adopt the convention that in expressions such as (1.7.3) we are to take the Cauchy principal value of the integral—that is,

$$\int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega') d\omega'}{\omega' - \omega} \equiv \lim_{\delta \rightarrow 0} \left[\int_{-\infty}^{\omega - \delta} \frac{\chi^{(1)}(\omega') d\omega'}{\omega' - \omega} + \int_{\omega + \delta}^{\infty} \frac{\chi^{(1)}(\omega') d\omega'}{\omega' - \omega} \right]. \quad (1.7.4)$$

We evaluate expression (1.7.3) using the techniques of contour integration, noting that the desired integral is given by $\text{Int} = \text{Int}(A) - \text{Int}(B) - \text{Int}(C)$ where $\text{Int}(A)$, $\text{Int}(B)$, and $\text{Int}(C)$ are the path integrals of $\chi^{(1)}(\omega')/(\omega' - \omega)$ over the paths shown in Fig. 1.7.1. Since $\chi^{(1)}(\omega')$ is analytic in the upper half plane, the only singularity of the integrand $\chi(\omega')/(\omega' - \omega)$ in the upper half-plane is a simple pole along the real axis at $\omega' = \omega$. We thus find that $\text{Int}(A) = 0$ by Cauchy's theorem since its closed path of integration contains no poles. Furthermore, $\text{Int}(B) = 0$ since the integration path increases as $|\omega'|$, whereas for large $|\omega'|$ the integrand scales as $\chi(\omega')/|\omega'|$, and thus the product will tend toward zero so long as $\chi(\omega')$ approaches zero for sufficiently large ω' . Finally, by the residue theorem $\text{Int}(C) = -\pi i \chi(\omega)$. By introducing these values into Eq. (1.7.3), we obtain the result

$$\chi^{(1)}(\omega) = \frac{-i}{\pi} \int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega') d\omega'}{\omega' - \omega}. \quad (1.7.5)$$

By separating $\chi^{(1)}(\omega)$ into its real and imaginary parts as $\chi^{(1)}(\omega) = \text{Re } \chi^{(1)}(\omega) + i \text{Im } \chi^{(1)}(\omega)$, we obtain one form of the Kramers–Kronig relations:

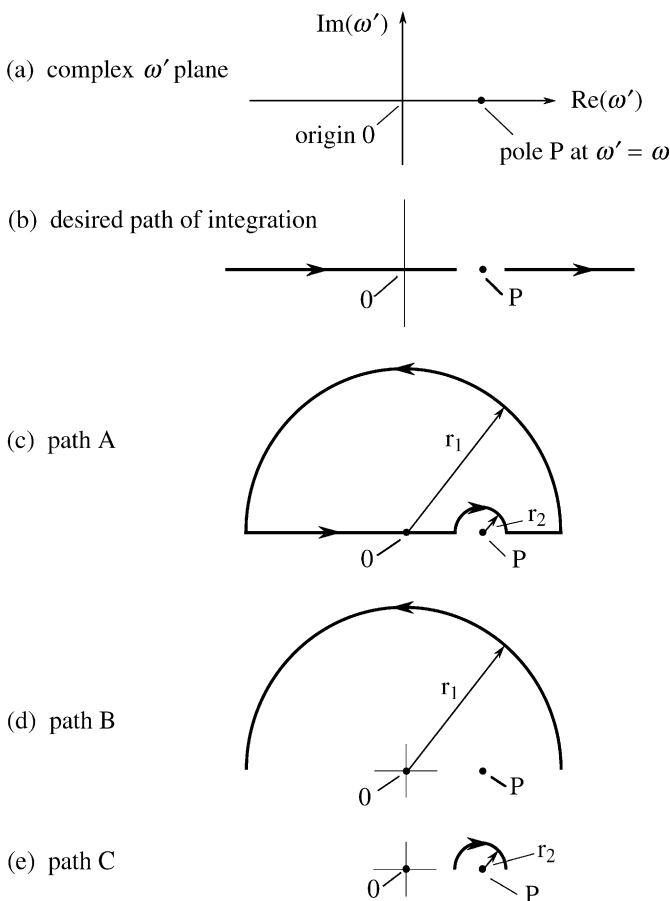


FIGURE 1.7.1 Diagrams used in the contour integration of Eq. (1.7.3). (a) shows the complex ω' plane, (b) shows the desired path of integration, and (c), (d), and (e) show paths over which the integral can be evaluated using the techniques of contour integration. In performing the integration the limits $r_1 \rightarrow \infty$ and $r_2 \rightarrow 0$ are taken.

$$\operatorname{Re} \chi^{(1)}(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Im} \chi^{(1)}(\omega') d\omega'}{\omega' - \omega}, \quad (1.7.6a)$$

$$\operatorname{Im} \chi^{(1)}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Re} \chi^{(1)}(\omega') d\omega'}{\omega' - \omega}. \quad (1.7.6b)$$

These integrals show how the real part of $\chi^{(1)}$ can be deduced from a knowledge of the frequency dependence of the imaginary part of $\chi^{(1)}$, and vice versa. Since it is usually easier to measure absorption spectra than the fre-

quency dependence of the refractive index, it can be quite useful to make use of Eq. (1.7.6a) as a means of predicting the frequency dependence of the real part of $\chi^{(1)}$.

The Kramers–Kronig relations can be rewritten to involve integration over only (physically meaningful) positive frequencies. From Eq. (1.7.2), we see that

$$\operatorname{Re} \chi^{(1)}(-\omega) = \operatorname{Re} \chi^{(1)}(\omega), \quad \operatorname{Im} \chi^{(1)}(-\omega) = -\operatorname{Im} \chi^{(1)}(\omega). \quad (1.7.7)$$

We can thus rewrite Eq. (1.7.6b) as follows:

$$\begin{aligned} \operatorname{Im} \chi^{(1)}(\omega) &= -\frac{1}{\pi} \int_{-\infty}^0 \frac{\operatorname{Re} \chi^{(1)}(\omega') d\omega'}{\omega' - \omega} - \frac{1}{\pi} \int_0^{\infty} \frac{\operatorname{Re} \chi^{(1)}(\omega') d\omega'}{\omega' - \omega} \\ &= \frac{1}{\pi} \int_0^{\infty} \frac{\operatorname{Re} \chi^{(1)}(\omega') d\omega'}{\omega' + \omega} - \frac{1}{\pi} \int_0^{\infty} \frac{\operatorname{Re} \chi^{(1)}(\omega') d\omega'}{\omega' - \omega} \end{aligned} \quad (1.7.8)$$

and hence

$$\operatorname{Im} \chi^{(1)}(\omega) = \frac{-2\omega}{\pi} \int_0^{\infty} \frac{\operatorname{Re} \chi^{(1)}(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (1.7.9a)$$

We similarly find that

$$\operatorname{Re} \chi^{(1)}(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \operatorname{Im} \chi^{(1)}(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (1.7.9b)$$

1.7.2. Kramers–Kronig Relations in Nonlinear Optics

Relations analogous to the usual Kramers–Kronig relations for the linear response can be deduced for some but not all nonlinear optical interactions. Let us first consider a nonlinear susceptibility of the form $\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3)$ with $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ and with ω_1, ω_2 , and ω_3 all positive and distinct. Such a susceptibility obeys a Kramers–Kronig relation in each of the three input frequencies, for example,

$$\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(\omega'_\sigma; \omega_1, \omega'_2, \omega_3)}{\omega'_2 - \omega_2} d\omega'_2, \quad (1.7.10)$$

where $\omega'_\sigma = \omega_1 + \omega'_2 + \omega_3$. Similar results hold for integrals involving ω'_1 and ω'_3 . The proof of this result proceeds in a manner strictly analogous to that of the linear Kramers–Kronig relation. In particular, we note from Eq. (1.6.11) that $\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3)$ is the Fourier transform of a causal response function, and hence $\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3)$ considered as a function of its three

independent variables ω_1, ω_2 , and ω_3 , is analytic in the region $\text{Im } \omega_1 \geq 0$, $\text{Im } \omega_2 \geq 0$, and $\text{Im } \omega_3 \geq 0$. We can then perform the integration indicated on the right-hand side of Eq. (1.7.10) as a contour integration closed in the upper part of the complex ω_2 plane, and obtain the indicated result. In fact, it is not at all surprising that a Kramers–Kronig-like relation should exist for the present situation; the expression $\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3)E(\omega_1)E(\omega_2)E(\omega_3)$ is linear in the field $E(\omega_2)$ and the physical system is causal, and thus the reasoning leading to the usual linear Kramers–Kronig relation is directly relevant to the present situation.

Note that in Eq. (1.7.10) all but one of the input frequencies are held fixed. Kramers–Kronig relations can also be formulated under more general circumstances. It can be shown (see, for instance, Section 6.2 of Hutchings *et al.*, 1992) by means of a somewhat intricate argument that

$$\begin{aligned} \chi^{(n)}(\omega_\sigma; \omega_1 + p_1\omega, \omega_2 + p_2\omega, \dots, \omega_n + p_n\omega) \\ = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(n)}(\omega'_\sigma; \omega_1 + p_1\omega', \omega_2 + p_2\omega', \dots, \omega_n + p_n\omega')}{\omega' - \omega} d\omega' \end{aligned} \quad (1.7.11)$$

where $p_i \geq 0$ for all i and where at least one p_i must be nonzero. Among the many special cases included in Eq. (1.7.11) are those involving the susceptibility for second-harmonic generation

$$\chi^{(2)}(2\omega; \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(2)}(2\omega'; \omega', \omega')}{\omega' - \omega} d\omega' \quad (1.7.12)$$

and for third-harmonic generation

$$\chi^{(3)}(3\omega; \omega, \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(3\omega'; \omega', \omega', \omega')}{\omega' - \omega} d\omega'. \quad (1.7.13)$$

Kramers–Kronig relations can also be formulated for the change in refractive index induced by an auxiliary beam, which is described by a susceptibility of the sort $\chi^{(3)}(\omega; \omega, \omega_1, -\omega_1)$. In particular, one can show (Hutchings *et al.*, 1992) that

$$\chi^{(3)}(\omega; \omega, \omega_1, -\omega_1) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(\omega'; \omega', \omega_1, -\omega_1)}{\omega' - \omega} d\omega'. \quad (1.7.14)$$

Probably the most important process for which it is not possible to form a Kramers–Kronig relation is for the self-induced change in refractive index, that is, for processes described by the nonlinear susceptibility $\chi^{(3)}(\omega; \omega, \omega, -\omega)$. Note that this susceptibility is not of the form

of Eq. (1.7.10) or of (1.7.11), because the first two applied frequencies are equal and because the third frequency is negative. Moreover, one can show by explicit calculation (see the problems at the end of this chapter) that for specific model systems the real and imaginary parts of $\chi^{(3)}$ are not related in the proper manner to satisfy the Kramers–Kronig relations.

To summarize the results of this section, we have seen that Kramers–Kronig relations, which are always valid in linear optics, are valid for some but not all nonlinear optical processes.

Problems

1. *Conversion from Gaussian to SI units.* For proustite $\chi_{yyy}^{(2)}$ has the value 1.3×10^{-7} cm/statvolt in Gaussian units. What is its value in MKS units? [Ans: 5.4×10^{-11} m/V.]
2. *Numerical estimate of nonlinear optical quantities.* A laser beam of frequency ω carrying 1 W of power is focused to a spot size of $30\text{-}\mu\text{m}$ diameter in a crystal having a refractive index of $n = 2$ and a second-order susceptibility of $\chi^{(2)} = 4 \times 10^{-11}$ m/V. Calculate numerically the amplitude $P(2\omega)$ of the component of the nonlinear polarization oscillating at frequency 2ω . Estimate numerically the amplitude of the dipole moment per atom $\mu(2\omega)$ oscillating at frequency 2ω . Compare this value with the atomic unit of dipole moment (ea_0 , where a_0 is the Bohr radius) and with the linear response of the atom, that is, with the component $\mu(\omega)$ of the dipole moment oscillating at frequency ω . We shall see in the next chapter that, under the conditions stated above, nearly all of the incident power can be converted to the second harmonic for a 1-cm-long crystal.
[Ans: $P(2\omega) = 4.7 \times 10^{-11}$ C/m³. Assuming that $N = 10^{28}$ atoms/m³, $\mu(2\omega) = 4.7 \times 10^{-39}$ Cm = $5.56 \times 10^{-10}ea_0$, where $ea_0 = 8.5 \times 10^{-30}$ Cm. By comparison, $P(\omega) = 9.7 \times 10^{-6}$ C/m³ and $\mu(\omega) = 9.7 \times 10^{-34}$ Cm = $1.14 \times 10^{-4}ea_0$, which shows that $\mu(2\omega)/\mu(\omega) = 4.9 \times 10^{-6}$.]
3. *Perturbation expansion.* Explain why it is unnecessary to include the term $\lambda^0 \tilde{x}^{(0)}$ in the power series of Eq. (1.4.6).
4. *Tensor properties of the anharmonic oscillator model.* Starting from Eq. (1.4.52), relevant to a collection of isotropic, centrosymmetric, anharmonic oscillators, show that the nonlinear susceptibility possesses the

following tensor properties:

$$\begin{aligned}\chi_{1122} &= \chi_{1212} = \chi_{1221} = \chi_{1133} = \chi_{1313} = \chi_{1331} = \chi_{2233} = \chi_{2323} \\ &= \chi_{2332} = \chi_{2211} = \chi_{2121} = \chi_{2112} = \chi_{3311} = \chi_{3131} = \chi_{3113} \\ &= \chi_{3322} = \chi_{3232} = \chi_{3223} = \frac{1}{3}\chi_{1111} = \frac{1}{3}\chi_{2222} = \frac{1}{3}\chi_{3333},\end{aligned}$$

with all other elements vanishing. Give a simple physical argument that explains why the vanishing elements do vanish. Also, give a simple physical argument that explains why χ_{ijhl} possesses off-diagonal tensor components, even though the medium is isotropic.

5. *Comparison of the centrosymmetric and noncentrosymmetric models.* For the noncentrosymmetric anharmonic oscillator described by Eq. (1.4.1), derive an expression for the third-order displacement $\tilde{x}^{(3)}$ and consequently for the third-order susceptibility $\chi_{1111}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p)$. Compare this result to that given by Eq. (1.4.52) for a purely centrosymmetric medium. Note that for a noncentrosymmetric medium both of these contributions can be present. Estimate the size of each of these contributions to see which is larger.
6. *Determination of d_{eff} .* Verify Eqs. (1.5.30a) and (1.5.30b).
7. *Formal properties of the third-order response.* Section 1.5 contains a description of some of the formal mathematical properties of the second-order susceptibility. For the present problem, you are to determine the analogous symmetry properties of the third-order susceptibility $\chi^{(3)}$. In your response, be sure to include the equations analogous to Eqs. (1.5.1), (1.5.2), (1.5.5), (1.5.6), (1.5.8), (1.5.9), and (1.5.19).
8. *Consequences of crystalline symmetry.* Through explicit consideration of the symmetry properties of each of the 32 point groups, verify the results presented in Tables 1.5.2 and 1.5.4 and in Fig. 1.5.3.
[Notes: This problem is lengthy and requires a more detailed knowledge of group theory and crystal symmetry than that presented in this text. For a list of recommended readings on these subjects, see the reference list to the present chapter. For a discussion of this problem, see also Butcher (1965).]
9. *Subtlety regarding crystal class 432.* According to Table 1.5.2, $\chi^{(2)}$ possesses nonvanishing tensor elements for crystal class 432, but according to Fig. 1.5.3 d_{il} for this crystal class vanishes identically. Justify these two statements by taking explicit account of the additional constraints that are implicit in the definition of the d_{il} matrix.
10. *Kramers–Kronig relations.* Show by explicit calculation that the linear susceptibility of an optical transition modeled in the two-level approx-

imation obeys the Kramers–Kronig relations, but that neither the total susceptibility χ nor the third-order susceptibility $\chi^{(3)}$ obeys these relations. Explain this result by finding the location of the poles of χ and of $\chi^{(3)}$.

[Hints: $\chi^{(1)}$ and $\chi^{(3)}$ are given by Eqs. (6.3.33) and χ is given by Eq. (6.3.23).]

11. *Kramers–Kronig relations.* For the classical anharmonic oscillator model of Eq. (1.4.20) show by explicit calculation that $\chi^{(2)}(2\omega; \omega, \omega)$ obeys the Kramers–Kronig relations in the form (1.7.12). Show also that $\chi^{(2)}(\omega_1; \omega_3, -\omega_2)$ does not satisfy Kramers–Kronig relations.
12. *Example of the third-order response.* The third-order polarization includes a term oscillating at the fundamental frequency and given by

$$P^{(3)}(\omega) = 3\epsilon_0\chi^{(3)}|E(\omega)|^2 E(\omega).$$

Assume that the field at frequency ω includes two contributions that propagate in the directions given by wave vectors \mathbf{k}_1 and \mathbf{k}_2 . Assume also that the second contribution is sufficiently weak that it can be treated linearly. Calculate the nonlinear polarization at the fundamental frequency and give the physical interpretation of its different terms.

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