This expression can be simplified by making use of the intrinsic permutation symmetry of the nonlinear susceptibility (this symmetry is discussed in more detail in Eq. (1.5.6) below), which requires that

$$\chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) = \chi_{ikj}^{(2)}(\omega_m + \omega_n, \omega_n, \omega_m).$$ (1.3.15)

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

$$P_i(\omega_3) = 2 \sum_{jk} \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2),$$ (1.3.16)

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

$$P_i(\omega_3) = 2\chi_{ixx}^{(2)}(\omega_3, \omega_1, \omega_2) E_x(\omega_1) E_x(\omega_2).$$ (1.3.17)

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. (1.3.13), we obtain

$$P_i(\omega_3) = \sum_{jk} \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_1) E_j(\omega_1) E_k(\omega_1).$$ (1.3.18)

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

$$P_i(\omega_3) = \chi_{ixx}^{(2)}(\omega_3, \omega_1, \omega_1) E_x(\omega_1)^2.$$ (1.3.19)

Note that a factor of two appears in Eqs. (1.3.16) and (1.3.17), which describe sum-frequency generation, but not in Eqs. (1.3.18) and (1.3.19), which describe second-harmonic generation. The fact that these expressions remain different even as ω_2 approaches ω_1 is 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 $P(2\omega_1)$ 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 (all 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. (1.3.13) can be performed formally to obtain the result

$$P_i(\omega_n + \omega_m) = D \sum_{jk} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m),$$ (1.3.20)

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 (1.3.13) 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 amplitude of the nonlinear polarization to a product of three electric field amplitudes according to the expression

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

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

$$P_i(\omega_o + \omega_n + \omega_m) = D \sum_{jkl} \chi_{ijkl}^{(3)}(\omega_o + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m)$$
$$\times E_j(\omega_o) E_k(\omega_n) E_l(\omega_m),$$ (1.3.22)

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 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 Owyoung (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

* 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).

possess many energy eigenvalues and hence more 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.

Noncentrosymmetric Media

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

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

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

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

where a is a parameter that characterizes the nonlinearity of the response. 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

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

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 of Eq. (1.4.3) is

* 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.
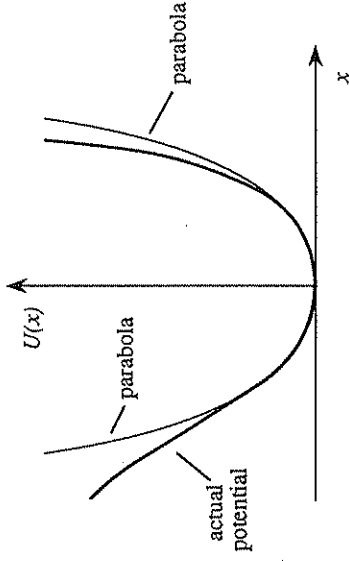
FIGURE 1.4.1   Potential energy function for a noncentrosymmetric medium.

contains both even and odd powers of 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; the reason is 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

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

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

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

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

$$\tilde{x} = \lambda\tilde{x}^{(1)} + \lambda^2\tilde{x}^{(2)} + \lambda^3\tilde{x}^{(3)} + \cdots. \qquad (1.4.6)$$

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 the terms proportional to λ, λ^2, and λ^3 lead respectively to the equations

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

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

$$\ddot{\tilde{x}}^{(3)} + 2\gamma\dot{\tilde{x}}^{(3)} + \omega_0^2\tilde{x}^{(3)} + 2a\tilde{x}^{(1)}\tilde{x}^{(2)} = 0.$$ (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 given by

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

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

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

where we have introduced the complex denominator function

$$D(\omega) = \omega_0^2 - \omega^2 - 2i\omega\gamma.$$ (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

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

We seek a steady-state solution of the form

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

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

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

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

to be

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

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

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

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

$$P^{(1)}(\omega_i) = \chi^{(1)}(\omega_i)E(\omega_i).$$ (1.4.15)

Since the linear contribution to the polarization is given by

$$P^{(1)}(\omega_i) = -Nex^{(1)}(\omega_i),$$ (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

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

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

$$P^{(2)}(2\omega_1) = \chi^{(2)}(2\omega_1, \omega_1, \omega_1)E(\omega_1)^2,$$ (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 given by

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

Comparison of these equations with Eq. (1.4.13) gives

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

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

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 $\omega_1 \to \omega_2$. The nonlinear susceptibility describing sum-frequency generation is obtained from the relations

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

and

$$P^{(2)}(\omega_1 + \omega_2) = -Ne\chi^{(2)}(\omega_1 + \omega_2). \tag{1.4.23}$$

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. (1.3.20). By comparison of these equations with (1.4.14b), the nonlinear susceptibility is seen to be given by

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

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

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

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

$$\chi^{(2)}(\omega_1 - \omega_2, \omega_1, \omega_2) = \frac{N(e^3/m^2)a}{D(\omega_1 - \omega_2)D(\omega_1)D(-\omega_2)}$$
$$= \frac{ma}{N^2 e^3}\chi^{(1)}(\omega_1 - \omega_2)\chi^{(1)}(\omega_1)\chi^{(1)}(-\omega_2), \tag{1.4.26}$$

and for optical rectification we find that

$$\chi^{(2)}(0, \omega_1, -\omega_1) = \frac{N(e^3/m^2)a}{D(0)D(\omega_1)D(-\omega_1)}$$
$$= \frac{ma}{N^2 e^3}\chi^{(1)}(0)\chi^{(1)}(\omega_1)\chi^{(1)}(-\omega_1). \tag{1.4.27}$$

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

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

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

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

$$\frac{ma}{N^2 e^3} \tag{1.4.29}$$

is nearly constant. In fact, the atomic number density N is nearly the same ($\sim 10^{22}$ 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 be 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. Consequently, one would expect that, to order of magnitude, $m\omega_0^2 d = mad^2$, or that

$$a = \frac{\omega_0^2}{d}. \tag{1.4.30}$$

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 noncentrosymmetric solids.

We can also use the estimate of the nonlinear coefficient a given by Eq. (1.4.30) to make an estimate of the size of the second-order susceptibility under 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

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

Using the values $\omega_0 = 1 \times 10^{16}$ rad/s, $d = 3$ Å, $e = 4.8 \times 10^{-10}$ esu, and $m = 9.1 \times 10^{-28}$ g, we find that

$$\chi^{(2)} \simeq 3 \times 10^{-8} \text{ esu}, \quad (1.4.32)$$

which is in good agreement with the measured values presented in Table 1.5.3 in the next section.

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

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

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

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

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 $\tilde{x} \to -\tilde{x}$, which it
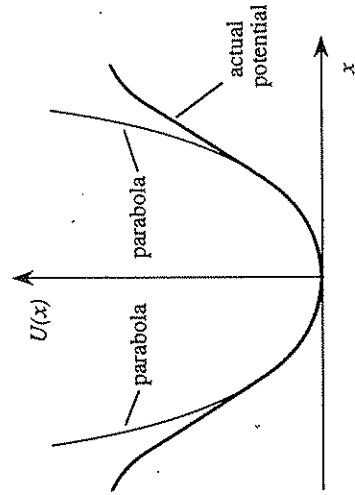

FIGURE 1.4.2   Potential energy function for a centrosymmetric medium.

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 $\tfrac{1}{2}m\omega_0^2\tilde{x}^2$. We assume that the electronic displacement $\tilde{x}$ never becomes so large that it is necessary to include higher-order terms in the potential.

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 noncentrosymmetric 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 which is isotropic (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

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

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:

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

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

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

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

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

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 before 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

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

where 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 before by

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

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. (1.4.41) into Eq. (1.4.40c), which becomes

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

Due to 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 (1.3.21),

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

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

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

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

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

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

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

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 $\tilde x$ is comparable to the atomic dimension d, that is, when $m\omega_0^2 d = mbd^3$, which implies that

$$b = \frac{\omega_0^2}{d^2}. \tag{1.4.54}$$

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

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

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

$$\chi^{(3)} \simeq 3 \times 10^{-14} \text{ esu.} \tag{1.4.56}$$

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 $\omega_1, \omega_2,$ and $\omega_3 = \omega_1 + \omega_2$. 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. (1.3.13)) by the expression

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

we therefore need to determine the six tensors

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

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.

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 in order to describe the nonlinear coupling. In this section, we shall 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.

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

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

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

$$P_i(-\omega_n - \omega_m) = P_i(\omega_n + \omega_m)^*. \tag{1.5.3}$$

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

$$E_j(-\omega_n) = E_j(\omega_n)^*, \tag{1.5.4a}$$
$$E_k(-\omega_m) = E_k(\omega_m)^*. \tag{1.5.4b}$$

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

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

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 discuss 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 $\chi_{ikj}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n)E_k(\omega_m)E_j(\omega_n)$. 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:

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

This property is known as intrinsic permutation symmetry.

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 $P_i(\omega_n + \omega_m)$ 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).

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 discussed 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 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

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

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

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

By an analogous procedure, one can show that

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

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.

Field Energy Density for a Nonlinear Medium

The fact 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

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

is given according to Poynting's theorem as

$$U = \frac{1}{8\pi}\,\overline{\tilde{\mathbf{D}}\cdot\tilde{\mathbf{E}}} = \frac{1}{8\pi}\sum_i \overline{\tilde{D}_i\tilde{E}_i},$$ (1.5.11)

where the overbar denotes a time average. Since the displacement vector is given by

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

where the dielectric tensor is given by

$$\epsilon_{ij}(\omega_n) = \delta_{ij} + 4\pi\chi_{ij}^{(1)}(\omega_n),$$ (1.5.13)

we can write the energy density as

$$U = \frac{1}{8\pi}\sum_i\sum_n E_i^*(\omega_n)E_i(\omega_n) + \frac{1}{2}\sum_{ij}\sum_n E_i^*(\omega_n)\chi_{ij}^{(1)}(\omega_n)E_j(\omega_n).$$ (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 (Kleinman, 1962; Armstrong et al., 1962; Pershan, 1963) associated with the polarization of the medium takes the more general form

$$U = \frac{1}{2}\sum_{ij}\sum_n \chi_{ij}^{(1)}(\omega_n)E_i^*(\omega_n)E_j(\omega_n)$$
$$+ \frac{1}{3}\sum_{ijk}\sum_{mn} \chi_{ijk}^{(2)\prime}(-\omega_n-\omega_m,\omega_m,\omega_n)E_i^*(\omega_m+\omega_n)E_j(\omega_n)E_k(\omega_n)$$
$$+ \frac{1}{4}\sum_{ijkl}\sum_{mno} \chi_{ijkl}^{(3)\prime}(-\omega_o-\omega_n-\omega_m,\omega_m,\omega_n,\omega_o)E_j(\omega_m)E_k(\omega_n)E_l(\omega_o) + \cdots$$
$$\times E_i^*(\omega_m+\omega_n+\omega_o)E_j(\omega_m)E_k(\omega_n)E_l(\omega_o) + \cdots.$$ (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 $\chi^{(n)\prime}$ 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 by (Pershan, 1963; Landau and Lifshitz, 1960) the expression

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

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

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

and for the nonlinear polarizations as*

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

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

We note that these last two expressions are identical to Eqs. (1.3.13) and (1.3.21), which define the nonlinear susceptibilities (except for the unimportant fact that the quantities $\chi^{(n)}$ and $\chi^{(n)\prime}$ use opposite conventions regarding the sign of the first frequency argument). Since the quantities $\chi^{(n)\prime}$ 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.

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 field.

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

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

$$\tilde{P}(t) = \chi^{(2)}\tilde{E}(t)^2,$$ (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 frequencies are permuted simultaneously, and leads to the conclusion that

$$\chi^{(2)}_{ijk}(\omega_3 = \omega_1 + \omega_2) = \chi^{(2)}_{jki}(\omega_1 = -\omega_2 + \omega_3) = \chi^{(2)}_{kij}(\omega_2 = \omega_3 - \omega_1)$$
$$= \chi^{(2)}_{ikj}(\omega_3 = \omega_2 + \omega_1) = \chi^{(2)}_{jik}(\omega_1 = \omega_3 - \omega_2)$$
$$= \chi^{(2)}_{kji}(\omega_2 = -\omega_1 + \omega_3).$$

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

$$\chi^{(2)}_{ijk}(\omega_3 = \omega_1 + \omega_2) = \chi^{(2)}_{jki}(\omega_3 = \omega_1 + \omega_2) = \chi^{(2)}_{kij}(\omega_3 = \omega_1 + \omega_2)$$
$$= \chi^{(2)}_{ikj}(\omega_3 = \omega_1 + \omega_2) = \chi^{(2)}_{jik}(\omega_3 = \omega_1 + \omega_2)$$
$$= \chi^{(2)}_{kji}(\omega_3 = \omega_1 + \omega_2).$$ (1.5.19)

This result is known as the Kleinman symmetry condition.

Contracted Notation

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

$$d_{ijk} = \tfrac{1}{2}\chi^{(2)}_{ijk}$$ (1.5.20)

and for simplicity suppress the frequency arguments. The nonlinear polarization can then be written as

$$P_i(\omega_n + \omega_m) = \sum_{jk}\sum_{(mn)} 2d_{ijk}E_j(\omega_n)E_k(\omega_m).$$ (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

jk:	11	22	33	23,32	31,13	12,21
l:	1	2	3	4	5	6

(1.5.22)

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

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

If we now *explicitly* introduce the Kleinman symmetry condition, i.e., 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

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

and that

$$d_{14} = d_{123} = d_{213} = d_{25}.$$ (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

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

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

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

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

As described above in relation to Eq. (1.3.19), the extra factor of 2 comes from the summation over n and m in Eq. (1.3.13).

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

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

and analogously for second-harmonic generation by

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

In each case, d_{eff} is obtained by evaluation of the summation $\sum_{jk}$ in the general equation (1.3.13).

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 crystals 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

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

under conditions (known as type II conditions) such that 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 azimuthual angle between the propagation vector and the xz crystalline plane.

Spatial Symmetry of the Nonlinear Medium

The form of the nonlinear susceptibility tensor is constrained by the symmetry properties of the nonlinear 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 nonlinear optical susceptibility is 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.

Inversion Symmetry

One of the symmetry properties that some but not all crystals possess is 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. While the result that $\chi^{(2)}$ vanishes for a centrosymmetric medium is general in nature, we will demonstrate this fact only for the special case of second-harmonic generation in a medium that responds instantaneously to the

* 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 the present chapter.

(a) $\bar{E}(t)$ applied field t

(b) $\bar{P}(t)$ linear response t

(c) $\bar{P}(t)$ nonlinear, centrosymmetric medium t

(d) $\bar{P}(t)$ nonlinear, noncentrosymmetric medium t

FIGURE 1.5.1   Waveforms associated with the atomic response.

applied optical field. We assume that the nonlinear polarization is given by

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

where the applied field is given by

$$\tilde{E}(t) = \mathscr{E}\cos\omega t.$$ (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

which shows that

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

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

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

This result can be understood intuitively by considering the motion of an electron in a nonparabolic potential well. Due to the nonlinearity of the associated restoring force, the atomic response will show significant harmonic distortion. Part (a) of Fig. 1.5.1 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 polarization 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 of a nonlinear, noncentrosymmetric medium having a potential energy function of the form shown in Fig. 1.4.1 (part d), 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-averaged response is nonzero, because the medium responds differently to an electric field pointing, say, in the upward direction than to one pointing downward.*

* Parts (a) and (b) of Fig. 1.5.1 are plots of the function sin ωt, part (c) is a plot of the function sin ωt − 0.25 sin $3\omega t$, and part (d) is a plot of −0.2 + sin ωt + 0.2 cos $2\omega t$.
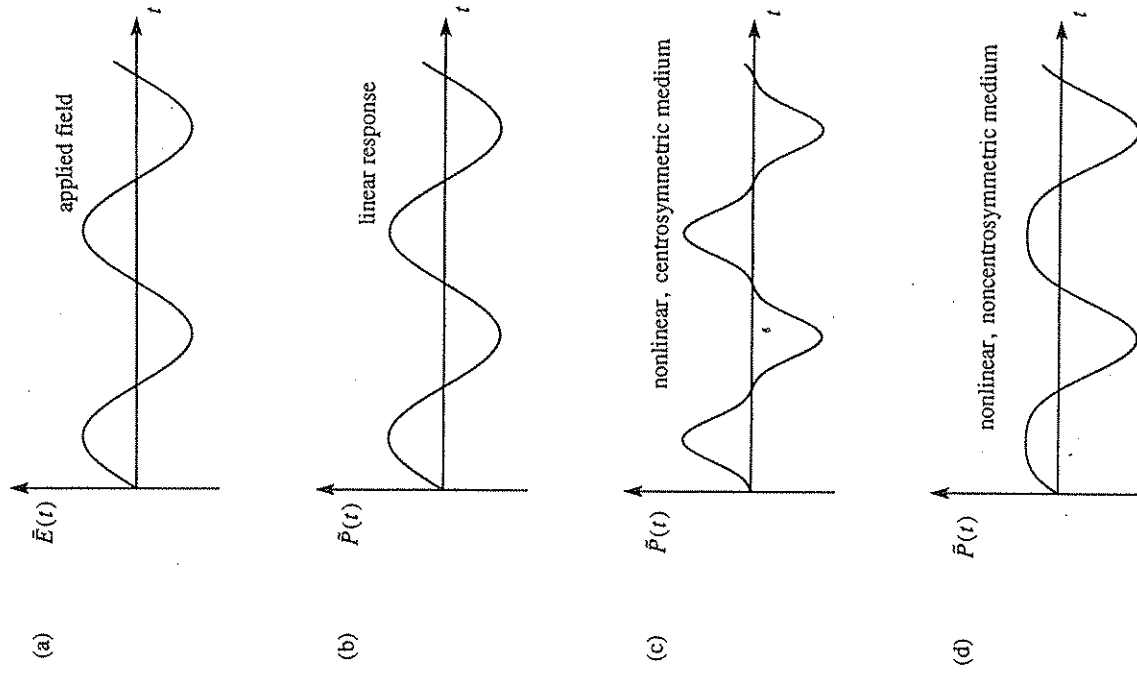
TABLE 1.5.1 Form of the second-order susceptibility tensor for each of the crystal classes. Each element is denoted by its cartesian indices.

Crystal system	Crystal class	Nonvanishing tensor elements
Triclinic	1	All elements are independent and nonzero
	1̄	Each element vanishes
Monoclinic	2	xyz, xzy, xxy, xyx, yxx, yyy, yzz, yzx, yxz, zyz, zzy, zyx (twofold axis parallel to ŷ)
	m	xxx, xyy, xzz, xxz, xzx, yyz, yzy, yxy, yyx, zxx, zyy, zzz, zxz, zzx (mirror plane perpendicular to ŷ)
	2/m	Each element vanishes
Orthorhombic	222	xyz, xzy, yzx, yxz, zxy, zyx
	mm2	xzx, xxz, yyz, yzy, zxx, zyy, zzz
	mmm	Each element vanishes
Tetragonal	4	xyz = −yxz, xzy = −yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = −zyx
	4̄	xyz = yxz, xzy = yzx, xzx = −yzy, xxz = −yyz, zxx = −zyy, zxy = zyx
	422	xyz = −yxz, xzy = −yzx, zxy = −zyx
	4mm	xzx = yzy, xxz = yyz, zxx = zyy, zzz
	4̄2m	xyz = yxz, xzy = yzx, zxy = zyx
	4/m, 4/mmm	Each element vanishes
Cubic	432	xyz = −xzy = yzx = −yxz = zxy = −zyx
	4̄3m	xyz = xzy = yzx = yxz = zxy = zyx
	23	xyz = yzx = zxy, xzy = yxz = zyx.
	m3, m3m	Each element vanishes
Trigonal	3	xxx = −xyy = −yyx = −yxy, xyz = −yxz, xzy = −yzx, xzx = yzy, xxz = yyz, yyy = −yxx = −xxy = −xyx, zxx = zyy, zzz, zxy = −zyx
	32	xxx = −xyy = −yxy = −yyx, xyz = −yxz, xzy = −yzx, zxy = −zyx, zxx = zyy, zzz, zxy = −zyx
	3m	xzx = yzy, xxz = yyz, zxx = zyy, zzz, yyy = −yxx = −xxy = −xyx (mirror plane perpendicular to x̂)
	3̄, 3̄m	Each element vanishes
Hexagonal	6	xyz = −yxz, xzy = −yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = −zyx
	6̄	xxx = −xyy = −yxy = −yyx, yyy = −yxx = −xxy = −xyx,
	622	xyz = −yxz, xzy = −yzx, zxy = −zyx
	6mm	xzx = yzy, xxz = yyz, zxx = zyy, zzz
	6̄m2	yyy = −yxx = −xxy = −xyx
	6/m, 6/mmm	Each element vanishes

Additional Spatial Symmetries

Any additional symmetry properties 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, which was performed originally by Butcher (1965) and was later corrected by Shang and Hsu (1987), are presented in Table 1.5.1. 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 1.5.1 can usefully be displayed graphically. These results, as adapted from Zernike and Midwinter (1973), are presented in Fig. 1.5.2. Note that the influence of Kleinman symmetry is also described in the figure. As an example of how to use the table, for a crystal of class 3m the form of the d_{il} matrix is

$$d_{il} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$
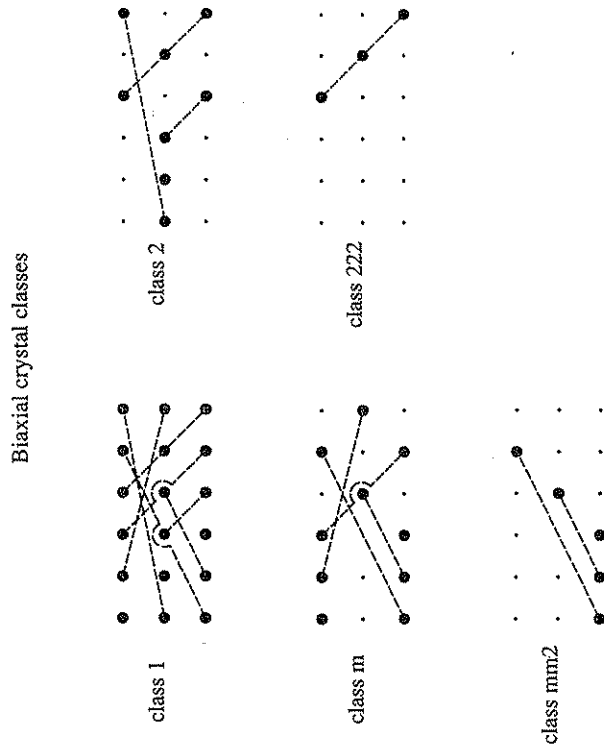
The spatial symmetry of the nonlinear optical medium also restricts the form of the third-order nonlinear optical susceptibility. The allowed form of the susceptibility has been calculated by Butcher (1965) and has been summarized by Hellwarth (1977); their results are presented in Table 1.5.2. Note that for the important special case of an isotropic optical material, the results presented in Table 1.5.2 agree with the result derived explicitly in the discussion of the nonlinear refractive index in Section 4.2.

The second-order nonlinear optical susceptibilities of a number of crystals are summarized in Table 1.5.3.

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

We remarked above 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.

Due to 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. 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
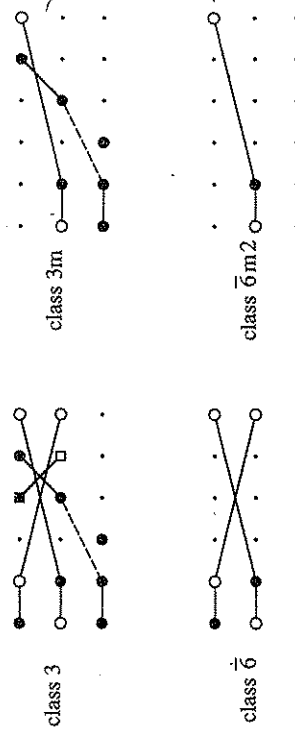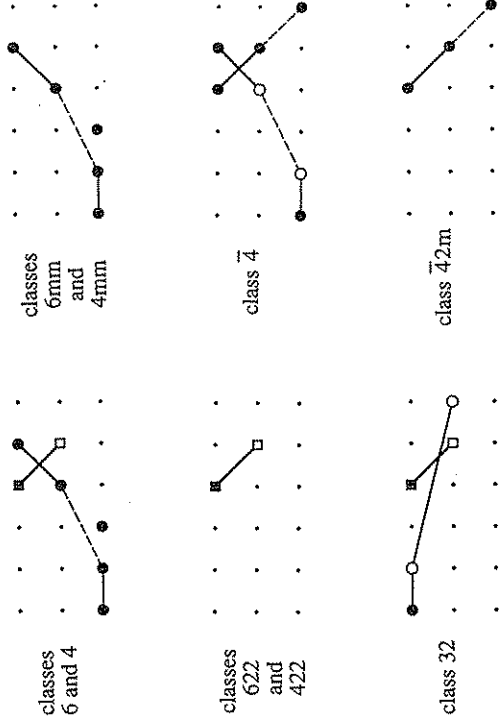
Biaxial crystal classes

class 1

class 2

class m

class 222

class mm2

Uniaxial crystal classes

class 3

class 3m

class 6̄

class 6̄m2

Uniaxial crystal classes (*Continued*)

classes 6 and 4

classes 6mm and 4mm

classes 622 and 422

class 4̄

class 32

class 4̄2m

Isotropic crystal classes

classes 4̄3m and 23

class 432 (all elements vanish)

FIGURE 1.5.2. (*Continued*)

FIGURE 1.5.2   Form of the d_{il} matrix for the 21 crystal classes that lack inversion symmetry. Small dot: zero coefficient; large symbol: 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.)
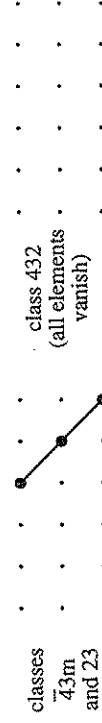
are independent. For second-harmonic generation, contracted notation can be used, and only 18 independent elements exist. When Kleinman's symmetry is valid, only 10 of these elements are independent. Furthermore, any crystalline symmetries of the nonlinear material can reduce this number still further.