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

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

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

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 \sum_{jkl} \sum_{(mno)} \chi^{(3)}_{ijkl}(\omega_0 + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) \times E_j(\omega_o) E_k(\omega_n) E_l(\omega_m). \tag{1.3.20}$$

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

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 D \sum_{jkl} \chi^{(3)}_{ijkl}(\omega_0 + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) \times E_j(\omega_0) E_k(\omega_n) E_l(\omega_m), \tag{1.3.21}$$

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

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* The role of symmetry in determining the nature of the nonlinear susceptibilty 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 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 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

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

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

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

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

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

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* 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.

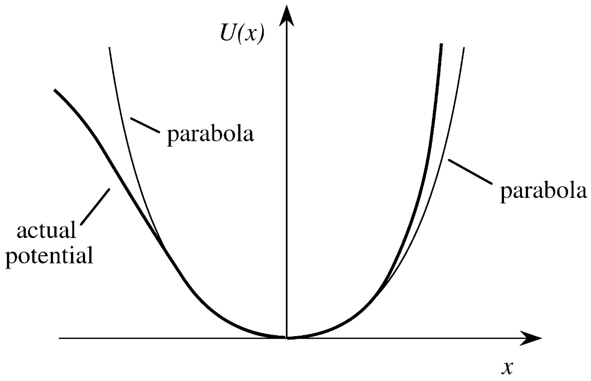

FIGURE 1.4.1 Potential energy function for a noncentrosymmetric medium.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where we have introduced the complex denominator function

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma. \tag{1.4.10}$$

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

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

We seek a steady-state solution of the form

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

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

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

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

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

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

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

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

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

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

Since the linear contribution to the polarization is given by

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

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

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

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

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

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

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

Comparison of these equations with Eq. (1.4.13) gives

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

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

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

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

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

and

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

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

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

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

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

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

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

and for optical rectification we find that

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

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

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

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

$$\frac{ma\epsilon_0^2}{N^2 e^3} \qquad (1.4.29)$$

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 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 $m\omega_0^2 d = mad^2$ or that

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

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

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

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

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

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

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

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

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

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 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

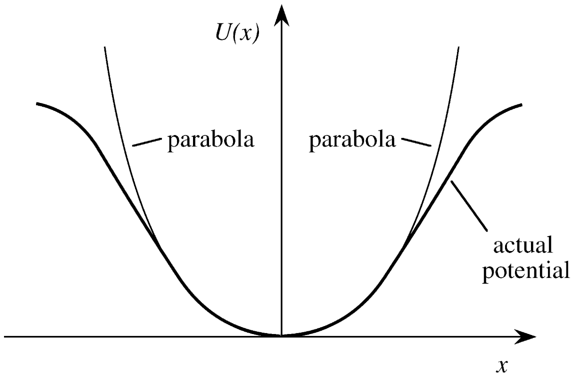

FIGURE 1.4.2 Potential energy function for a centrosymmetric medium.

(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

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

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

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

We assume that the applied field is given by

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

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

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

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:

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

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

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

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

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

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

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

where

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

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

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

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

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

Here the linear susceptibility is given by

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

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

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

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,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 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

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

we therefore need to determine the six tensors

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

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.

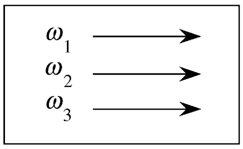

FIGURE 1.5.1 Optical waves of frequencies ω_1, ω_2, and $\omega_3 = \omega_1 + \omega_2$ interact in a lossless second-order nonlinear optical medium.