

Chapter 3

Quantum-Mechanical Theory of the Nonlinear Optical Susceptibility

3.1 Introduction

In this chapter, we use the laws of quantum mechanics to derive explicit expressions for the nonlinear optical susceptibility. The motivation for obtaining these expressions is at least three-fold: (1) these expressions display the functional form of the nonlinear optical susceptibility and hence show how the susceptibility depends on material parameters such as dipole transition moments and atomic energy levels, (2) these expressions display the internal symmetries of the susceptibility, and (3) these expressions can be used to make predictions of the numerical values of the nonlinear susceptibilities. These numerical predictions are particularly reliable for the case of atomic vapors, because the atomic parameters (such as atomic energy levels and dipole transition moments) that appear in the quantum-mechanical expressions are often known with high accuracy. In addition, since the energy levels of free atoms are very sharp (as opposed to the case of most solids, where allowed energies have the form of broad bands), it is possible to obtain very large values of the nonlinear susceptibility through the technique of resonance enhancement. The idea behind resonance enhancement of the nonlinear optical susceptibility is shown schematically in Fig. 3.1.1 for the case of third-harmonic generation. In part (a) of this figure, we show the process of third-harmonic generation in terms of the virtual levels introduced in Chapter 1. In part (b) we also show real atomic levels, indicated by solid horizontal lines. If one of the real atomic levels is nearly coincident with one of the virtual levels of the indicated process, the coupling between the radiation and the atom becomes particularly strong and the nonlinear optical susceptibility becomes large.

Three possible strategies for enhancing the efficiency of third-harmonic generation through the technique of resonance enhancement are illustrated in Fig. 3.1.2. In part (a), the one-photon transition is nearly resonant, in part (b) the two-photon transition is nearly resonant, and in part (c) the three-photon transition is nearly resonant. The formulas derived later in this chapter

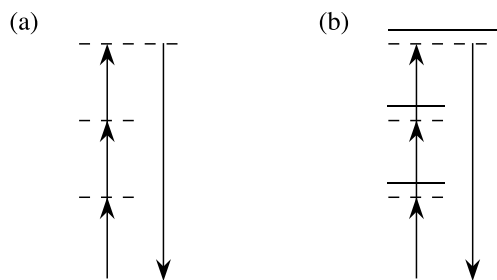


FIGURE 3.1.1: Third-harmonic generation described in terms of virtual levels (a) and with real atomic levels indicated (b).

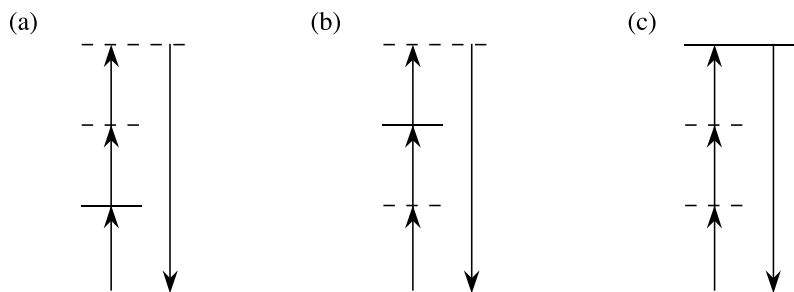


FIGURE 3.1.2: Three strategies for enhancing the process of third-harmonic generation.

demonstrate that all three procedures are equally effective at increasing the value of the third-order nonlinear susceptibility. However, the method shown in part (b) is usually the preferred way in which to generate the third-harmonic field with high efficiency, for the following reason. For the case of a one-photon resonance (part a), the incident field experiences linear absorption and is rapidly attenuated as it propagates through the medium. Similarly, for the case of the three-photon resonance (part c), the generated field experiences linear absorption. However, for the case of a two-photon resonance (part b), there is no linear absorption to limit the efficiency of the process.

3.2 Schrödinger Equation Calculation of the Nonlinear Optical Susceptibility

In this section, we present a derivation of the nonlinear optical susceptibility based on quantum-mechanical perturbation theory of the atomic wave function. The expressions that we derive using this formalism can be used to make accurate predictions of the *nonresonant* response of atomic and molecular systems. Relaxation processes, which are important for the case of

near-resonant excitation, cannot be adequately described by this formalism. Relaxation processes are discussed later in this chapter in connection with the density matrix formulation of quantum mechanics. Even though the density matrix formalism provides results that are more generally valid, the calculation of the nonlinear susceptibility is much more complicated when performed using this method. For this reason, we first present a calculation of the nonlinear susceptibility based on the properties of the atomic wavefunction, since this method is somewhat simpler and for this reason gives a clearer picture of the underlying physics of the nonlinear interaction.

One of the fundamental assumptions of quantum mechanics is that all of the properties of the atomic system can be described in terms of the atomic wavefunction $\psi(\mathbf{r}, t)$, which is the solution to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi. \quad (3.2.1)$$

Here \hat{H} is the Hamiltonian operator*

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (3.2.2)$$

which is written as the sum of the Hamiltonian \hat{H}_0 for a free atom and an interaction Hamiltonian, $\hat{V}(t)$, which describes the interaction of the atom with the electromagnetic field. We usually take the interaction Hamiltonian to be of the form

$$\hat{V}(t) = -\hat{\boldsymbol{\mu}} \cdot \tilde{\mathbf{E}}(t), \quad (3.2.3)$$

where $\hat{\boldsymbol{\mu}} = -e\hat{\mathbf{r}}$ is the electric-dipole moment operator and $-e$ is the charge of the electron.

3.2.1 Energy Eigenstates

For the case in which no external field is applied to the atom, the Hamiltonian \hat{H} is simply equal to \hat{H}_0 , and Schrödinger's equation (3.2.1) possesses solutions in the form of energy eigenstates. These states are also known as stationary states, because the time of evolution of these states is given by a simple exponential phase factor. These states have the form

$$\psi_n(\mathbf{r}, t) = u_n(\mathbf{r})e^{-i\omega_n t}. \quad (3.2.4a)$$

* We use a caret above a quantity to indicate that the quantity such as \hat{H} is a quantum-mechanical operator. For the most part, in this book we work in the coordinate representation, in which case quantum-mechanical operators are represented by ordinary numbers for positions and by differential operators for momenta.

By substituting this form into the Schrödinger equation (3.2.1), we find that the spatially varying part of the wavefunction $u_n(\mathbf{r})$ must satisfy the eigenvalue equation (known as the time-independent Schrödinger equation)

$$\hat{H}_0 u_n(\mathbf{r}) = E_n u_n(\mathbf{r}), \quad (3.2.4b)$$

where $E_n = \hbar\omega_n$. Here n is a label used to distinguish the various solutions. For future convenience, we assume that these solutions are chosen in such a manner that they constitute a complete, orthonormal set satisfying the condition

$$\int u_m^* u_n d^3r = \delta_{mn}. \quad (3.2.5)$$

3.2.2 Perturbation Solution to Schrödinger's Equation

For the general case in which the atom is exposed to an electromagnetic field, Schrödinger's equation (3.2.1) usually cannot be solved exactly. In such cases, it is often adequate to solve Schrödinger's equation through the use of perturbation theory. In order to solve Eq. (3.2.1) systematically in terms of a perturbation expansion, we replace the Hamiltonian (3.2.2) by

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t), \quad (3.2.6)$$

where λ is a continuously varying parameter ranging from zero to unity that characterizes the strength of the interaction; the value $\lambda = 1$ corresponds to the actual physical situation. We now seek a solution to Schrödinger's equation in the form of a power series in λ :

$$\psi(\mathbf{r}, t) = \psi^{(0)}(\mathbf{r}, t) + \lambda \psi^{(1)}(\mathbf{r}, t) + \lambda^2 \psi^{(2)}(\mathbf{r}, t) + \dots \quad (3.2.7)$$

By requiring that the solution be of this form for any value of λ , we assure that $\psi^{(N)}$ will be that part of the solution which is of order N in the interaction energy V . We now introduce Eq. (3.2.7) into Eq. (3.2.1) and require that all terms proportional to λ^N satisfy the equality separately. We thereby obtain the set of equations

$$i\hbar \frac{\partial \psi^{(0)}}{\partial t} = \hat{H}_0 \psi^{(0)}, \quad (3.2.8a)$$

$$i\hbar \frac{\partial \psi^{(N)}}{\partial t} = \hat{H}_0 \psi^{(N)} + \hat{V} \psi^{(N-1)}, \quad N = 1, 2, 3, \dots \quad (3.2.8b)$$

Eq. (3.2.8a) is simply Schrödinger's equation for the atom in the absence of its interaction with the applied field; we assume for definiteness that initially the atom is in state g (typically the ground state) so that the solution to this equation can be represented as

$$\psi^{(0)}(\mathbf{r}, t) = u_g(\mathbf{r}) e^{-iE_g t/\hbar}. \quad (3.2.9)$$

The remaining equations in the perturbation expansion (Eq. (3.2.8b)) are readily solved by making use of the fact that the energy eigenfunctions for the free atom constitute a complete set of basis functions, in terms of which any function can be expanded. In particular, we represent the N th-order contribution to the wavefunction $\psi^{(N)}(\mathbf{r}, t)$ as the sum

$$\psi^{(N)}(\mathbf{r}, t) = \sum_l a_l^{(N)}(t) u_l(\mathbf{r}) e^{-i\omega_l t}. \quad (3.2.10)$$

Here $a_l^{(N)}(t)$ gives the probability amplitude that, to N th order in the perturbation, the atom is in energy eigenstate l at time t . If Eq. (3.2.10) is substituted into Eq. (3.2.8b), we find that the probability amplitudes obey the system of equations

$$i\hbar \sum_l \dot{a}_l^{(N)} u_l(\mathbf{r}) e^{-i\omega_l t} = \sum_l a_l^{(N-1)} \hat{V} u_l(\mathbf{r}) e^{-i\omega_l t}, \quad (3.2.11)$$

where the dot denotes a total time derivative. This equation relates all of the probability amplitudes of order N (the left-hand side) to all of the amplitudes of order $N - 1$ (the right-hand side). To simplify this equation, we multiply each side from the left by u_m^* and integrate the resulting equation over all space. Then through use of the orthonormality condition (3.2.5), we obtain the equation

$$\dot{a}_m^{(N)}(t) = (i\hbar)^{-1} \sum_l a_l^{(N-1)}(t) V_{ml}(t) e^{i\omega_{ml}t}, \quad (3.2.12)$$

where we have introduced the frequency difference $\omega_{ml} \equiv \omega_m - \omega_l$ and where we have introduced the matrix elements of the perturbing Hamiltonian, which are defined by

$$V_{ml} \equiv \langle m | \hat{V} | l \rangle = \int u_m^* \hat{V} u_l d^3r. \quad (3.2.13)$$

The form of Eq. (3.2.12) demonstrates the usefulness of the perturbation technique; once the probability amplitudes of order $N - 1$ are determined, the amplitudes of the next higher order (N) can be obtained by straightforward time integration. In this manner a simple constructive procedure can be used to obtain correction terms to the wave function of arbitrarily high order. In particular, we find that

$$a_m^{(N)}(t) = (i\hbar)^{-1} \sum_l \int_{-\infty}^t dt' V_{ml}(t') a_l^{(N-1)}(t') e^{i\omega_{ml}t'}. \quad (3.2.14)$$

We shall eventually be interested in determining the linear, second-order, and third-order optical susceptibilities. To do so, we shall require explicit expressions for the probability amplitudes up to third order in the perturbation expansion. We now determine the form of these amplitudes.

To determine the first-order amplitudes $a_m^{(1)}(t)$, we set $a_l^{(0)}$ in Eq. (3.2.14) equal to δ_{lg} , corresponding to an atom known to be in state g in zeroth order. We represent the optical field $\tilde{\mathbf{E}}(t)$ as a discrete sum of (positive and negative) frequency components as

$$\tilde{\mathbf{E}}(t) = \sum_p \mathbf{E}(\omega_p) e^{-i\omega_p t}. \quad (3.2.15)$$

Through use of Eqs. (3.2.3) and (3.2.15), we can then replace $V_{ml}(t')$ by $-\sum_p \boldsymbol{\mu}_{ml} \cdot \mathbf{E}(\omega_p) \exp(-i\omega_p t')$, where $\boldsymbol{\mu}_{ml} = \int u_m^* \hat{\boldsymbol{\mu}} u_l d^3r$ is known as the electric-dipole transition moment. We next evaluate the integral appearing in Eq. (3.2.14) and assume that the contribution from the lower limit of integration vanishes*; we thereby find that

$$a_m^{(1)}(t) = \frac{1}{\hbar} \sum_p \frac{\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)}{\omega_{mg} - \omega_p} e^{i(\omega_{mg} - \omega_p)t}. \quad (3.2.16)$$

We next determine the second-order correction to the probability amplitudes by using Eq. (3.2.14) once again, but with N set equal to 2. We introduce Eq. (3.2.16) for $a_m^{(1)}$ into the right-hand side of this equation and perform the integration to find that

$$a_n^{(2)}(t) = \frac{1}{\hbar^2} \sum_{pq} \sum_m \frac{[\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)][\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} e^{i(\omega_{ng} - \omega_p - \omega_q)t}. \quad (3.2.17)$$

Analogously, through an additional use of Eq. (3.2.14), we find that the third-order correction to the probability amplitude is given by

$$a_v^{(3)}(t) = \frac{1}{\hbar^3} \sum_{pqr} \sum_{mn} \frac{[\boldsymbol{\mu}_{vn} \cdot \mathbf{E}(\omega_r)][\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)][\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg} - \omega_p - \omega_q - \omega_r)(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \times e^{i(\omega_{vg} - \omega_p - \omega_q - \omega_r)t}. \quad (3.2.18)$$

3.2.3 Linear Susceptibility

Let us use the results just obtained to describe the linear optical properties of a material system. According to the rules of quantum mechanics, the expectation value of the electric-dipole moment is given by

$$\langle \hat{\mathbf{p}} \rangle = \langle \psi | \hat{\boldsymbol{\mu}} | \psi \rangle, \quad (3.2.19)$$

* We note that there is no mathematical justification for ignoring the lower limit of integration. This mathematical difficulty does not occur within the context of the density-matrix formalism of quantum mechanics, to be developed later in this chapter.

where ψ is given by the perturbation expansion (3.2.7) with λ set equal to one. We thus find that the lowest-order contribution to $\langle \tilde{\mathbf{p}} \rangle$ (i.e., the contribution linear in the applied field amplitude) is given by

$$\langle \tilde{\mathbf{p}}^{(1)} \rangle = \langle \psi^{(0)} | \hat{\boldsymbol{\mu}} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{\boldsymbol{\mu}} | \psi^{(0)} \rangle, \quad (3.2.20)$$

where $\psi^{(0)}$ is given by Eq. (3.2.9) and $\psi^{(1)}$ is given by Eqs. (3.2.10) and (3.2.16). By substituting these forms into Eq. (3.2.20) we find that

$$\langle \tilde{\mathbf{p}}^{(1)} \rangle = \frac{1}{\hbar} \sum_p \sum_m \left(\frac{\boldsymbol{\mu}_{gm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{\omega_{mg} - \omega_p} e^{-i\omega_p t} + \frac{[\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]^* \boldsymbol{\mu}_{mg}}{\omega_{mg}^* - \omega_p} e^{i\omega_p t} \right). \quad (3.2.21)$$

In writing Eq. (3.2.21) in the form shown, we have formally allowed for the possibility that the transition frequency ω_{mg} is a complex quantity. We have done this because a crude way of incorporating damping phenomena into the theory is to take ω_{mg} to be the complex quantity $\omega_{mg} = (E_m - E_g)/\hbar - i\Gamma_m/2$, where Γ_m is the population decay rate of the upper level m . This procedure is not totally acceptable, because it cannot describe the cascade of population among the excited states nor can it describe dephasing processes that are not accompanied by the transfer of population. Nonetheless, for the remainder of the present section, we shall allow the transition frequency ω_{mg} to be a complex quantity in order to provide an indication of how damping effects could be incorporated into the present theory.

Eq. (3.2.21) is written as a summation over all positive and negative field frequencies ω_p . This result is easier to interpret if we formally replace ω_p by $-\omega_p$ in the second term, in which case the expression becomes

$$\langle \tilde{\mathbf{p}}^{(1)} \rangle = \frac{1}{\hbar} \sum_p \sum_m \left(\frac{\boldsymbol{\mu}_{gm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{\omega_{mg} - \omega_p} + \frac{[\boldsymbol{\mu}_{gm} \cdot \mathbf{E}(\omega_p)] \boldsymbol{\mu}_{mg}}{\omega_{mg}^* + \omega_p} \right) e^{-i\omega_p t}. \quad (3.2.22)$$

We now use this result to calculate the form of the linear susceptibility. We take the linear polarization to be $\tilde{\mathbf{P}}^{(1)} = N \langle \tilde{\mathbf{p}}^{(1)} \rangle$, where N is the number density of atoms. We next express the polarization in terms of its complex amplitude as $\tilde{\mathbf{P}}^{(1)} = \sum_p \mathbf{P}^{(1)}(\omega_p) \exp(-i\omega_p t)$. Finally, we introduce the linear susceptibility defined through the relation $P_i^{(1)}(\omega_p) = \epsilon_0 \sum_j \chi_{ij}^{(1)} E_j(\omega_p)$. We thereby find that

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_m \left(\frac{\mu_{gm}^i \mu_{mg}^j}{\omega_{mg} - \omega_p} + \frac{\mu_{gm}^j \mu_{mg}^i}{\omega_{mg}^* + \omega_p} \right). \quad (3.2.23)$$

The first and second terms in Eq. (3.2.23) can be interpreted as the resonant and antiresonant contributions to the susceptibility, as illustrated in Fig. 3.2.1. In this figure we have indicated where level m would have to be located in order for the corresponding term to become resonant. Note that if g denotes the ground state, it is impossible for the second term to become resonant, which is why it is called the antiresonant contribution.

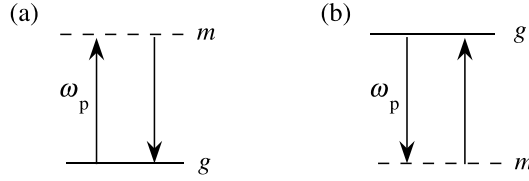


FIGURE 3.2.1: The resonant (a) and anti-resonant (b) contributions to the linear susceptibility of Eq. (3.2.23).

3.2.4 Second-Order Susceptibility

The expression for the second-order susceptibility is derived in a manner analogous to that used for the linear susceptibility. The second-order contribution (i.e., the contribution second order in \hat{V}) to the induced dipole moment per atom is given by

$$\langle \tilde{\mathbf{p}}^{(2)} \rangle = \langle \psi^{(0)} | \hat{\boldsymbol{\mu}} | \psi^{(2)} \rangle + \langle \psi^{(1)} | \hat{\boldsymbol{\mu}} | \psi^{(1)} \rangle + \langle \psi^{(2)} | \hat{\boldsymbol{\mu}} | \psi^{(0)} \rangle, \quad (3.2.24)$$

where $\psi^{(0)}$ is given by Eq. (3.2.9), and $\psi^{(1)}$ and $\psi^{(2)}$ are given by Eqs. (3.2.10), (3.2.16), and (3.2.17). We find that $\langle \tilde{\mathbf{p}}^{(2)} \rangle$ is given explicitly by

$$\begin{aligned} \langle \tilde{\mathbf{p}}^{(2)} \rangle = & \frac{1}{\hbar^2} \sum_{pq} \sum_{mn} \left(\frac{\boldsymbol{\mu}_{gn} [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} e^{-i(\omega_p + \omega_q)t} \right. \\ & + \frac{[\boldsymbol{\mu}_{ng} \cdot \mathbf{E}(\omega_q)]^* \boldsymbol{\mu}_{nm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng}^* - \omega_q)(\omega_{mg} - \omega_p)} e^{-i(\omega_p - \omega_q)t} \\ & \left. + \frac{[\boldsymbol{\mu}_{ng} \cdot \mathbf{E}(\omega_q)]^* [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_p)]^* \boldsymbol{\mu}_{mg}}{(\omega_{ng}^* - \omega_q)(\omega_{mg}^* - \omega_p - \omega_q)} e^{i(\omega_p + \omega_q)t} \right). \end{aligned} \quad (3.2.25)$$

As in the case of the linear susceptibility, this equation can be rendered more transparent by replacing ω_q by $-\omega_q$ in the second term and by replacing ω_q by $-\omega_q$ and ω_p by $-\omega_p$ in the third term; these substitutions are permissible because the expression is to be summed over frequencies ω_p and ω_q . We thereby obtain an expression in which each term has the same frequency dependence:

$$\begin{aligned} \langle \tilde{\mathbf{p}}^{(2)} \rangle = & \frac{1}{\hbar^2} \sum_{pq} \sum_{mn} \left(\frac{\boldsymbol{\mu}_{gn} [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \right. \\ & + \frac{[\boldsymbol{\mu}_{gn} \cdot \mathbf{E}(\omega_q)] \boldsymbol{\mu}_{nm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng}^* + \omega_q)(\omega_{mg} - \omega_p)} \\ & \left. + \frac{[\boldsymbol{\mu}_{gn} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_p)] \boldsymbol{\mu}_{mg}}{(\omega_{ng}^* + \omega_q)(\omega_{mg}^* + \omega_p + \omega_q)} \right) e^{-i(\omega_p + \omega_q)t}. \end{aligned} \quad (3.2.26)$$

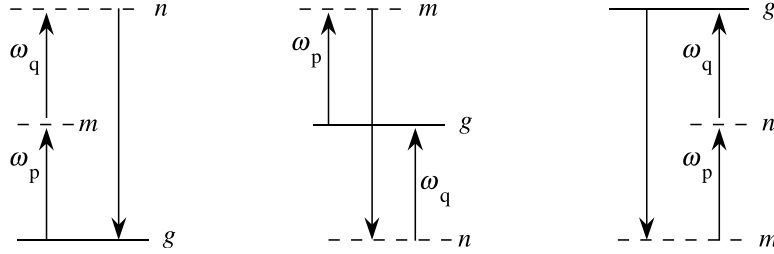


FIGURE 3.2.2: Resonance structure of the three terms of the second-order susceptibility of Eq. (3.2.27).

We next take the second-order polarization to be $\tilde{\mathbf{P}}^{(2)} = N \langle \tilde{\mathbf{p}}^{(2)} \rangle$ and represent it in terms of its frequency components as $\tilde{\mathbf{P}}^{(2)} = \sum_r \mathbf{P}^{(2)}(\omega_r) \exp(-i\omega_r t)$. We also introduce the standard definition of the second-order susceptibility (see also Eq. (1.3.13)):

$$P_i^{(2)} = \epsilon_0 \sum_{jk} \sum_{(pq)} \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) E_j(\omega_q) E_k(\omega_p)$$

and find that the second-order susceptibility is given by

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^2} \mathcal{P}_I \sum_{mn} & \left(\frac{\mu_{gn}^i \mu_{nm}^j \mu_{mg}^k}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \right. \\ & + \frac{\mu_{gn}^j \mu_{nm}^i \mu_{mg}^k}{(\omega_{ng}^* + \omega_q)(\omega_{mg} - \omega_p)} \\ & \left. + \frac{\mu_{gn}^j \mu_{nm}^k \mu_{mg}^i}{(\omega_{ng}^* + \omega_q)(\omega_{mg}^* + \omega_p + \omega_q)} \right). \end{aligned} \quad (3.2.27)$$

In this expression, the symbol \mathcal{P}_I denotes the intrinsic permutation operator. This operator tells us to average the expression that follows it over both permutations of the frequencies ω_p and ω_q of the applied fields. The Cartesian indices j and k are to be permuted simultaneously. We introduce the intrinsic permutation operator into Eq. (3.2.27) to ensure that the resulting expression obeys the condition of intrinsic permutation symmetry, as described in the discussion of Eqs. (1.4.52) and (1.5.6). The nature of the expression (3.2.27) for the second-order susceptibility can be understood in terms of the energy level diagrams depicted in Fig. 3.2.2, which show where the levels m and n would have to be located in order for each term in the expression to become resonant.

The quantum-mechanical expression for the second-order susceptibility given by Eq. (3.2.27) is sometimes called a sum-over-states expression because it involves a sum over all of the excited states of the atom. This expression actually is comprised of six terms; through use of the intrinsic permutation operator \mathcal{P}_I , we have been able to express the susceptibility in the

form (3.2.27), in which only three terms are displayed explicitly. For the case of highly non-resonant excitation, such that the resonance frequencies ω_{mg} and ω_{ng} can be taken to be real quantities, the expression for $\chi^{(2)}$ can be simplified still further. In particular, under such circumstances Eq. (3.2.27) can be expressed as

$$\chi_{ijk}^{(2)}(\omega_\sigma, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^2} \mathcal{P}_F \sum_{mn} \frac{\mu_{gn}^i \mu_{nm}^j \mu_{mg}^k}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_p)}, \quad (3.2.28)$$

where $\omega_\sigma = \omega_p + \omega_q$. Here we have introduced the full permutation operator, \mathcal{P}_F , defined such that the expression that follows it is to be summed over all permutations of the frequencies ω_p , ω_q , and $-\omega_\sigma$ —that is, over all input and output frequencies. The Cartesian indices are to be permuted along with the frequencies. The final result is then to be divided by the number of permutations of the input frequencies. The equivalence of Eqs. (3.2.27) and (3.2.28) can be verified by explicitly expanding the right-hand side of each equation into all six terms. The six permutations denoted by the operator \mathcal{P}_F are

$$\begin{aligned} (-\omega_\sigma, \omega_q, \omega_p) &\rightarrow (-\omega_\sigma, \omega_p, \omega_q), (\omega_q, -\omega_\sigma, \omega_p), (\omega_q, \omega_p, -\omega_\sigma), \\ &(\omega_p, -\omega_\sigma, \omega_q), (\omega_p, \omega_q, -\omega_\sigma). \end{aligned}$$

Since we can express the nonlinear susceptibility in the form of Eq. (3.2.28), we have proven the statement made in Section 1.5 that the second-order susceptibility of a lossless medium possesses full permutation symmetry.

3.2.5 Third-Order Susceptibility

We now calculate the third-order susceptibility. The dipole moment per atom, correct to third order in perturbation theory, is given by

$$\langle \tilde{\mathbf{p}}^{(3)} \rangle = \langle \psi^{(0)} | \hat{\boldsymbol{\mu}} | \psi^{(3)} \rangle + \langle \psi^{(1)} | \hat{\boldsymbol{\mu}} | \psi^{(2)} \rangle + \langle \psi^{(2)} | \hat{\boldsymbol{\mu}} | \psi^{(1)} \rangle + \langle \psi^{(3)} | \hat{\boldsymbol{\mu}} | \psi^{(0)} \rangle. \quad (3.2.29)$$

Formulas for $\psi^{(0)}$, $\psi^{(1)}$, $\psi^{(2)}$, $\psi^{(3)}$, are given by Eqs. (3.2.9), (3.2.10), (3.2.16), (3.2.17), and (3.2.18). We thus find that

$$\begin{aligned} \langle \tilde{\mathbf{p}}^{(3)} \rangle &= \frac{1}{\hbar^3} \sum_{pqr} \sum_{mnv} \\ &\times \left(\frac{\boldsymbol{\mu}_{gv} [\boldsymbol{\mu}_{vn} \cdot \mathbf{E}(\omega_r)] [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} e^{-i(\omega_p + \omega_q + \omega_r)t} \right. \\ &\left. + \frac{[\boldsymbol{\mu}_{vg} \cdot \mathbf{E}(\omega_r)]^* \boldsymbol{\mu}_{vn} [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg}^* - \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} e^{-i(\omega_p + \omega_q - \omega_r)t} \right) \end{aligned}$$

$$\begin{aligned}
 & + \frac{[\boldsymbol{\mu}_{vg} \cdot \mathbf{E}(\omega_r)]^* [\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_q)]^* \boldsymbol{\mu}_{nm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg}^* - \omega_r)(\omega_{ng}^* - \omega_r - \omega_q)(\omega_{mg} - \omega_p)} e^{-i(\omega_p - \omega_q - \omega_r)t} \\
 & + \frac{[\boldsymbol{\mu}_{vg} \cdot \mathbf{E}(\omega_r)]^* [\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_q)]^* [\boldsymbol{\mu}_{mn} \cdot \mathbf{E}(\omega_p)]^* \boldsymbol{\mu}_{mg}}{(\omega_{vg}^* - \omega_r)(\omega_{ng}^* - \omega_r - \omega_q)(\omega_{mg}^* - \omega_r - \omega_q - \omega_p)} e^{+i(\omega_p + \omega_q + \omega_r)t} \Big).
 \end{aligned} \tag{3.2.30}$$

Since the expression is summed over all positive and negative values of ω_p , ω_q , and ω_r , we can replace these quantities by their negatives in those expressions where the complex conjugate of a field amplitude appears. We thereby obtain the expression

$$\begin{aligned}
 \langle \tilde{\mathbf{p}}^{(3)} \rangle = & \frac{1}{\hbar^3} \sum_{pqr} \sum_{mnv} \\
 & \times \left(\frac{\boldsymbol{\mu}_{gv} [\boldsymbol{\mu}_{vn} \cdot \mathbf{E}(\omega_r)] [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right. \\
 & + \frac{[\boldsymbol{\mu}_{gv} \cdot \mathbf{E}(\omega_r)] \boldsymbol{\mu}_{vn} [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \\
 & + \frac{[\boldsymbol{\mu}_{gv} \cdot \mathbf{E}(\omega_r)] [\boldsymbol{\mu}_{vn} \cdot \mathbf{E}(\omega_q)] \boldsymbol{\mu}_{nm} [\boldsymbol{\mu}_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} \\
 & \left. + \frac{[\boldsymbol{\mu}_{gv} \cdot \mathbf{E}(\omega_r)] [\boldsymbol{\mu}_{vn} \cdot \mathbf{E}(\omega_q)] [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_p)] \boldsymbol{\mu}_{mg}}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg}^* + \omega_r + \omega_q + \omega_p)} \right) \\
 & \times e^{-i(\omega_p + \omega_q + \omega_r)t}.
 \end{aligned} \tag{3.2.31}$$

We now use this result to calculate the third-order susceptibility: We let $\tilde{\mathbf{P}}^{(3)} = N \langle \tilde{\mathbf{p}}^{(3)} \rangle = \sum_s \mathbf{P}^{(3)}(\omega_s) \exp(-i\omega_s t)$ and introduce the definition (1.3.21) of the third-order susceptibility:

$$P_k(\omega_p + \omega_q + \omega_r) = \epsilon_0 \sum_{hij} \sum_{(pqr)} \chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) E_j(\omega_r) E_i(\omega_q) E_h(\omega_p).$$

We thereby obtain the result

$$\begin{aligned}
 & \chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) \\
 & = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_I \sum_{mnv} \left[\frac{\boldsymbol{\mu}_{gv}^k \boldsymbol{\mu}_{vn}^j \boldsymbol{\mu}_{nm}^i \boldsymbol{\mu}_{mg}^h}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right. \\
 & \quad \left. + \frac{\boldsymbol{\mu}_{gv}^j \boldsymbol{\mu}_{vn}^k \boldsymbol{\mu}_{nm}^i \boldsymbol{\mu}_{mg}^h}{(\omega_{vg}^* + \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right]
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\mu_{gv}^j \mu_{vn}^i \mu_{nm}^k \mu_{mg}^h}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} \\
& + \frac{\mu_{gv}^j \mu_{vn}^i \mu_{nm}^h \mu_{mg}^k}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg}^* + \omega_r + \omega_q + \omega_p)} \Big]. \quad (3.2.32)
\end{aligned}$$

Here we have again made use of the intrinsic permutation operator \mathcal{P}_I defined following Eq. (3.2.27). The complete expression for the third-order susceptibility actually contains 24 terms, of which only four are displayed explicitly in Eq. (3.2.33); the others can be obtained through permutations of the frequencies (and Cartesian indices) of the applied fields. The locations of the resonances in the displayed terms of this expression are illustrated in Fig. 3.2.3.

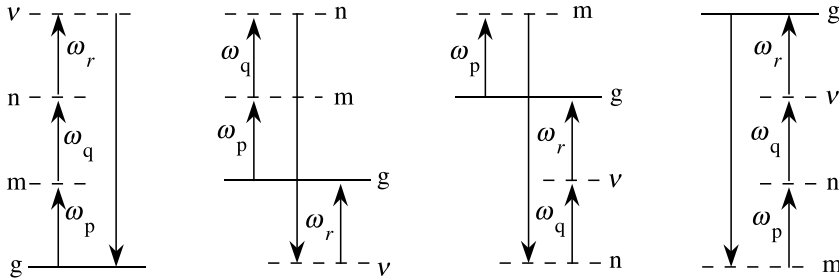


FIGURE 3.2.3: Locations of the resonances of each term in the expression (3.2.32) for the third-order susceptibility.

As in the case of the second-order susceptibility, the expression for $\chi^{(3)}$ can be written very compactly for the case of highly nonresonant excitation such that the imaginary parts of the resonance frequencies (recall that $\omega_{lg} = (E_l - E_g)/\hbar - i\Gamma_l/2$) can be ignored. In this case, the expression for $\chi^{(3)}$ can be written as

$$\begin{aligned}
& \chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) \\
& = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_F \sum_{mnv} \frac{\mu_{gv}^k \mu_{vn}^j \mu_{nm}^i \mu_{mg}^h}{(\omega_{vg} - \omega_\sigma)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)}, \quad (3.2.33)
\end{aligned}$$

where $\omega_\sigma = \omega_p + \omega_q + \omega_r$ and where we have made use of the full permutation operator \mathcal{P}_F defined following Eq. (3.2.28).

3.2.6 Third-Harmonic Generation in Alkali Metal Vapors

As an example of the use of Eq. (3.2.33), we next calculate the nonlinear optical susceptibility describing third-harmonic generation in a vapor of sodium atoms. Except for minor changes

in notation, our treatment follows that of the original treatment of Miles and Harris (1973). We assume that the incident radiation is linearly polarized in the z direction. Consequently, the nonlinear polarization will have only a z component, and we can suppress the tensor nature of the nonlinear interaction. If we represent the applied field as

$$\tilde{E}(\mathbf{r}, t) = E_1(\mathbf{r})e^{-i\omega t} + \text{c.c.}, \quad (3.2.34)$$

we find that the nonlinear polarization can be represented as

$$\tilde{P}(\mathbf{r}, t) = P_3(\mathbf{r})e^{-i3\omega t} + \text{c.c.}, \quad (3.2.35)$$

where

$$P_3(\mathbf{r}) = \epsilon_0 \chi^{(3)}(3\omega) E_1^3. \quad (3.2.36)$$

Here $\chi^{(3)}(3\omega)$ is an abbreviated notation for the quantity $\chi^{(3)}(3\omega = \omega + \omega + \omega)$. The nonlinear susceptibility describing third-harmonic generation is given, ignoring damping effects, by

$$\begin{aligned} \chi^{(3)}(3\omega) = & \frac{N}{\epsilon_0 \hbar^3} \sum_{mnv} \mu_{gv} \mu_{vn} \mu_{nm} \mu_{mg} \\ & \times \left[\frac{1}{(\omega_{vg} - 3\omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} \right. \\ & + \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} \\ & + \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} - \omega)} \\ & \left. + \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} + 3\omega)} \right]. \end{aligned} \quad (3.2.37)$$

Eq. (3.2.37) can be readily evaluated through use of the known energy-level structure and dipole transition moments of the sodium atom. Fig. 3.2.4 shows an energy-level diagram of the low-lying states of the sodium atom and a photon energy-level diagram describing the process of third-harmonic generation. We see that only the first contribution to Eq. (3.2.37) can become fully resonant. This term becomes fully resonant when ω is nearly equal to ω_{mg} , 2ω is nearly equal to ω_{ng} , and 3ω is nearly equal to ω_{vg} . In performing the summation over excited levels m , n , and v , the only levels that contribute are those that obey the selection rule $\Delta l = \pm 1$ for electric-dipole transitions. In particular, since the ground state is an s state, the matrix element μ_{mg} will be nonzero only if m denotes a p state. Similarly, since m denotes a p state, the matrix element μ_{nm} will be nonzero only if n denotes an s or a d state. In either case, v must denote a p state, since only in this case can both μ_{vn} and μ_{gv} be nonzero. The two types of coupling schemes that contribute to $\chi^{(3)}$ are shown in Fig. 3.2.5.

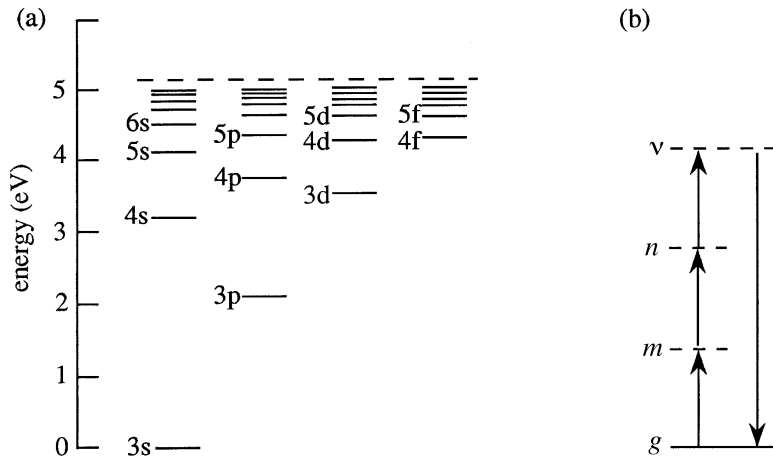


FIGURE 3.2.4: (a) Energy-level diagram of the sodium atom. (b) The third-harmonic generation process.

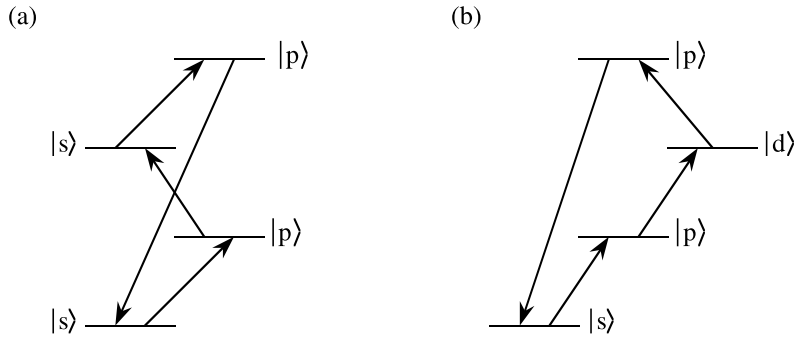


FIGURE 3.2.5: Two coupling schemes that contribute to the third-order susceptibility.

Through use of tabulated values of the matrix elements for the sodium atom, Miles and Harris (1973) calculated numerically the value of $\chi^{(3)}$ as a function of the vacuum wavelength $\lambda = 2\pi c/\omega$ of the incident laser field. The results of this calculation are shown in Fig. 3.2.6. A number of strong resonances in the nonlinear susceptibility are evident. Each such resonance is labeled by the quantum number of the level and the type of resonance that leads to the resonance enhancement. The peak labeled $3p(3\omega)$, for example, is due to a three-photon resonance with the $3p$ level of sodium. Miles and Harris also presented experimental results that confirm predictions of their theory.

Because atomic vapors are centrosymmetric, they cannot produce a second-order response. Nonetheless, the presence of a static electric field can break the inversion symmetry of the material medium, allowing processes such as sum-frequency generation to occur. These effects can be particularly large if the optical fields excite the high-lying Rydberg levels of an atomic

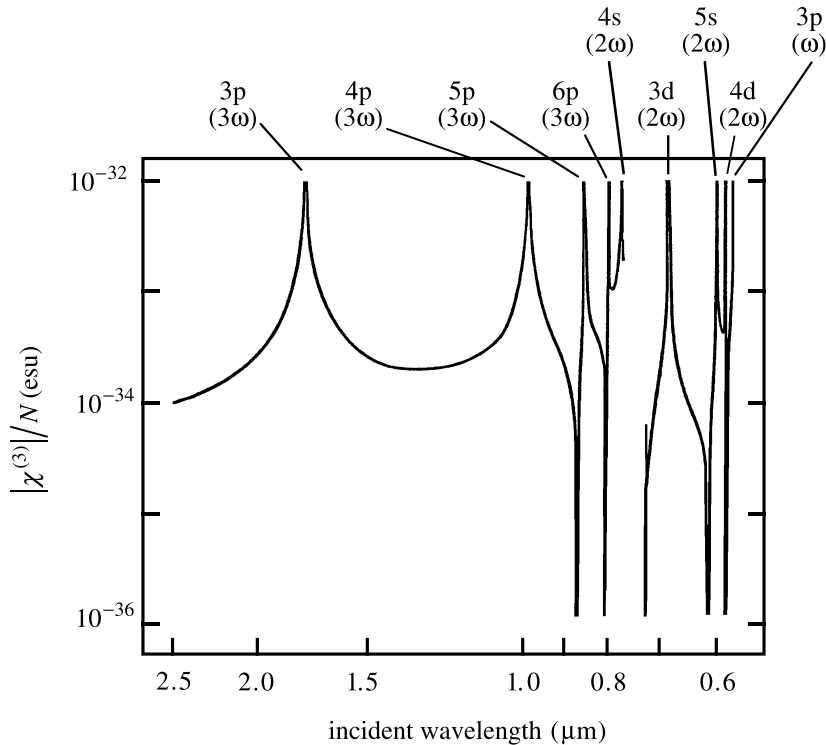


FIGURE 3.2.6: The nonlinear susceptibility describing third-harmonic generation in atomic sodium vapor plotted versus the vacuum wavelength of the fundamental radiation (after Miles and Harris, 1973).

system. The details of this process have been described theoretically by Boyd and Xiang (1982), with experimental confirmation presented by Gauthier et al. (1983) and Boyd et al. (1984).

3.3 Density Matrix Formulation of Quantum Mechanics

In the present section through Section 3.7, we calculate the nonlinear optical susceptibility through use of the density matrix formulation of quantum mechanics. We use this formalism because it is capable of treating effects, such as collisional broadening of the atomic resonances, that cannot be treated by the simple theoretical formalism based on the atomic wave function. We need to be able to treat such effects for a number of related reasons. We saw in the previous section that nonlinear effects become particularly large when one of the frequencies of the incident laser field, or when sums or differences of these frequencies, becomes equal to a transition frequency of the atomic system. But the formalism of the previous section does not allow us to describe the width of these resonances, and thus it cannot tell us how accurately we need to set the laser frequency to that of the atomic resonance. The wavefunction formalism also does not

tell us how strongly the response is modified when the laser frequency lies within the width of the resonance.

Let us begin by reviewing how the density matrix formalism follows from the basic laws of quantum mechanics.* If a quantum-mechanical system (such as an atom) is known to be in a particular quantum-mechanical state that we designate s , we can describe all of the physical properties of the system in terms of the wavefunction $\psi_s(\mathbf{r}, t)$ appropriate to this state. This wavefunction obeys the Schrödinger equation

$$i\hbar \frac{\partial \psi_s(\mathbf{r}, t)}{\partial t} = \hat{H} \psi_s(\mathbf{r}, t), \quad (3.3.1)$$

where \hat{H} denotes the Hamiltonian operator of the system. We assume that \hat{H} can be represented as

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (3.3.2)$$

where \hat{H}_0 is the Hamiltonian for a free atom and $\hat{V}(t)$ represents the interaction energy. In order to determine how the wavefunction evolves in time, it is often helpful to make explicit use of the fact that the energy eigenstates of the free-atom Hamiltonian \hat{H}_0 form a complete set of basis functions. We can hence represent the wavefunction of state s as

$$\psi_s(\mathbf{r}, t) = \sum_n C_n^s(t) u_n(\mathbf{r}), \quad (3.3.3)$$

where, as we noted in Section 3.2, the functions $u_n(\mathbf{r})$ are the energy eigensolutions to the time-independent Schrödinger equation

$$\hat{H}_0 u_n(\mathbf{r}) = E_n u_n(\mathbf{r}), \quad (3.3.4)$$

which are assumed to be orthonormal in that they obey the relation

$$\int u_m^*(\mathbf{r}) u_n(\mathbf{r}) d^3r = \delta_{mn}. \quad (3.3.5)$$

The expansion coefficient $C_n^s(t)$ gives the probability amplitude that the atom, which is known to be in state s , is in energy eigenstate n at time t . The time evolution of $\psi_s(\mathbf{r}, t)$ can be specified in terms of the time evolution of each of the expansion coefficient $C_n^s(t)$. To determine how these coefficients evolve in time, we introduce the expansion (3.3.3) into Schrödinger's equation (3.3.1) to obtain

$$i\hbar \sum_n \frac{dC_n^s(t)}{dt} u_n(\mathbf{r}) = \sum_n C_n^s(t) \hat{H} u_n(\mathbf{r}). \quad (3.3.6)$$

* The reader who is already familiar with the density matrix formalism can skip directly to Section 3.4.

Each side of this equation involves a summation over all of the energy eigenstates of the system. In order to simplify this equation, we multiply each side from the left by $u_m^*(\mathbf{r})$ and integrate over all space. The summation on the left-hand side of the resulting equation reduces to a single term through use of the orthogonality condition of Eq. (3.3.5). The right-hand side is simplified by introducing the matrix elements of the Hamiltonian operator \hat{H} , defined through

$$H_{mn} = \int u_m^*(\mathbf{r}) \hat{H} u_n(\mathbf{r}) d^3r. \quad (3.3.7)$$

We thereby obtain the result

$$i\hbar \frac{d}{dt} C_m^s(t) = \sum_n H_{mn} C_n^s(t). \quad (3.3.8)$$

This equation is entirely equivalent to the Schrödinger equation (3.3.1), but it is written in terms of the probability amplitudes $C_n^s(t)$.

The expectation value of any observable quantity can be calculated in terms of the wavefunction of the system. A basic postulate of quantum mechanics states that any observable quantity A is associated with a Hermitian operator \hat{A} . The expectation value of A is then obtained according to the prescription

$$\langle A \rangle = \int \psi_s^* \hat{A} \psi_s d^3r. \quad (3.3.9)$$

Here the angular brackets denote a quantum-mechanical average. This relationship can alternatively be written in Dirac notation as

$$\langle A \rangle = \langle \psi_s | \hat{A} | \psi_s \rangle = \langle s | \hat{A} | s \rangle, \quad (3.3.10)$$

where we shall use either $|\psi_s\rangle$ or $|s\rangle$ to denote the state s . The expectation value $\langle A \rangle$ can be expressed in terms of the probability amplitudes $C_n^s(t)$ by introducing Eq. (3.3.3) into Eq. (3.3.9) to obtain

$$\langle A \rangle = \sum_{mn} C_m^{s*} C_n^s A_{mn}, \quad (3.3.11)$$

where we have introduced the matrix elements A_{mn} of the operator \hat{A} , defined through

$$A_{mn} = \langle u_m | \hat{A} | u_n \rangle = \int u_m^* \hat{A} u_n d^3r. \quad (3.3.12)$$

As long as the initial state and the Hamiltonian operator \hat{H} for the system are known, the formalism described by Eqs. (3.3.1) through (3.3.12) is capable of providing a complete description of the time evolution of the system and of all of its observable properties. However,

there are circumstances under which the state of the system is not known in a precise manner. An example is a collection of atoms in an atomic vapor, where the atoms can interact with one another by means of collisions. Each time a collision occurs, the wave function of each interacting atom is modified. If the collisions are sufficiently weak, the modification may involve only an overall change in the phase of the wave function. However, since it is computationally infeasible to keep track of the phase of each atom within the atomic vapor, from a practical point of view the state of each atom is not known.

Under such circumstances, where the precise state of the system is unknown, the density matrix formalism can be used to describe the system in a statistical sense. Let us denote by $p(s)$ the probability that the system is in the state s . The quantity $p(s)$ is to be understood as a classical rather than a quantum-mechanical probability. Hence $p(s)$ simply reflects our lack of knowledge of the actual quantum-mechanical state of the system; it is not a consequence of any sort of quantum-mechanical uncertainty relation. In terms of $p(s)$, we define the elements of the density matrix of the system by

$$\rho_{nm} = \sum_s p(s) C_m^{s*} C_n^s. \quad (3.3.13)$$

This relation can also be written symbolically as

$$\rho_{nm} = \overline{C_m^{*} C_n}, \quad (3.3.14)$$

where the overbar denotes an ensemble average, that is, an average over all of the possible states of the system. In either form, the indices n and m are understood to run over all of the energy eigenstates of the system.

The elements of the density matrix have the following physical interpretation: The diagonal elements ρ_{nn} give the probability that the system is in energy eigenstate n . The off-diagonal elements have a somewhat more abstract interpretation: ρ_{nm} gives the “coherence” between levels n and m , in the sense that ρ_{nm} will be nonzero only if the system is in a coherent superposition of energy eigenstate n and m . We show below that the off-diagonal elements of the density matrix are, in certain circumstances, proportional to the induced electric dipole moment of the atom.

The density matrix is useful because it can be used to calculate the expectation value of any observable quantity. Since the expectation value of an observable quantity A for a system known to be in the quantum state s is given according to Eq. (3.3.11) by $\langle A \rangle = \sum_{mn} C_m^{s*} C_n^s A_{mn}$, the expectation value for the case in which the exact state of the system is not known is obtained by averaging Eq. (3.3.11) over all possible states of the system, to yield

$$\overline{\langle A \rangle} = \sum_s p(s) \sum_{nm} C_m^{s*} C_n^s A_{mn}. \quad (3.3.15)$$

The notation used on the left-hand side of this equation means that we are calculating the ensemble average of the quantum-mechanical expectation value of the observable quantity A .^{*} Through use of Eq. (3.3.13), this quantity can alternatively be expressed as

$$\overline{\langle A \rangle} = \sum_{nm} \rho_{nm} A_{mn}. \quad (3.3.16)$$

The double summation in the equation can be simplified as follows:

$$\sum_{nm} \rho_{nm} A_{mn} = \sum_n \left(\sum_m \rho_{nm} A_{mn} \right) = \sum_n (\hat{\rho} \hat{A})_{nn} \equiv \text{Tr}(\hat{\rho} \hat{A}),$$

where we have introduced the trace operation, which is defined for any operator \hat{M} by $\text{Tr} \hat{M} = \sum_n M_{nn}$. The expectation value of A is hence given by

$$\overline{\langle A \rangle} = \text{Tr}(\hat{\rho} \hat{A}). \quad (3.3.17)$$

The notation used in these equations is that $\hat{\rho}$ denotes the density operator, whose n, m matrix component is denoted ρ_{nm} ; $\hat{\rho} \hat{A}$ denotes the product of $\hat{\rho}$ with the operator \hat{A} ; and $(\hat{\rho} \hat{A})_{nn}$ denotes the n, n component of the matrix representation of this product.

We have just seen that the expectation value of any observable quantity can be determined straightforwardly in terms of the density matrix. In order to determine how any expectation value evolves in time, it is thus necessary only to determine how the density matrix itself evolves in time. By direct time differentiation of Eq. (3.3.13), we find that

$$\dot{\rho}_{nm} = \sum_s \frac{dp(s)}{dt} C_m^{s*} C_n^s + \sum_s p(s) \left(C_m^{s*} \frac{dC_n^s}{dt} + \frac{dC_m^{s*}}{dt} C_n^s \right). \quad (3.3.18)$$

For the present, let us assume that $p(s)$ does not vary in time, so that the first term in this expression vanishes. We can then evaluate the second term straightforwardly by using Schrödinger's equation for the time evolution of the probability amplitudes equation (3.3.8). From this equation we obtain the expressions

$$\begin{aligned} C_m^{s*} \frac{dC_n^s}{dt} &= \frac{-i}{\hbar} C_m^{s*} \sum_v H_{nv} C_v^s, \\ C_n^s \frac{dC_m^{s*}}{dt} &= \frac{i}{\hbar} C_n^s \sum_v H_{mv}^* C_v^{s*} = \frac{i}{\hbar} C_n^s \sum_v H_{vm} C_v^{s*}. \end{aligned}$$

* In later sections of this chapter, we shall follow conventional notation and omit the overbar from expressions such as $\overline{\langle A \rangle}$, allowing the angular brackets to denote both a quantum and a classical average.

These results are now substituted into Eq. (3.3.18) (with the first term on the right-hand side omitted) to obtain

$$\dot{\rho}_{nm} = \sum_s p(s) \frac{i}{\hbar} \sum_v (C_n^s C_v^{s*} H_{vm} - C_m^{s*} C_v^s H_{nv}). \quad (3.3.19)$$

The right-hand side of this equation can be written more compactly by introducing the form (3.3.13) for the density matrix to obtain

$$\dot{\rho}_{nm} = \frac{i}{\hbar} \sum_v (\rho_{nv} H_{vm} - H_{nv} \rho_{vm}). \quad (3.3.20)$$

Finally, the summation over v can be performed formally to write this result as

$$\dot{\rho}_{nm} = \frac{i}{\hbar} (\hat{\rho} \hat{H} - \hat{H} \hat{\rho})_{nm} = \frac{-i}{\hbar} [\hat{H}, \hat{\rho}]_{nm}. \quad (3.3.21)$$

We have written the last form in terms of the commutator, defined for any two operators \hat{A} and \hat{B} by $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

Eq. (3.3.21) describes how the density matrix evolves in time as the result of interactions that are included in the Hamiltonian \hat{H} . However, as mentioned above, there are certain interactions (such as those resulting from collisions between atoms) that cannot conveniently be included in a Hamiltonian description. Such interactions can lead to a change in the state of the system, and hence to a nonvanishing value of $dp(s)/dt$. We include such effects in the formalism by adding phenomenological damping terms to the equation of motion (3.3.21). There is more than one way to model such decay processes. We shall often model such processes by taking the density matrix equations to have the form

$$\dot{\rho}_{nm} = \frac{-i}{\hbar} [\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm} (\rho_{nm} - \rho_{nm}^{(\text{eq})}). \quad (3.3.22)$$

Here the second term on the right-hand side is a phenomenological damping term, which indicates that ρ_{nm} relaxes to its equilibrium value $\rho_{nm}^{(\text{eq})}$ at rate γ_{nm} . Since γ_{nm} is a decay rate, we assume that $\gamma_{nm} = \gamma_{mn}$. In addition, we make the physical assumption that

$$\rho_{nm}^{(\text{eq})} = 0 \quad \text{for } n \neq m. \quad (3.3.23)$$

We are thereby asserting that in thermal equilibrium the excited states of the system may contain population (i.e., $\rho_{nn}^{(\text{eq})}$ can be nonzero) but that thermal excitation, which is expected to be an incoherent process, cannot produce any coherent superpositions of atomic states ($\rho_{nm}^{(\text{eq})} = 0$ for $n \neq m$).

An alternative method of describing decay phenomena is to assume that the off-diagonal elements of the density matrix are damped in the manner described above, but to describe the

damping of the diagonal elements by allowing population to decay from higher-lying levels to lower-lying levels. In such a case, the density matrix equations of motion are given by

$$\dot{\rho}_{nm} = -i\hbar^{-1}[\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm}\rho_{nm}, \quad n \neq m, \quad (3.3.24a)$$

$$\dot{\rho}_{nn} = -i\hbar^{-1}[\hat{H}, \hat{\rho}]_{nn} + \sum_{E_m > E_n} \Gamma_{nm}\rho_{mm} - \sum_{E_m < E_n} \Gamma_{mn}\rho_{nn}. \quad (3.3.24b)$$

Here Γ_{nm} gives the rate per atom at which population decays from level m to level n , and, as above, γ_{nm} gives the damping rate of the ρ_{nm} coherence.

The damping rates γ_{nm} for the off-diagonal elements of the density matrix are not entirely independent of the damping rates of the diagonal elements. In fact, under quite general conditions the off-diagonal elements can be represented as

$$\gamma_{nm} = \frac{1}{2}(\Gamma_n + \Gamma_m) + \gamma_{nm}^{(\text{col})}. \quad (3.3.25)$$

Here, Γ_n and Γ_m denote the total decay rates of population out of levels n and m , respectively. In the notation of Eq. (3.3.24b), for example, Γ_n is given by the expression

$$\Gamma_n = \sum_{n' (E_{n'} < E_n)} \Gamma_{n'n}. \quad (3.3.26)$$

The quantity $\gamma_{nm}^{(\text{col})}$ in Eq. (3.3.25) is the dipole dephasing rate due to processes (such as elastic collisions) that are not associated with the transfer of population; $\gamma_{nm}^{(\text{col})}$ is sometimes called the proper dephasing rate. To see why Eq. (3.3.25) depends upon the population decay rates in the manner indicated, we note that if level n has lifetime $\tau_n = 1/\Gamma_n$, the probability to be in level n must decay as

$$|C_n(t)|^2 = |C_n(0)|^2 e^{-\Gamma_n t}, \quad (3.3.27)$$

and thus the probability amplitude must vary in time as

$$C_n(t) = C_n(0) e^{-i\omega_n t} e^{-\Gamma_n t/2}. \quad (3.3.28)$$

Likewise, the probability amplitude of being in level m must vary as

$$C_m(t) = C_m(0) e^{-i\omega_m t} e^{-\Gamma_m t/2}. \quad (3.3.29)$$

Thus, the coherence between the two levels must vary as

$$C_n^*(t)C_m(t) = C_n^*(0)C_m(0) e^{-i\omega_{mn}t} e^{-(\Gamma_n + \Gamma_m)t/2}. \quad (3.3.30)$$

But since the ensemble average of $C_n^*C_m$ is just ρ_{mn} , whose damping rate is denoted γ_{mn} , it follows that

$$\gamma_{mn} = \frac{1}{2}(\Gamma_n + \Gamma_m). \quad (3.3.31)$$

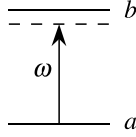


FIGURE 3.3.1: A two-level atom.

3.3.1 Example: Two-Level Atom

As an example of the use of the density matrix formalism, we apply it to the simple case illustrated in Fig. 3.3.1, in which only the two atomic states a and b interact appreciably with the incident optical field. The wavefunction describing state s of such an atom is given by

$$\psi_s(\mathbf{r}, t) = C_a^s(t)u_a(\mathbf{r}) + C_b^s(t)u_b(\mathbf{r}), \quad (3.3.32)$$

and thus the density matrix describing the atom is the two-by-two matrix given explicitly by

$$\begin{bmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{bmatrix} = \begin{bmatrix} \overline{C_a C_a^*} & \overline{C_a C_b^*} \\ \overline{C_b C_a^*} & \overline{C_b C_b^*} \end{bmatrix}. \quad (3.3.33)$$

The matrix representation of the electric-dipole-moment operator is

$$\hat{\mu} \Rightarrow \begin{bmatrix} 0 & \mu_{ab} \\ \mu_{ba} & 0 \end{bmatrix}, \quad (3.3.34)$$

where $\mu_{ij} = \mu_{ji}^* = -e\langle i|\hat{z}|j\rangle$, $-e$ is the electron charge, and \hat{z} is the position operator for the electron. We have set the diagonal elements of the electric-dipole-moment operator equal to zero on the basis of the implicit assumption that states a and b have definite parity, in which case $\langle a|\hat{\mathbf{r}}|a\rangle$ and $\langle b|\hat{\mathbf{r}}|b\rangle$ vanish identically as a consequence of symmetry considerations. The expectation value of the dipole moment is given according to Eq. (3.3.17) by $\langle \hat{\mu} \rangle = \text{Tr}(\hat{\rho}\hat{\mu})$. Explicitly, $\hat{\rho}\hat{\mu}$ is represented as

$$\hat{\rho}\hat{\mu} \Rightarrow \begin{bmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{bmatrix} \begin{bmatrix} 0 & \mu_{ab} \\ \mu_{ba} & 0 \end{bmatrix} = \begin{bmatrix} \rho_{ab}\mu_{ba} & \rho_{aa}\mu_{ab} \\ \rho_{bb}\mu_{ba} & \rho_{ba}\mu_{ab} \end{bmatrix} \quad (3.3.35)$$

and thus the expectation value of the induced dipole moment is given by

$$\overline{\langle \mu \rangle} = \text{Tr}(\hat{\rho}\hat{\mu}) = \rho_{ab}\mu_{ba} + \rho_{ba}\mu_{ab}. \quad (3.3.36)$$

As stated in connection with Eq. (3.3.14), the expectation value of the dipole moment is seen to depend upon the off-diagonal elements of the density matrix.

The density matrix treatment of the two-level atom is developed more fully in Chapter 6.

3.4 Perturbation Solution of the Density Matrix Equation of Motion

In the last section, we saw that the density matrix equation of motion with the phenomenological inclusion of damping is given by

$$\dot{\rho}_{nm} = \frac{-i}{\hbar} [\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm} (\rho_{nm} - \rho_{nm}^{(\text{eq})}). \quad (3.4.1)$$

In general, this equation cannot be solved exactly for physical systems of interest, and for this reason it is useful to develop a perturbative technique for solving it. This technique presupposes that, as in Eq. (3.3.2) in the preceding section, the Hamiltonian can be split into two parts as

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (3.4.2)$$

where \hat{H}_0 represents the Hamiltonian of the free atom and $\hat{V}(t)$ represents the energy of interaction of the atom with the externally applied radiation field. This interaction is assumed to be weak in the sense that the expectation value and matrix elements of \hat{V} are much smaller than the expectation value of \hat{H}_0 . We usually assume that this interaction energy is given adequately by the electric-dipole approximation as

$$\hat{V} = -\hat{\boldsymbol{\mu}} \cdot \tilde{\mathbf{E}}(t), \quad (3.4.3)$$

where $\hat{\boldsymbol{\mu}} = -e\hat{\mathbf{r}}$ denotes the electric-dipole moment operator of the atom. However, for generality and for compactness of notation, we shall introduce Eq. (3.4.3) only when necessary.

When Eq. (3.4.2) is introduced into Eq. (3.4.1), the commutator $[\hat{H}, \hat{\rho}]$ splits into two terms. We examine first the commutator of \hat{H}_0 with $\hat{\rho}$. We assume that the states n represent the energy eigenfunctions u_n of the unperturbed Hamiltonian \hat{H}_0 and thus satisfy the equation $\hat{H}_0 u_n = E_n u_n$ (see also Eq. (3.3.4)). As a consequence, the matrix representation of \hat{H}_0 is diagonal—that is,

$$H_{0,nm} = E_n \delta_{nm}. \quad (3.4.4)$$

The commutator can thus be expanded as

$$\begin{aligned} [\hat{H}_0, \hat{\rho}]_{nm} &= (\hat{H}_0 \hat{\rho} - \hat{\rho} \hat{H}_0)_{nm} = \sum_v (H_{0,nv} \rho_{vm} - \rho_{nv} H_{0,v,m}) \\ &= \sum_v (E_n \delta_{nv} \rho_{vm} - \rho_{nv} \delta_{vm} E_v) \\ &= E_n \rho_{nm} - E_m \rho_{nm} = (E_n - E_m) \rho_{nm}. \end{aligned} \quad (3.4.5)$$

For future convenience, we define the transition frequency (in angular frequency units) as

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}. \quad (3.4.6)$$

Through use of Eqs. (3.4.2), (3.4.5), and (3.4.6), the density matrix equation of motion (3.4.1) thus becomes

$$\dot{\rho}_{nm} = -i\omega_{nm}\rho_{nm} - \frac{i}{\hbar}[\hat{V}, \hat{\rho}]_{nm} - \gamma_{nm}(\rho_{nm} - \rho_{nm}^{(\text{eq})}). \quad (3.4.7)$$

We can also expand the commutator of \hat{V} with $\hat{\rho}$ to obtain the density matrix equation of motion in the form*

$$\dot{\rho}_{nm} = -i\omega_{nm}\rho_{nm} - \frac{i}{\hbar} \sum_v (V_{nv}\rho_{vm} - \rho_{nv}V_{vm}) - \gamma_{nm}(\rho_{nm} - \rho_{nm}^{(\text{eq})}). \quad (3.4.8)$$

For most problems of physical interest, Eq. (3.4.8) cannot be solved analytically. We therefore seek a solution in the form of a perturbation expansion. In order to carry out this procedure, we replace V_{ij} in Eq. (3.4.8) by λV_{ij} , where λ is a parameter ranging between zero and one that characterizes the strength of the perturbation. The value $\lambda = 1$ is taken to represent the actual physical situation. We now seek a solution to Eq. (3.4.8) in the form of a power series in λ —that is,

$$\rho_{nm} = \rho_{nm}^{(0)} + \lambda\rho_{nm}^{(1)} + \lambda^2\rho_{nm}^{(2)} + \cdots. \quad (3.4.9)$$

We require that Eq. (3.4.9) be a solution of Eq. (3.4.8) for any value of the parameter λ . In order for this condition to hold, the coefficients of each power of λ must satisfy Eq. (3.4.8) separately. We thereby obtain the set of equations

$$\dot{\rho}_{nm}^{(0)} = -i\omega_{nm}\rho_{nm}^{(0)} - \gamma_{nm}(\rho_{nm}^{(0)} - \rho_{nm}^{(\text{eq})}), \quad (3.4.10a)$$

$$\dot{\rho}_{nm}^{(1)} = -(i\omega_{nm} + \gamma_{nm})\rho_{nm}^{(1)} - i\hbar^{-1}[\hat{V}, \hat{\rho}^{(0)}]_{nm}, \quad (3.4.10b)$$

$$\dot{\rho}_{nm}^{(2)} = -(i\omega_{nm} + \gamma_{nm})\rho_{nm}^{(2)} - i\hbar^{-1}[\hat{V}, \hat{\rho}^{(1)}]_{nm}, \quad (3.4.10c)$$

and so on. This system of equations can now be integrated directly, since, if the set of equations is solved in the order shown, each equation contains only linear homogeneous terms and inhomogeneous terms that are already known.

* In this section, we are describing the time evolution of the system in the Schrödinger picture. It is sometimes convenient to describe the time evolution instead in the interaction picture. To find the analogous equation of motion in the interaction picture, we define new quantities σ_{nm} and $\sigma_{nm}^{(\text{eq})}$ through

$$\rho_{nm} = \sigma_{nm}e^{-i\omega_{nm}t}, \quad \rho_{nm}^{(\text{eq})} = \sigma_{nm}^{(\text{eq})}e^{-i\omega_{nm}t}.$$

In terms of these new quantities, Eq. (3.4.8) becomes

$$\dot{\sigma}_{nm} = -\frac{i}{\hbar} \sum_v [V_{nv}\sigma_{vm}e^{i\omega_{nv}t} - \sigma_{nv}e^{i\omega_{vm}t}V_{vm}] - \gamma_{nm}(\sigma_{nm} - \sigma_{nm}^{(\text{eq})}).$$

Eq. (3.4.10a) describes the time evolution of the system in the absence of any external field. We take the steady-state solution to this equation to be

$$\rho_{nm}^{(0)} = \rho_{nm}^{(\text{eq})}, \quad (3.4.11a)$$

where (for reasons given earlier; see Eq. (3.3.23))

$$\rho_{nm}^{(\text{eq})} = 0 \quad \text{for} \quad n \neq m. \quad (3.4.11b)$$

Now that $\rho_{nm}^{(0)}$ is known, Eq. (3.4.10b) can be integrated. To do so, we make a change of variables by representing $\rho_{nm}^{(1)}$ as

$$\rho_{nm}^{(1)}(t) = S_{nm}^{(1)}(t)e^{-(i\omega_{nm} + \gamma_{nm})t}. \quad (3.4.12)$$

The time derivative $\dot{\rho}_{nm}^{(1)}$ can be represented in terms of $S_{nm}^{(1)}$ as

$$\dot{\rho}_{nm}^{(1)} = -(i\omega_{nm} + \gamma_{nm})S_{nm}^{(1)}e^{-(i\omega_{nm} + \gamma_{nm})t} + \dot{S}_{nm}^{(1)}e^{-(i\omega_{nm} + \gamma_{nm})t}. \quad (3.4.13)$$

These forms are substituted into Eq. (3.4.10b), which then becomes

$$\dot{S}_{nm}^{(1)} = \frac{-i}{\hbar} [\hat{V}, \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t}. \quad (3.4.14)$$

This equation can be integrated to give

$$S_{nm}^{(1)} = \int_{-\infty}^t \frac{-i}{\hbar} [\hat{V}(t'), \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} dt'. \quad (3.4.15)$$

This expression is now substituted back into Eq. (3.4.12) to obtain

$$\rho_{nm}^{(1)}(t) = \int_{-\infty}^t \frac{-i}{\hbar} [\hat{V}(t'), \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})(t'-t)} dt'. \quad (3.4.16)$$

In similar way, all of the higher-order corrections to the density matrix can be obtained. These expressions are formally identical to Eq. (3.4.16). The expression for $\rho_{nm}^{(N)}$, for example, is obtained by replacing $\hat{\rho}^{(0)}$ with $\hat{\rho}^{(N-1)}$ on the right-hand side of Eq. (3.4.16).

3.5 Density Matrix Calculation of the Linear Susceptibility

As a first application of the perturbation solution to the density matrix equations of motion, we calculate the linear susceptibility of an atomic system. The relevant starting equation for this calculation is Eq. (3.4.16), which we write in the form

$$\rho_{nm}^{(1)}(t) = e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^t dt' \frac{-i}{\hbar} [\hat{V}(t'), \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'}. \quad (3.5.1)$$

As before, the interaction Hamiltonian is given by Eq. (3.4.3) as

$$\hat{V}(t') = -\hat{\boldsymbol{\mu}} \cdot \tilde{\mathbf{E}}(t'), \quad (3.5.2)$$

and we assume that the unperturbed density matrix is given by (see also Eqs. (3.4.11))

$$\rho_{nm}^{(0)} = 0 \quad \text{for } n \neq m. \quad (3.5.3)$$

We represent the applied field as

$$\tilde{\mathbf{E}}(t) = \sum_p \mathbf{E}(\omega_p) e^{-i\omega_p t}. \quad (3.5.4)$$

The first step is to obtain an explicit expression for the commutator appearing in Eq. (3.5.1):

$$\begin{aligned} [\hat{V}(t), \hat{\rho}^{(0)}]_{nm} &= \sum_v [V(t)_{nv} \rho_{vm}^{(0)} - \rho_{nv}^{(0)} V(t)_{vm}] \\ &= - \sum_v [\boldsymbol{\mu}_{nv} \rho_{vm}^{(0)} - \rho_{nv}^{(0)} \boldsymbol{\mu}_{vm}] \cdot \tilde{\mathbf{E}}(t) \\ &= -(\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \boldsymbol{\mu}_{nm} \cdot \tilde{\mathbf{E}}(t). \end{aligned} \quad (3.5.5)$$

Here the second form is obtained by introducing $\hat{V}(t)$ explicitly from Eq. (3.5.2), and the third form is obtained by performing the summation over all v and utilizing the condition (3.5.3). This expression for the commutator is introduced into Eq. (3.5.1) to obtain

$$\rho_{nm}^{(1)}(t) = \frac{i}{\hbar} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \boldsymbol{\mu}_{nm} \cdot e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^t \tilde{\mathbf{E}}(t') e^{(i\omega_{nm} + \gamma_{nm})t'} dt'. \quad (3.5.6)$$

We next introduce Eq. (3.5.4) for $\tilde{\mathbf{E}}(t)$ to obtain

$$\begin{aligned} \rho_{nm}^{(1)}(t) &= \frac{i}{\hbar} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \boldsymbol{\mu}_{nm} \cdot \sum_p \mathbf{E}(\omega_p) \\ &\quad \times e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^t e^{[i(\omega_{nm} - \omega_p) + \gamma_{nm}]t'} dt'. \end{aligned} \quad (3.5.7)$$

The second line of this expression can be evaluated explicitly as

$$e^{-(i\omega_{nm} + \gamma_{nm})t} \left(\frac{e^{[i(\omega_{nm} - \omega_p) + \gamma_{nm}]t'}}{i(\omega_{nm} - \omega_p) + \gamma_{nm}} \right) \Big|_{-\infty}^t = \frac{e^{-i\omega_p t}}{i(\omega_{nm} - \omega_p) + \gamma_{nm}}, \quad (3.5.8)$$

and $\rho_{nm}^{(1)}$ is thus seen to be given by

$$\rho_{nm}^{(1)} = \hbar^{-1} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \sum_p \frac{\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_p) e^{-i\omega_p t}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}. \quad (3.5.9)$$

We next use this result to calculate the expectation value of the induced dipole moment*:

$$\begin{aligned}\langle \tilde{\boldsymbol{\mu}}(t) \rangle &= \text{Tr}(\hat{\rho}^{(1)} \hat{\boldsymbol{\mu}}) = \sum_{nm} \rho_{nm}^{(1)} \boldsymbol{\mu}_{mn} \\ &= \sum_{nm} \hbar^{-1} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \sum_p \frac{\boldsymbol{\mu}_{mn} [\boldsymbol{\mu}_{nm} \cdot \mathbf{E}(\omega_p)] e^{-i\omega_p t}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}.\end{aligned}\quad (3.5.10)$$

We decompose $\langle \tilde{\boldsymbol{\mu}}(t) \rangle$ into its frequency components according to

$$\langle \tilde{\boldsymbol{\mu}}(t) \rangle = \sum_p \langle \boldsymbol{\mu}(\omega_p) \rangle e^{-i\omega_p t} \quad (3.5.11)$$

and define the linear susceptibility tensor $\boldsymbol{\chi}^{(1)}(\omega)$ by the equation

$$\mathbf{P}(\omega_p) = N \langle \boldsymbol{\mu}(\omega_p) \rangle = \epsilon_0 \boldsymbol{\chi}^{(1)}(\omega_p) \cdot \mathbf{E}(\omega_p), \quad (3.5.12)$$

where N denotes the atomic number density. By comparing this equation with Eq. (3.5.10), we find that the linear susceptibility is given by

$$\boldsymbol{\chi}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \frac{\boldsymbol{\mu}_{mn} \boldsymbol{\mu}_{nm}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}. \quad (3.5.13)$$

The result given by Eqs. (3.5.12) and (3.5.13) can be written in Cartesian component form as

$$P_i(\omega_p) = N \langle \mu_i(\omega_p) \rangle = \sum_j \epsilon_0 \chi_{ij}^{(1)}(\omega_p) E_j(\omega_p) \quad (3.5.14)$$

with

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}. \quad (3.5.15)$$

We see that the linear susceptibility is proportional to the population difference $\rho_{mm}^{(0)} - \rho_{nn}^{(0)}$; thus, if levels m and n contain equal populations, the $m \rightarrow n$ transition does not contribute to the linear susceptibility.

Eq. (3.5.15) is an extremely compact way of representing the linear susceptibility. At times it is more intuitive to express the susceptibility in an expanded form. We first rewrite Eq. (3.5.15) as

$$\begin{aligned}\chi_{ij}^{(1)}(\omega_p) &= \frac{N}{\epsilon_0 \hbar} \sum_{nm} \rho_{mm}^{(0)} \frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} \\ &\quad - \frac{N}{\epsilon_0 \hbar} \sum_{nm} \rho_{nn}^{(0)} \frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}.\end{aligned}\quad (3.5.16)$$

* Here and throughout the remainder of this chapter we are omitting the bar over quantities such as $\overline{\langle \mu \rangle}$ for simplicity of notation. Hence, the angular brackets are meant to imply both a quantum and an ensemble average.

We next interchange the dummy indices n and m in the second summation so that the two summations can be recombined as

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} \rho_{mm}^{(0)} \left[\frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} - \frac{\mu_{nm}^i \mu_{mn}^j}{(\omega_{mn} - \omega_p) - i\gamma_{mn}} \right]. \quad (3.5.17)$$

We now use the fact that $\omega_{mn} = -\omega_{nm}$ and $\gamma_{nm} = \gamma_{mn}$ to write this result as

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} \rho_{mm}^{(0)} \left[\frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} + \frac{\mu_{nm}^i \mu_{mn}^j}{(\omega_{nm} + \omega_p) + i\gamma_{nm}} \right]. \quad (3.5.18)$$

In order to interpret this result, let us first make the simplifying assumption that all of the population is in one level (typically the ground state), which we denote as level a . Mathematically, this assumption can be stated as

$$\rho_{aa}^{(0)} = 1, \quad \rho_{mm}^{(0)} = 0 \quad \text{for } m \neq a. \quad (3.5.19)$$

We now perform the summation over m in Eq. (3.5.18) to obtain

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_n \left[\frac{\mu_{an}^i \mu_{na}^j}{(\omega_{na} - \omega_p) - i\gamma_{na}} + \frac{\mu_{na}^i \mu_{an}^j}{(\omega_{na} + \omega_p) + i\gamma_{na}} \right]. \quad (3.5.20)$$

We see that for positive frequencies (i.e., for $\omega_p > 0$), only the first term can become resonant. The second term is known as the antiresonant or counterrotating term. We can often drop the second term, especially when ω_p is close to one of the resonance frequencies of the atom. Let us assume that ω_p is nearly resonant with the transition frequency ω_{na} . Then to good approximation the linear susceptibility is given by

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \frac{\mu_{an}^i \mu_{na}^j}{(\omega_{na} - \omega_p) - i\gamma_{na}} = \frac{N}{\epsilon_0 \hbar} \mu_{an}^i \mu_{na}^j \frac{(\omega_{na} - \omega_p) + i\gamma_{na}}{(\omega_{na} - \omega_p)^2 + \gamma_{na}^2}. \quad (3.5.21)$$

The real and imaginary parts of this expression are shown in Fig. 3.5.1. We see that the imaginary part of χ_{ij} has the form of a Lorentzian line shape with a linewidth (full width at half maximum) equal to $2\gamma_{na}$.

3.5.1 Linear Response Theory

Linear response theory plays a key role in the understanding of many optical phenomena, and for this reason we devote the remainder of this section to the interpretation of the results just derived. Let us first specialize our results to the case of an isotropic material. As a consequence of symmetry considerations, \mathbf{P} must be parallel to \mathbf{E} in such a medium, and we

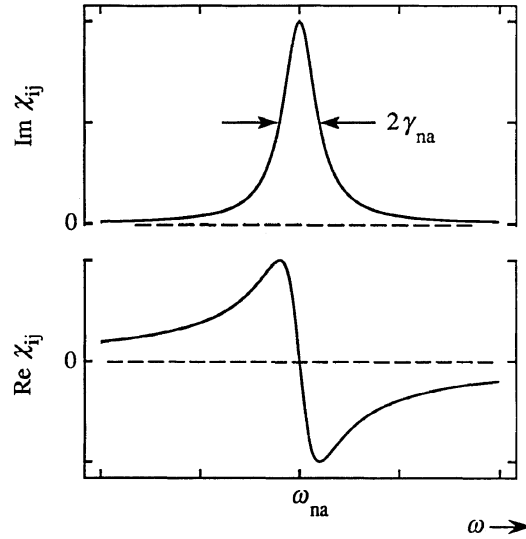


FIGURE 3.5.1: Resonance nature of the linear susceptibility.

can therefore express the linear susceptibility as the scalar quantity $\chi^{(1)}(\omega)$ defined through $\mathbf{P}(\omega) = \epsilon_0 \chi^{(1)}(\omega) \mathbf{E}(\omega)$ and given by

$$\chi^{(1)}(\omega) = \frac{N}{\epsilon_0 \hbar} \sum_n \frac{1}{3} |\boldsymbol{\mu}_{na}|^2 \left[\frac{1}{(\omega_{na} - \omega) - i\gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i\gamma_{na}} \right]. \quad (3.5.22)$$

For simplicity we are assuming the case of a $J = 0$ (nondegenerate) ground state and $J = 1$ excited states. We have included the factor of $\frac{1}{3}$ for the following reason: The summation over n includes all of the magnetic sublevels of the atomic excited states. However, on average only one-third of the $a \rightarrow n$ transitions will have their dipole transition moments parallel to the polarization vector of the incident field, and hence only one-third of these transitions contribute effectively to the susceptibility.

It is useful to introduce the *oscillator strength* of the $a \rightarrow n$ transition. This quantity is defined by

$$f_{na} = \frac{2m\omega_{na} |\boldsymbol{\mu}_{na}|^2}{3\hbar e^2}. \quad (3.5.23)$$

Standard books on quantum mechanics (see, for example, Bethe and Salpeter, 1977) show that this quantity obeys the *oscillator strength sum rule*—that is,

$$\sum_n f_{na} = 1. \quad (3.5.24)$$

If a is the atomic ground state, the frequency ω_{na} is necessarily positive, and the sum rule hence shows that the oscillator strength is a positive quantity bounded by unity—that is, $0 \leq f_{na} \leq 1$. The expression (3.5.22) for the linear susceptibility can be written in terms of the oscillator strength as

$$\begin{aligned}\chi^{(1)}(\omega) &= \sum_n \frac{N f_{na} e^2}{2\epsilon_0 m \omega_{na}} \left[\frac{1}{(\omega_{na} - \omega) - i\gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i\gamma_{na}} \right] \\ &\simeq \sum_n f_{na} \left[\frac{N e^2 / \epsilon_0 m}{\omega_{na}^2 - \omega^2 - 2i\omega\gamma_{na}} \right].\end{aligned}\quad (3.5.25)$$

In the latter form, the expression in square brackets is formally identical to the expression for the linear susceptibility predicted by the classical Lorentz model of the atom (see also Eq. (1.4.17)). We see that the quantum-mechanical prediction differs from that of the Lorentz model only in that in the quantum-mechanical theory there can be more than one resonance frequency ω_{na} . The strength of each such transition is given by the value of the oscillator strength.

Let us next see how to calculate the refractive index and absorption coefficient. The refractive index $n(\omega)$ is related to the linear dielectric constant $\epsilon^{(1)}(\omega)$ and linear susceptibility $\chi^{(1)}(\omega)$ through

$$n(\omega) = \sqrt{\epsilon^{(1)}(\omega)} = \sqrt{1 + \chi^{(1)}(\omega)} \simeq 1 + \frac{1}{2}\chi^{(1)}(\omega). \quad (3.5.26)$$

In obtaining the last expression, we have assumed that the medium is sufficiently dilute (i.e., N sufficiently small) that $\chi^{(1)} \ll 1$. For the remainder of the present section, we shall assume that this assumption is valid, both so that we can use Eq. (3.5.26) as written and also so that we can ignore local-field corrections (cf. Section 3.9). The significance of the refractive index $n(\omega)$ is that the propagation of a plane wave through the material system is described by

$$\tilde{E}(z, t) = E_0 e^{i(kz - \omega t)} + \text{c.c.}, \quad (3.5.27)$$

where the propagation constant k is given by

$$k = n(\omega)\omega/c. \quad (3.5.28)$$

Hence, the intensity $I = nc\epsilon_0 \langle \tilde{E}(z, t)^2 \rangle$ of this wave varies with position in the medium according to

$$I(z) = I_0 e^{-\alpha z}, \quad (3.5.29)$$

where the *absorption coefficient* α is given by

$$\alpha = 2n''\omega/c, \quad (3.5.30)$$

and where we have defined the real and imaginary parts of the refractive index as $n(\omega) = n' + in''$. Alternatively, through use of Eq. (3.5.26), we can represent the absorption coefficient in terms of the susceptibility as

$$\alpha = \chi^{(1)''} \omega / c, \quad (3.5.31a)$$

where $\chi^{(1)}(\omega) = \chi^{(1)'} + i\chi^{(1)''}$. Through use of Eq. (3.5.25), we find that the absorption coefficient of the material system is given by

$$\alpha \approx \sum_n \frac{f_{na} N e^2}{2m\epsilon_0 c \gamma_{na}} \left[\frac{\gamma_{na}^2}{(\omega_{na} - \omega)^2 + \gamma_{na}^2} \right]. \quad (3.5.31b)$$

In obtaining this result, we have replaced ω in Eq. (3.5.31a) by ω_{na} , which is valid for a narrow resonance.

It is often useful to describe the response of a material system to an applied field in terms of microscopic rather than macroscopic quantities. We define the atomic polarizability $\gamma^{(1)}(\omega)$ as the coefficient relating the induced dipole moment $\langle \mu(\omega) \rangle$ and the applied field $\mathbf{E}(\omega)^*$:

$$\langle \mu(\omega) \rangle = \gamma^{(1)}(\omega) \mathbf{E}(\omega). \quad (3.5.32)$$

The susceptibility and polarizability are related (when local-field corrections can be ignored) through

$$\chi^{(1)}(\omega) = N \gamma^{(1)}(\omega), \quad (3.5.33)$$

and we thus find from Eq. (3.5.22) that the polarizability is given by

$$\gamma^{(1)}(\omega) = \frac{1}{\epsilon_0 \hbar} \sum_n \frac{1}{3} |\mu_{na}|^2 \left[\frac{1}{(\omega_{na} - \omega) - i\gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i\gamma_{na}} \right]. \quad (3.5.34)$$

Another microscopic quantity that is often encountered is the absorption cross section σ , which is defined through the relation

$$\alpha = N \sigma. \quad (3.5.35)$$

The cross section can hence be interpreted as the effective area of an atom for removing radiation from an incident beam of light. By comparison with Eqs. (3.5.31a) and (3.5.33), we see that the absorption cross section is related to the atomic polarizability $\gamma^{(1)} = \gamma^{(1)'} + i\gamma^{(1)''}$ through

$$\sigma = \gamma^{(1)''} \omega / c. \quad (3.5.36)$$

* Note that many authors use the symbol α to denote the polarizability. We use the present notation to avoid confusion with the absorption coefficient.

Eq. (3.5.34) shows how the polarizability can be calculated in terms of the transition frequencies ω_{na} , the dipole transition moments μ_{na} , and the dipole dephasing rates γ_{na} . The transition frequencies and dipole moments are inherent properties of any atomic system and can be obtained either by solving Schrödinger's equation for the atom or through laboratory measurement. The dipole dephasing rate, however, depends not only on the inherent atomic properties but also on the local environment. We saw in Eq. (3.3.25) that the dipole dephasing rate γ_{mn} can be represented as

$$\gamma_{nm} = \frac{1}{2}(\Gamma_n + \Gamma_m) + \gamma_{nm}^{(\text{col})}. \quad (3.5.37)$$

Next we calculate the maximum values that the polarizability and absorption cross section can attain. We consider the case of resonant excitation ($\omega = \omega_{na}$) of some excited level n . We find, through use of Eq. (3.5.34) and dropping the nonresonant contribution, that the polarizability is purely imaginary and is given by

$$\gamma_{\text{res}}^{(1)} = \frac{i|\mu_{n'a}|^2}{\epsilon_0 \hbar \gamma_{n'a}}. \quad (3.5.38)$$

We have let n' designate the state associated with level n that is excited by the incident light. Note that the factor of $\frac{1}{3}$ no longer appears in Eq. (3.5.38), because we are now considering a particular state of the upper level and are no longer summing over n . The polarizability will take on its maximum possible value if $\gamma_{n'a}$ is as small as possible, which according to Eq. (3.5.37) occurs when $\gamma_{n'a}^{(\text{col})} = 0$. If a is the atomic ground state, as we have been assuming, its decay rate Γ_a must vanish, and thus the minimum possible value of $\gamma_{n'a}$ is $\frac{1}{2}\Gamma_{n'}$.

The population decay rate out of state n' is usually dominated by spontaneous emission. If state n' can decay only to the ground state, this decay rate is equal to the Einstein A coefficient and is given by

$$\Gamma_{n'} = \frac{\omega_{na}^3 |\mu_{n'a}|^2}{3\pi \epsilon_0 \hbar c^3}. \quad (3.5.39)$$

If $\gamma_{n'a} = \frac{1}{2}\Gamma_{n'}$ is inserted into Eq. (3.5.38), we find that the maximum possible value that the polarizability can possess is

$$\gamma_{\text{max}}^{(1)} = i6\pi \left(\frac{\lambda}{2\pi} \right)^3. \quad (3.5.40)$$

We find the value of the absorption cross section associated with this value of the polarizability through use of Eq. (3.5.36):

$$\sigma_{\text{max}} = \frac{3\lambda^2}{2\pi}. \quad (3.5.41)$$

These results show that under resonant excitation an atomic system possesses an effective linear dimension approximately equal to an optical wavelength.

Recall that the treatment given in this subsection assumes the case of a $J = 0$ lower level and a $J = 1$ upper level. More generally, when J_a is the total angular momentum quantum number of the lower level and J_b is that of the upper level, the maximum on-resonance cross section can be shown to have the form

$$\sigma_{\max} = \frac{g_b}{g_a} \frac{\lambda^2}{2\pi}, \quad (3.5.42)$$

where $g_b = 2J_b + 1$ is the degeneracy of the upper level and $g_a = 2J_a + 1$ is that of the lower level. Furthermore, we have implicitly assumed in the treatment given above that the lower-level sublevels are equally populated, as they would be in thermal equilibrium. If the ground level sublevels are not equally populated, due for instance to optical pumping effects, the result of Eq. (3.5.42) needs to be modified further. To account for these effects, this equation is to be multiplied by a numerical factor that lies between 0 and 3. The cross section vanishes, for example, for an atom that is optically pumped so that the direction of the dipole transition moment is perpendicular to that of the electric field vector of the incident radiation, and it attains its maximum value when these directions are parallel. These considerations are described in greater detail by Siegman (1986).

3.6 Density Matrix Calculation of the Second-Order Susceptibility

In this section we calculate the second-order (i.e., $\chi^{(2)}$) susceptibility of an atomic system. We present the calculation in considerable detail, for the following two reasons: (1) the second-order susceptibility is intrinsically important for many applications; and (2) the calculation of the third-order susceptibility proceeds along lines that are analogous to those followed in the present derivation. However, the expression for the third-order susceptibility $\chi^{(3)}$ is so complicated (it contains 48 terms) that it is not feasible to show all of the steps in the calculation of $\chi^{(3)}$. Thus the present development serves as a template for the calculation of higher-order susceptibilities.

From the perturbation expansion (3.4.16), the general result for the second-order correction to $\hat{\rho}$ is given by

$$\rho_{nm}^{(2)} = e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^t \frac{-i}{\hbar} [\hat{V}, \hat{\rho}^{(1)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} dt', \quad (3.6.1)$$

where the commutator can be expressed (by analogy with Eq. (3.5.5)) as

$$[\hat{V}, \hat{\rho}^{(1)}]_{nm} = - \sum_v (\mu_{nv} \rho_{vm}^{(1)} - \rho_{nv}^{(1)} \mu_{vm}) \cdot \tilde{\mathbf{E}}(t). \quad (3.6.2)$$

In order to evaluate this commutator, the first-order solution given by Eq. (3.5.9) is written with changes in the dummy indices as

$$\rho_{vm}^{(1)} = \hbar^{-1} (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \sum_p \frac{\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_p)}{(\omega_{vm} - \omega_p) - i\gamma_{vm}} e^{-i\omega_p t} \quad (3.6.3)$$

and as

$$\rho_{nv}^{(1)} = \hbar^{-1} (\rho_{vv}^{(0)} - \rho_{nn}^{(0)}) \sum_p \frac{\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_p)(\omega_p)}{(\omega_{nv} - \omega_p) - i\gamma_{nv}} e^{-i\omega_p t}. \quad (3.6.4)$$

The applied optical field $\tilde{\mathbf{E}}(t)$ is expressed as

$$\tilde{\mathbf{E}}(t) = \sum_q \mathbf{E}(\omega_q) e^{-i\omega_q t}. \quad (3.6.5)$$

The commutator of Eq. (3.6.2) thus becomes

$$\begin{aligned} [\hat{V}, \hat{\rho}^{(1)}]_{nm} &= -\hbar^{-1} \sum_v (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \\ &\quad \times \sum_{pq} \frac{[\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_q)][\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_p)]}{(\omega_{vm} - \omega_q) - i\gamma_{vm}} e^{-i(\omega_p + \omega_q)t} \\ &\quad + \hbar^{-1} \sum_v (\rho_{vv}^{(0)} - \rho_{nn}^{(0)}) \\ &\quad \times \sum_{pq} \frac{[\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_p)][\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_q)]}{(\omega_{nv} - \omega_p) - i\gamma_{nv}} e^{-i(\omega_p + \omega_q)t}. \end{aligned} \quad (3.6.6)$$

This expression is now inserted into Eq. (3.6.1), and the integration is performed to obtain

$$\begin{aligned} \rho_{nm}^{(2)} &= \sum_v \sum_{pq} e^{-i(\omega_p + \omega_q)t} \\ &\quad \times \left\{ \frac{\rho_{mm}^{(0)} - \rho_{vv}^{(0)}}{\hbar^2} \frac{[\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_q)][\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_p)]}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right. \\ &\quad \left. - \frac{\rho_{vv}^{(0)} - \rho_{nn}^{(0)}}{\hbar^2} \frac{[\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_q)][\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_q)]}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{nv} - \omega_p) - i\gamma_{nv}]} \right\} \\ &\equiv \sum_v \sum_{pq} K_{nmv} e^{-i(\omega_p + \omega_q)t}. \end{aligned} \quad (3.6.7)$$

We have given the complicated expression in curly braces the label K_{nmv} because it appears in many subsequent equations.

We next calculate the expectation value of the atomic dipole moment, which (according to Eq. (3.3.16)) is given by

$$\langle \tilde{\mu} \rangle = \sum_{nm} \rho_{nm} \mu_{mn}. \quad (3.6.8)$$

We are interested in the various frequency components of $\langle \tilde{\mu} \rangle$, whose complex amplitudes $\langle \mu(\omega_r) \rangle$ are defined through

$$\langle \tilde{\mu} \rangle = \sum_r \langle \mu(\omega_r) \rangle e^{-i\omega_r t}. \quad (3.6.9)$$

Then, in particular, the complex amplitude of the component of the atomic dipole moment oscillating at frequency $\omega_p + \omega_q$ is given by

$$\langle \mu(\omega_p + \omega_q) \rangle = \sum_{nm} \sum_{(pq)} K_{nmv} \mu_{mn}, \quad (3.6.10)$$

and consequently the complex amplitude of the component of the nonlinear polarization oscillating at frequency $\omega_p + \omega_q$ is given by

$$\mathbf{P}^{(2)}(\omega_p + \omega_q) = N \langle \mu(\omega_p + \omega_q) \rangle = N \sum_{nm} \sum_{(pq)} K_{nmv} \mu_{mn}. \quad (3.6.11)$$

We define the nonlinear susceptibility through the equation

$$P_i^{(2)}(\omega_p + \omega_q) = \epsilon_0 \sum_{jk} \sum_{(pq)} \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) E_j(\omega_q) E_k(\omega_p), \quad (3.6.12)$$

using the same notation as that used earlier (see also Eq. (1.3.13)). By comparison of Eqs. (3.6.7), (3.6.11), and (3.6.12), we obtain a tentative expression for the susceptibility tensor given by

$$\begin{aligned} \chi_{ijk}^{(2)[\text{tent}]}(\omega_p + \omega_q, \omega_q, \omega_p) &= \frac{N}{\epsilon_0 \hbar^2} \\ &\times \sum_{mnv} \left\{ (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \frac{\mu_{mn}^i \mu_{nv}^j \mu_{vm}^k}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right. \\ &\quad \left. - (\rho_{vv}^{(0)} - \rho_{nn}^{(0)}) \frac{\mu_{mn}^i \mu_{vm}^j \mu_{nv}^k}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{nv} - \omega_p) - i\gamma_{nv}]} \right\}. \end{aligned} \quad (3.6.13)$$

We have labeled the two terms that appear in this expression (a) and (b) so that we can keep track of how these terms contribute to our final expression for the second-order susceptibility.

Eq. (3.6.13) can be used in conjunction with Eq. (3.6.12) to make proper predictions of the nonlinear polarization, which is a physically meaningful quantity. However, Eq. (3.6.13) does not possess intrinsic permutation symmetry (cf. Section 1.5), which we require the susceptibility to possess. We therefore define the nonlinear susceptibility to be one-half the sum of the right-hand side of Eq. (3.6.13) with an analogous expression obtained by simultaneously interchanging ω_p with ω_q and j with k . We thereby obtain the result

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) &= \frac{N}{2\epsilon_0\hbar^2} \\
 &\times \sum_{mnv} \left\{ (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \left[\frac{\mu_{mn}^i \mu_{nv}^j \mu_{vm}^k}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right] \right. \\
 &+ \frac{\mu_{mn}^i \mu_{nv}^k \mu_{vm}^j}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_q) - i\gamma_{vm}]} \Big] \\
 &- (\rho_{vv}^{(0)} - \rho_{nn}^{(0)}) \left[\frac{\mu_{mn}^i \mu_{vm}^j \mu_{nv}^k}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{nv} - \omega_p) - i\gamma_{nv}]} \right. \\
 &+ \frac{\mu_{mn}^i \mu_{vm}^k \mu_{nv}^j}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{nv} - \omega_q) - i\gamma_{nv}]} \Big] \Big\}. \tag{3.6.14}
 \end{aligned}$$

(a_1)
 (a_2)
 (b_1)
 (b_2)

This expression displays intrinsic permutation symmetry and gives the nonlinear susceptibility in a reasonably compact fashion. It is clear from its form that certain contributions to the susceptibility vanish when two of the levels associated with the contribution contain equal populations. We shall examine the nature of this cancellation in greater detail below (see Eq. (3.6.17)). Note that the population differences that appear in this expression are always associated with the two levels separated by a one-photon resonance, as we can see by inspection of the detuning factors that appear in the denominator.

The expression for the second-order nonlinear susceptibility can be rewritten in several different forms, all of which are equivalent but provide different insights in to the resonant nature of the nonlinear coupling. Since the indices m , n , and v are summed over, they constitute dummy indices. We can therefore replace the indices v , n , and m in the last two terms of Eq. (3.6.14) by m , v , and n , respectively, so that the population difference term is the same as that of the first two terms. We thereby recast the second-order susceptibility into

the form

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) &= \frac{N}{2\epsilon_0\hbar^2} \sum_{mnv} (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \\
 &\times \left\{ \frac{\mu_{mn}^i \mu_{nv}^j \mu_{vm}^k}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right. \quad (a_1) \\
 &+ \frac{\mu_{mn}^i \mu_{nv}^k \mu_{vm}^j}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_q) - i\gamma_{vm}]} \quad (a_2) \\
 &- \frac{\mu_{nv}^i \mu_{mn}^j \mu_{vm}^k}{[(\omega_{vn} - \omega_p - \omega_q) - i\gamma_{vn}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \quad (b_1) \\
 &\left. - \frac{\mu_{nv}^i \mu_{mn}^k \mu_{vm}^j}{[(\omega_{vn} - \omega_p - \omega_q) - i\gamma_{vn}][(\omega_{vm} - \omega_q) - i\gamma_{vm}]} \right\}. \quad (b_2) \quad (3.6.15)
 \end{aligned}$$

We can make this result more transparent by making another change in dummy indices: we replace indices m , v , and n by l , m , and n , respectively. In addition, we replace ω_{lm} , ω_{ln} , and ω_{mn} by $-\omega_{ml}$, $-\omega_{nl}$, and $-\omega_{nm}$, respectively, whenever one of them appears. Also, we reorder the product of matrix elements in the numerator so that the subscripts n , m , and l are “chained” in the sense shown and thereby obtain the result

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) &= \frac{N}{2\epsilon_0\hbar^2} \sum_{lmn} (\rho_{ll}^{(0)} - \rho_{mm}^{(0)}) \\
 &\times \left\{ \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right. \quad (a_1) \\
 &+ \frac{\mu_{ln}^i \mu_{nm}^k \mu_{ml}^j}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \quad (a_2) \\
 &+ \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \quad (b_1) \\
 &\left. + \frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \right\}. \quad (b_2) \quad (3.6.16)
 \end{aligned}$$

One way of interpreting this result is to consider where levels l , m , and n would have to be located in order for each of the terms to become resonant. The positions of these energies are illustrated in Fig. 3.6.1. For definiteness, we have drawn the figure with ω_p and ω_q positive. In each case the magnitude of the contribution to the nonlinear susceptibility is proportional to the population difference between levels l and m .

In order to illustrate how to make use of Eq. (3.6.16) and to examine the nature of the cancellation that can occur when more than one of the atomic levels contains population, we consider

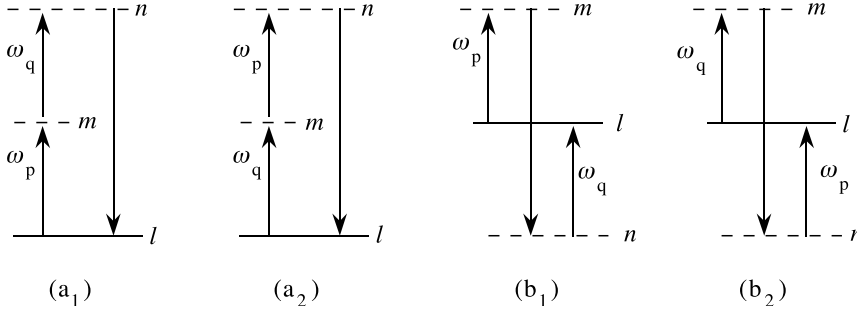


FIGURE 3.6.1: The resonance structure of Eq. (3.6.16).

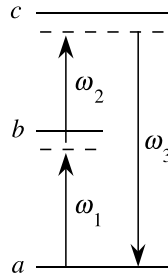


FIGURE 3.6.2: Three-level atomic system.

the simple three-level atomic system illustrated in Fig. 3.6.2. We assume that only levels a , b , and c interact appreciably with the optical fields and that the applied field at frequency ω_1 is nearly resonant with the $a \rightarrow b$ transition, the applied field at frequency ω_2 is nearly resonant with the $b \rightarrow c$ transition, and the generated field frequency $\omega_3 = \omega_1 + \omega_2$ is nearly resonant with the $c \rightarrow a$ transition. If we now perform the summation over the dummy indices l , m , and n in Eq. (3.6.16) and retain only those terms in which both factors in the denominator are resonant, we find that the nonlinear susceptibility is given by

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_3, \omega_2, \omega_1) &= \frac{N}{2\epsilon_0 \hbar^2} \left\{ (\rho_{aa}^{(0)} - \rho_{bb}^{(0)}) \left[\frac{\mu_{ac}^i \mu_{cb}^j \mu_{ba}^k}{[(\omega_{ca} - \omega_3) - i\gamma_{ca}][(\omega_{ba} - \omega_1) - i\gamma_{ba}]} \right] \right. \\
 &\quad \left. + (\rho_{cc}^{(0)} - \rho_{bb}^{(0)}) \left[\frac{\mu_{ac}^i \mu_{cb}^j \mu_{ba}^k}{[(\omega_{ca} - \omega_3) - i\gamma_{ca}][(\omega_{cb} - \omega_2) - i\gamma_{cb}]} \right] \right\}. \quad (3.6.17)
 \end{aligned}$$

Here the first term comes from the first term in Eq. (3.6.16), and the second term comes from the last (fourth) term in Eq. (3.6.16). Note that the first term vanishes if $\rho_{aa}^{(0)} = \rho_{bb}^{(0)}$ and that the

second term vanishes if $\rho_{bb}^{(0)} = \rho_{cc}^{(0)}$. If all three populations are equal, the resonant contribution vanishes identically.

For some purposes it is useful to express the general result (3.6.16) for the second-order susceptibility in terms of a summation over populations rather than a summation over population differences. In order to cast the susceptibility in such a form, we change the dummy indices l, m , and n to n, l , and m in the summation containing $\rho_{mm}^{(0)}$ but leave them unchanged in the summation containing $\rho_{ll}^{(0)}$. We thereby obtain the result

$$\begin{aligned}
 \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) &= \frac{N}{2\epsilon_0\hbar^2} \sum_{lmn} \rho_{ll}^{(0)} \left\{ \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right. & (a_1) \\
 &+ \frac{\mu_{ln}^i \mu_{nm}^k \mu_{ml}^j}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} & (a_2) \\
 &+ \frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][(\omega_{nl} + \omega_p) + i\gamma_{nl}]} & (a'_1) \\
 &+ \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][(\omega_{nl} + \omega_q) + i\gamma_{nl}]} & (a'_2) \\
 &+ \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} & (b_1) \\
 &+ \frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} & (b_2) \\
 &+ \frac{\mu_{ln}^k \mu_{nm}^j \mu_{ml}^i}{[(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][(\omega_{nl} + \omega_p) + i\gamma_{nl}]} & (b'_1) \\
 &+ \frac{\mu_{ln}^j \mu_{nm}^k \mu_{ml}^i}{[(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][(\omega_{nl} + \omega_q) + i\gamma_{nl}]} \left. \right\}. & (b'_2)
 \end{aligned}
 \tag{3.6.18}$$

As before, we can interpret this result by considering the conditions under which each term of the equation can become resonant. Fig. 3.6.3 shows where the energy levels l, m , and n would have to be located in order for each term to become resonant, under the assumption the ω_p and ω_q are both positive. Note that the unprimed diagrams are the same as those of Fig. 3.6.1 (which represents Eq. (3.6.16)), but that diagrams b'_1 and b'_2 represent new resonances not present in Fig. 3.6.1.

Another way of making sense of the general eight-term expression for $\chi^{(2)}$ Eq. (3.6.18) is to keep track of how the density matrix is modified in each order of perturbation theory. Through

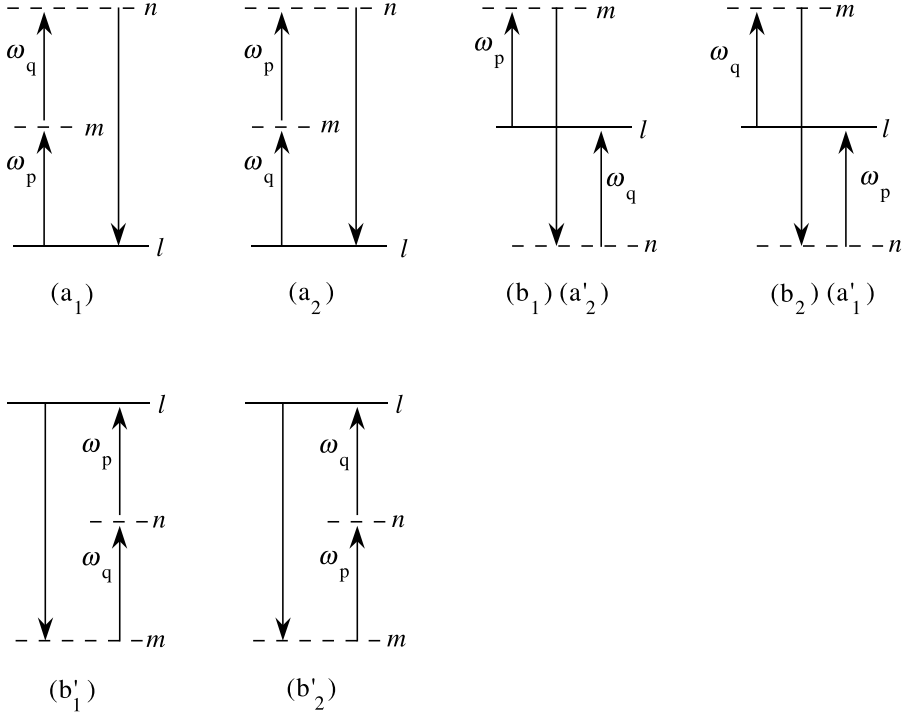


FIGURE 3.6.3: The resonances of Eq. (3.6.18).

examination of Eqs. (3.6.1) through (3.6.7), we find that the terms of type a , a' , b , b' occur as the result of the following perturbation expansion:

$$\begin{aligned}
 \text{(a): } \rho_{mm}^{(0)} &\rightarrow \rho_{vm}^{(1)} \rightarrow \rho_{nm}^{(2)}, & \text{(a'): } \rho_{vv}^{(0)} &\rightarrow \rho_{vm}^{(1)} \rightarrow \rho_{nm}^{(2)}, \\
 \text{(b): } \rho_{vv}^{(0)} &\rightarrow \rho_{nv}^{(1)} \rightarrow \rho_{nm}^{(2)}, & \text{(b'): } \rho_{nn}^{(0)} &\rightarrow \rho_{nv}^{(1)} \rightarrow \rho_{nm}^{(2)}.
 \end{aligned}$$

However, in writing Eq. (3.6.18) in the displayed form, we have changed the dummy indices appearing in it. In terms of these new indices, the perturbation expansion is

$$\begin{aligned}
 \text{(a): } \rho_{ll}^{(0)} &\rightarrow \rho_{ml}^{(1)} \rightarrow \rho_{nl}^{(2)}, & \text{(a'): } \rho_{ll}^{(0)} &\rightarrow \rho_{ln}^{(1)} \rightarrow \rho_{mn}^{(2)}, \\
 \text{(b): } \rho_{ll}^{(0)} &\rightarrow \rho_{ml}^{(1)} \rightarrow \rho_{mn}^{(2)}, & \text{(b'): } \rho_{ll}^{(0)} &\rightarrow \rho_{ln}^{(1)} \rightarrow \rho_{lm}^{(2)}.
 \end{aligned} \tag{3.6.19}$$

Note that the various terms differ in whether it is the left or right index that is changed by each elementary interaction and by the order in which such a modification occurs.

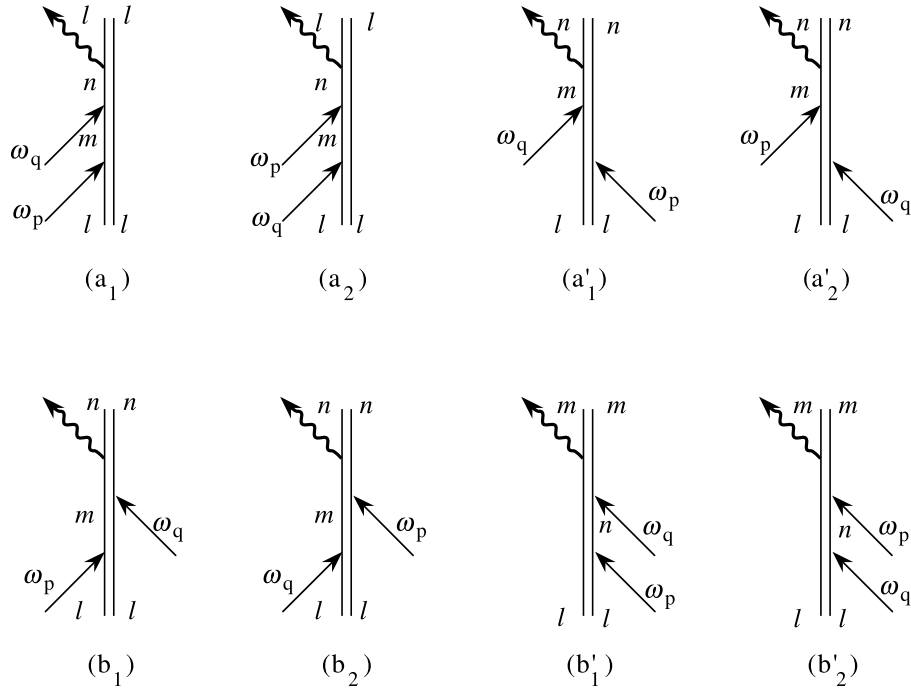


FIGURE 3.6.4: Double-sided Feynman diagrams.

A convenient way of keeping track of the order in which the elementary interactions occur is by means of double-sided Feynman diagrams. These diagrams represent the way in which the density operator is modified by the interaction of the atom with the laser field. We represent the density operator as

$$\hat{\rho} = \overline{|\psi\rangle\langle\psi|}, \quad (3.6.20)$$

where $|\psi\rangle$ represents the key vector for some state of the system, $\langle\psi|$ (the bar vector) represents the Hermitian adjoint of $|\psi\rangle$, and the overbar represents an ensemble average. The elements of the density matrix are related to the density operator $\hat{\rho}$ through the equation

$$\rho_{nm} = \langle n|\hat{\rho}|m\rangle. \quad (3.6.21)$$

Fig. 3.6.4 gives a pictorial description of the modification of the density matrix as indicated by the expressions (3.6.19). The left-hand side of each diagram indicates the time evolution of $|\psi\rangle$, and the right-hand side indicates the time evolution of $\langle\psi|$, with time increasing verti-

cally upward. Each interaction with the applied field is indicated by a solid arrow labeled by the field frequency. The trace operation, which corresponds to calculating the output field, is indicated by the wavy arrow.* It should be noted that there are several different conventions concerning the rules for drawing double-sided Feynman diagrams (Boyd and Mukamel, 1984; Prior, 1984; Yee and Gustafson, 1978).

3.6.1 $\chi^{(2)}$ in the Limit of Nonresonant Excitation

When all of the frequencies ω_p , ω_q , and $\omega_p + \omega_q$ differ significantly from any resonance frequency of the atomic system, the imaginary contributions to the denominators in Eq. (3.6.18) can be ignored. In this case, the expression for $\chi^{(2)}$ can be simplified. In particular, terms (a'_2) and (b_1) can be combined into a single term, and similarly for terms (a'_1) and (b_2) . We note that the numerators of terms (a'_2) and (b_1) are identical and that their denominators can be combined as follows:

$$\begin{aligned}
 & \frac{1}{(\omega_{mn} - \omega_p - \omega_q)(\omega_{nl} + \omega_q)} + \frac{1}{(-\omega_{mn} + \omega_p + \omega_q)(\omega_{ml} - \omega_p)} \\
 &= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[\frac{1}{\omega_{nl} + \omega_q} - \frac{1}{\omega_{ml} - \omega_p} \right] \\
 &= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[\frac{\omega_{ml} - \omega_p - \omega_{nl} - \omega_q}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \right] \\
 &= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[\frac{\omega_{mn} - \omega_p - \omega_q}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \right] \\
 &= \frac{1}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)}. \tag{3.6.22}
 \end{aligned}$$

The same procedure can be performed on terms (a'_1) and (b_2) ; the only difference between this case and the one treated in Eq. (3.6.22) is that ω_p and ω_q have switched roles. The frequency dependence is thus

$$\frac{1}{(\omega_{nl} + \omega_p)(\omega_{ml} - \omega_q)}. \tag{3.6.23}$$

* In drawing Fig. 3.6.4, we have implicitly assumed that all of the applied field frequencies are positive, which corresponds to the absorption of an incident photon. The interaction with a negative field frequency which corresponds to the emission of a photon, is sometimes indicated by a solid arrow pointing diagonally upward and away from (rather than toward) the central double line.

The expression for $\chi^{(2)}$ in the off-resonance case thus becomes

$$\begin{aligned}
 & \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) \\
 &= \frac{N}{2\epsilon_0 \hbar^2} \sum_{lmn} \rho_{ll}^{(0)} \left\{ \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{(\omega_{nl} - \omega_p - \omega_q)(\omega_{ml} - \omega_p)} \right. \quad (a_1) \\
 & \quad + \frac{\mu_{ln}^i \mu_{nm}^k \mu_{ml}^j}{(\omega_{nl} - \omega_p - \omega_q)(\omega_{ml} - \omega_q)} \quad (a_2) \\
 & \quad + \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \quad (b_1), (a'_2) \\
 & \quad + \frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{(\omega_{nl} + \omega_p)(\omega_{ml} - \omega_q)} \quad (b_2), (a'_1) \\
 & \quad + \frac{\mu_{ln}^k \mu_{nm}^j \mu_{ml}^i}{(\omega_{ml} + \omega_p + \omega_q)(\omega_{nl} + \omega_p)} \quad (b'_1) \\
 & \quad \left. + \frac{\mu_{ln}^j \mu_{nm}^k \mu_{ml}^i}{(\omega_{ml} + \omega_p + \omega_q)(\omega_{nl} + \omega_q)} \right\}. \quad (b'_2) \quad (3.6.24)
 \end{aligned}$$

Note that only six terms appear in this expression for the off-resonance susceptibility, whereas eight terms appear in the general expression of Eq. (3.6.18). One can verify by explicit calculation that Eq. (3.6.24) satisfies the condition of full permutation symmetry (see also Eq. (1.5.7)). In addition, one can see by inspection that Eq. (3.6.24) is identical to the result obtained above (Eq. (3.2.27)) based on perturbation theory of the atomic wavefunction.

There are several diagrammatic methods that can be used to interpret this expression. One of the simplest is to plot the photon energies on an atomic energy-level diagram. This method displays the conditions under which each contribution can become resonant. The results of such an analysis gives exactly the same diagrams displayed in Fig. 3.6.3. Eq. (3.6.24) can also be understood in terms of a diagrammatic approach introduced by Ward (1965).

3.7 Density Matrix Calculation of the Third-Order Susceptibility

We now turn to the calculation of the third-order susceptibility. The third-order correction to the density matrix is given by the perturbation expansion of Eq. (3.4.16) as

$$\rho_{nm}^{(3)} = e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^t \frac{-i}{\hbar} [\hat{V}, \hat{\rho}^{(2)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} dt', \quad (3.7.1)$$

where the commutator can be represented explicitly as

$$[\hat{V}, \hat{\rho}^{(2)}]_{nm} = - \sum_v (\boldsymbol{\mu}_{nv} \rho_{vm}^{(2)} - \rho_{nv}^{(2)} \boldsymbol{\mu}_{vm}) \cdot \tilde{\mathbf{E}}(t). \quad (3.7.2)$$

Expressions for $\rho_{vm}^{(2)}$ and $\rho_{nv}^{(2)}$ are available from Eq. (3.6.7). Since these expressions are very complicated, we use the abbreviated notation introduced there:

$$\rho_{vm}^{(2)} = \sum_l \sum_{pq} K_{vml} e^{-i(\omega_p + \omega_q)t}, \quad (3.7.3)$$

where K_{vml} has been displayed explicitly. We also represent the electric field as

$$\tilde{\mathbf{E}}(t) = \sum_r \mathbf{E}(\omega_r) e^{-i\omega_r t}. \quad (3.7.4)$$

The commutator thus becomes

$$\begin{aligned} [\hat{V}, \hat{\rho}^{(2)}]_{nm} = & - \sum_{vl} \sum_{pqr} [\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_r)] K_{vml} e^{-i(\omega_p + \omega_q + \omega_r)t} \\ & + \sum_{vl} \sum_{pqr} [\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_r)] K_{nvl} e^{-i(\omega_p + \omega_q + \omega_r)t}. \end{aligned} \quad (3.7.5)$$

The integration of Eq. (3.7.1) with the commutator given by Eq. (3.7.5) can now be performed. We obtain

$$\begin{aligned} \rho_{nm}^{(3)} = & \frac{1}{\hbar} \sum_{vl} \sum_{pqr} \left\{ \frac{[\boldsymbol{\mu}_{nv} \cdot \mathbf{E}(\omega_r)] K_{vml}}{(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}} \right. \\ & \left. - \frac{[\boldsymbol{\mu}_{vm} \cdot \mathbf{E}(\omega_r)] K_{nvl}}{(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}} \right\} e^{-i(\omega_p + \omega_q + \omega_r)t}. \end{aligned} \quad (3.7.6)$$

The nonlinear polarization oscillating at frequency $\omega_p + \omega_q + \omega_r$ is given by

$$\mathbf{P}(\omega_p + \omega_q + \omega_r) = N \langle \boldsymbol{\mu}(\omega_p + \omega_q + \omega_r) \rangle, \quad (3.7.7)$$

where

$$\langle \tilde{\boldsymbol{\mu}} \rangle = \sum_{nm} \rho_{nm} \boldsymbol{\mu}_{mn} \equiv \sum_s \langle \boldsymbol{\mu}(\omega_s) \rangle e^{-i\omega_s t}. \quad (3.7.8)$$

We express the nonlinear polarization in terms of the third-order susceptibility defined by (see also Eq. (1.3.21))

$$\begin{aligned} P_k(\omega_p + \omega_q + \omega_r) = & \epsilon_0 \sum_{hij} \sum_{pqr} \chi_{kjih}^{(3)}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) \\ & \times E_j(\omega_r) E_i(\omega_q) E_h(\omega_p). \end{aligned} \quad (3.7.9)$$

By combining Eqs. (3.7.6) through (3.7.9), we find that the third-order susceptibility is given by

$$\begin{aligned}
 \chi_{kjih}^{(3)}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) &= \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_I \sum_{nmvl} \\
 &\left\{ \frac{(\rho_{mm}^{(0)} - \rho_{ll}^{(0)}) \mu_{mn}^k \mu_{nv}^j \mu_{vl}^i \mu_{lm}^h}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{vm} - \omega_p - \omega_q) - i\gamma_{vm}][(\omega_{lm} - \omega_p) - i\gamma_{lm}]} \right. \\
 &- \frac{(\rho_{ll}^{(0)} - \rho_{vv}^{(0)}) \mu_{mn}^k \mu_{nv}^j \mu_{lm}^i \mu_{vl}^h}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{vm} - \omega_p - \omega_q) - i\gamma_{vm}][(\omega_{vl} - \omega_p) - i\gamma_{vl}]} \\
 &- \frac{(\rho_{vv}^{(0)} - \rho_{ll}^{(0)}) \mu_{mn}^k \mu_{vm}^j \mu_{nl}^i \mu_{lv}^h}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv}][(\omega_{lv} - \omega_p) - i\gamma_{lv}]} \\
 &\left. + \frac{(\rho_{ll}^{(0)} - \rho_{nn}^{(0)}) \mu_{mn}^k \mu_{vm}^j \mu_{lv}^i \mu_{nl}^h}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv}][(\omega_{nl} - \omega_p) - i\gamma_{nl}]} \right\}. \quad (3.7.10)
 \end{aligned}
 \tag{a} \tag{b} \tag{c} \tag{d}$$

Here we have again made use of the intrinsic permutation operator \mathcal{P}_I , whose meaning is that everything to the right of it is to be averaged over all possible permutations of the input frequencies ω_p , ω_q , and ω_r , with the cartesian indices h, i, j permuted simultaneously. Next, we rewrite this equation as eight separate terms by changing the dummy indices so that l is always the index of $\rho_{ii}^{(0)}$. We also require that only positive resonance frequencies appear if the energies are ordered so that $E_v > E_n > E_m > E_l$, and we arrange the matrix elements so that they appear in “natural” order, $l \rightarrow m \rightarrow n \rightarrow v$ (reading right to left). We obtain

$$\begin{aligned}
 \chi_{kjih}^{(3)}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) &= \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_I \sum_{vnml} \rho_{ll}^{(0)} \\
 &\times \left\{ \frac{\mu_{lv}^k \mu_{vn}^j \mu_{nm}^i \mu_{ml}^h}{[(\omega_{vl} - \omega_p - \omega_q - \omega_r) - i\gamma_{vl}][(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right. \\
 &+ \frac{\mu_{lv}^h \mu_{vn}^k \mu_{nm}^j \mu_{ml}^i}{[(\omega_{nv} - \omega_p - \omega_q - \omega_r) - i\gamma_{nv}][(\omega_{mv} - \omega_p - \omega_q) - i\gamma_{mv}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \\
 &+ \frac{\mu_{lv}^i \mu_{vn}^k \mu_{nm}^j \mu_{ml}^h}{[(\omega_{nv} - \omega_p - \omega_q - \omega_r) - i\gamma_{nv}][(\omega_{vm} + \omega_p + \omega_q) + i\gamma_{vm}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \\
 &+ \frac{\mu_{lv}^h \mu_{vn}^i \mu_{nm}^k \mu_{ml}^j}{[(\omega_{mn} - \omega_p - \omega_q - \omega_r) - i\gamma_{mn}][(\omega_{nl} + \omega_p + \omega_q) + i\gamma_{nl}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \\
 &\left. + \frac{\mu_{lv}^j \mu_{vn}^k \mu_{nm}^i \mu_{ml}^h}{[(\omega_{vn} + \omega_p + \omega_q + \omega_r) + i\gamma_{vn}][(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right\}
 \end{aligned}
 \tag{a1} \tag{a2} \tag{b1} \tag{b2} \tag{c1}$$

$$\begin{aligned}
& + \frac{\mu_{lv}^h \mu_{vn}^j \mu_{nm}^k \mu_{ml}^i}{[(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i\gamma_{nm}][(\omega_{mv} - \omega_p - \omega_q) - i\gamma_{mv}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \quad (c_2) \\
& + \frac{\mu_{lv}^i \mu_{vn}^j \mu_{nm}^k \mu_{ml}^h}{[(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i\gamma_{nm}][(\omega_{vm} + \omega_p + \omega_q) + i\gamma_{mv}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \quad (d_1) \\
& + \frac{\mu_{lv}^h \mu_{vn}^i \mu_{nm}^j \mu_{ml}^k}{[(\omega_{ml} + \omega_p + \omega_q + \omega_r) + i\gamma_{ml}][(\omega_{nl} + \omega_p + \omega_q) + i\gamma_{nl}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \quad (d_2)
\end{aligned}
\tag{3.7.11}$$

For the general case in which ω_p , ω_q , and ω_r are distinct, six permutations of the field frequencies occur, and thus the expression for $\chi^{(3)}$ consists of 48 different terms once the permutation operator \mathcal{P}_I is expanded. The resonance structure of this expression can be understood in terms of the energy level diagrams shown in Fig. 3.7.1. Furthermore, the nature of the perturbation

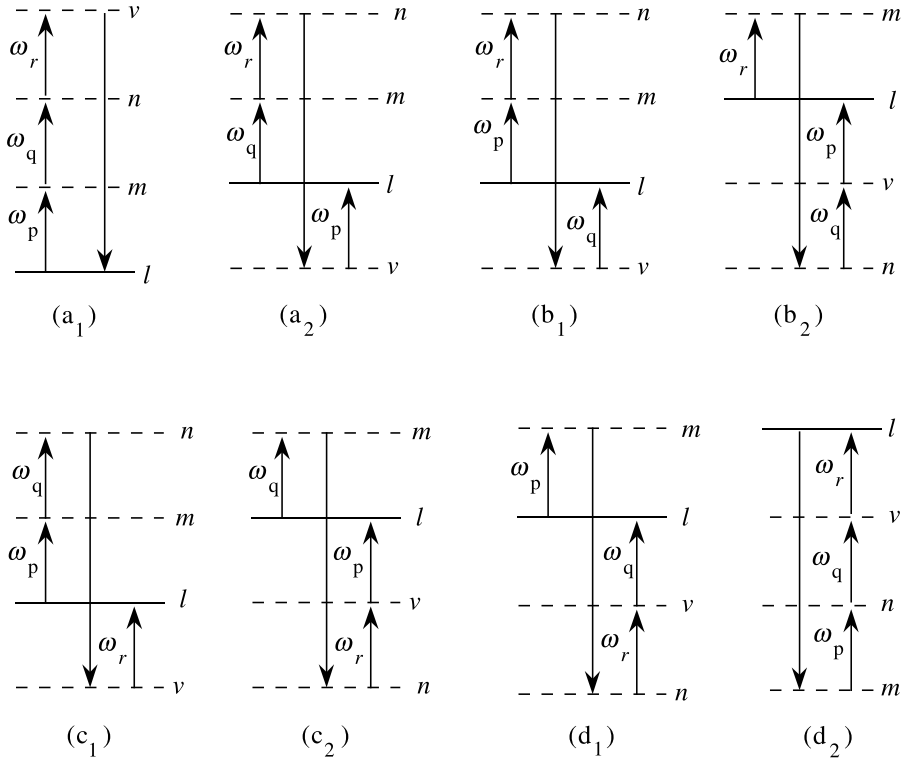


FIGURE 3.7.1: The resonance structure of the expression (3.7.11) for the third-order nonlinear susceptibility.

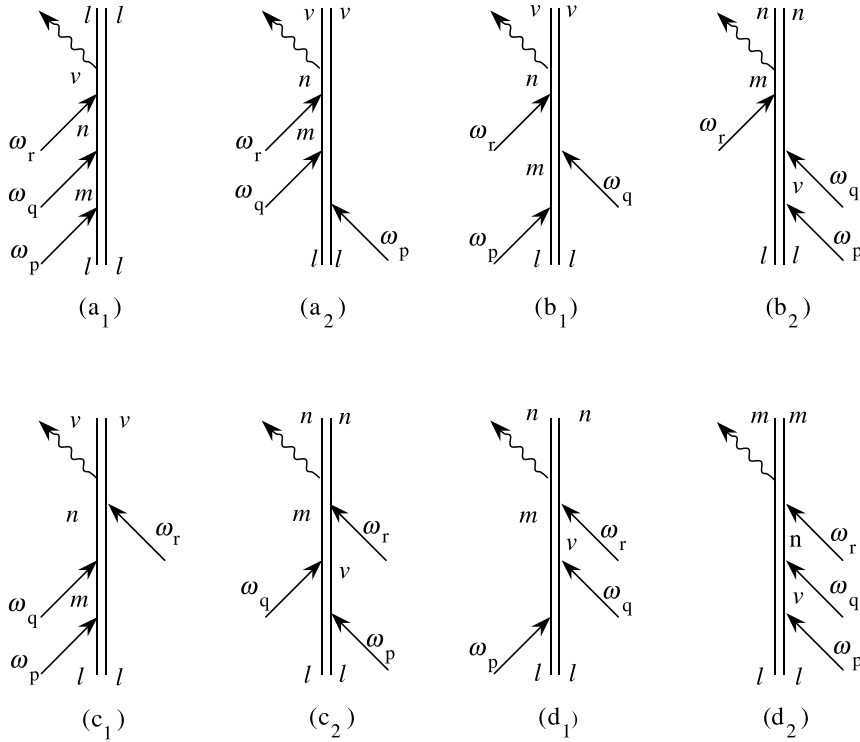


FIGURE 3.7.2: Double-sided Feynman diagrams associated with the various terms in Eq. (3.7.11).

expansion leading to Eq. (3.7.11) can be understood in terms of the double-sided Feynman diagrams shown in Fig. 3.7.2.

We saw in Section 3.2 that the general expression for the third-order susceptibility calculated using perturbation theory applied to the atomic wavefunction contained 24 terms. Eq. (3.2.33) shows four of these terms explicitly; the other terms are obtained from the six permutations of the frequencies of the applied field. It can be shown that Eq. (3.7.11) reduces to Eq. (3.2.33) in the limit of nonresonant excitation, where the imaginary contributions ($i\gamma_{\alpha\beta}$) appearing in Eq. (3.7.11) can be ignored. One can demonstrate this fact by means of a calculation similar to that used to derive Eq. (3.6.23), which applies to the case of the second-order susceptibility (see Problem 5 at the end of this chapter).

In fact, even in the general case in which the imaginary contributions $i\gamma_{\alpha\beta}$ appearing in Eq. (3.7.11) are retained, it is possible to rewrite the 48-term expression (3.7.11) in the form of the 24-term expression (3.2.33) by allowing the coefficient of each of the 24 terms to be weakly frequency-dependent. These frequency-dependent coefficients usually display resonances at frequencies other than those that appear in Fig. 3.7.1, and these new resonances occur only if the line-broadening mechanism is collisional (rather than radiative). The nature

of these *collision-induced resonances* has been discussed by Bloembergen et al. (1978), Prior (1984), and Rothberg (1987).

3.8 Electromagnetically Induced Transparency

Electromagnetically induced transparency (EIT) is a powerful technique that can be used to render a material system transparent to resonant laser radiation while retaining the large and desirable nonlinear optical properties associated with the resonant response of a material system. EIT was first described theoretically by Harris et al. (1990), although EIT shares some features with processes described earlier by Gray et al. (1978) and by Tewari and Agarwal (1986). EIT also shares some similarity with the process known as lasing without inversion (Harris, 1989; Kocharovskaya and Khanis, 1988; Scully et al., 1989). EIT has been observed both in atomic systems (Boller et al., 1991; Field et al., 1991) and in solids (Ham et al., 1997; Zhao et al., 1997). Laboratory studies have confirmed that EIT can be used to enhance the efficiency of nonlinear optical processes including nonlinear frequency conversion (Hakuta et al., 1991; Jain et al., 1996) and optical phase conjugation (Hemmer et al., 1995; Li and Xiao, 1996). Moreover, EIT plays a key role in the generation of “slow light” (Budker et al., 1999; Boyd and Gauthier, 2002; Hau et al., 1999; Inouye et al., 2000; Kash et al., 1999). In addition, it has been predicted that EIT can enhance the properties of a much broader range of processes, including squeezed-light generation (Lukin et al., 1999) and low-light-level photonic switching (Harris and Yamamoto, 1998; Imamoğlu et al., 1997). More information about EIT can be found in the review articles on EIT cited at the end of this chapter.

Let us analyze a prototypical example of EIT. The situation is illustrated in part (a) of Fig. 3.8.1. Laser fields at frequencies ω and ω_s are applied to an atomic system with the intent of generating radiation at the sum frequency $\omega_4 = 2\omega + \omega_s$. One would normally expect that strong absorption of light at frequency ω_4 would severely limit the efficiency of the sum-frequency generation process. However, we shall see that by allowing the field at frequency ω_s to be a strong saturating field one is able to eliminate absorption at the $a \rightarrow d$ transition frequency while maintaining a large four-wave-mixing susceptibility.

Our goal is to treat the sum-frequency generation process illustrated in part (a) of Fig. 3.8.1 and to show how it can be excited more efficiently through use of EIT techniques. As a first step, we examine how absorption at a specified frequency can be essentially eliminated by means of the EIT process. Later in this section we shall return to the study of sum-frequency generation and show that the nonlinear response leading to this process can remain large even when linear absorption at the output frequency is eliminated.

We thus first examine how linear absorption at frequency ω_4 is modified by an intense saturating field of amplitude E_s at frequency ω_s , as illustrated in part (b) of Fig. 3.8.1. To treat

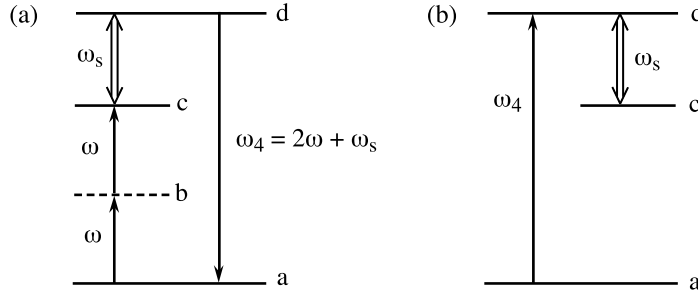


FIGURE 3.8.1: Typical situation for observing electromagnetically induced transparency.

this problem, we need to include states a , d , and c in the atomic wavefunction. Common sense might suggest that we thus express the wavefunction as

$$\psi(\mathbf{r}, t) = C'_a(t)u_a(\mathbf{r})e^{-i\omega_a t} + C'_d(t)u_d(\mathbf{r})e^{-i\omega_d t} + C'_c(t)u_c(\mathbf{r})e^{-i\omega_c t}, \quad (3.8.1)$$

where $\hbar\omega_j$ is the energy of level j , and solve Schrödinger's equation to determine the time evolution of the expansion coefficients $C'_a(t)$, $C'_d(t)$, and $C'_c(t)$. But in fact the calculation proceeds much more simply if instead we work in the *interaction picture* and represent the wavefunction as

$$\psi(\mathbf{r}, t) = C_a(t)u_a(\mathbf{r}) + C_d(t)u_d(\mathbf{r})e^{-i\omega_4 t} + C_c(t)u_c(\mathbf{r})e^{-i(\omega_4 - \omega_s)t}. \quad (3.8.2)$$

In fact, this representation makes sense because in a driven system the coefficients are expected to oscillate at the driving frequency, not at the resonance frequency. We require that $\psi(\mathbf{r}, t)$ obey Schrödinger's equation in the form

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad \text{with} \quad \hat{H} = \hat{H}_0 + \hat{V}, \quad (3.8.3)$$

where in the rotating-wave and electric-dipole approximations we can express the interaction energy as

$$\hat{V} = -\hat{\mu}(E_4 e^{-i\omega_4 t} + E_s^* e^{i\omega_s t}). \quad (3.8.4)$$

We next proceed to derive equations of motion for the coefficients C_j . We begin by introducing the wave function (3.8.2) into Schrödinger's equation (3.8.3) to obtain

$$\begin{aligned} i\hbar [\dot{C}_a u_a + \dot{C}_d u_d e^{-i\omega_4 t} - i\omega_4 C_d u_d e^{-i\omega_4 t} + \dot{C}_c u_c e^{-i(\omega_4 - \omega_s)t} \\ - i(\omega_4 - \omega_s) C_c u_c e^{-i(\omega_4 - \omega_s)t}] \\ = C_a \hbar\omega_a u_a + C_d \hbar\omega_d u_d e^{-i\omega_4 t} + C_c \hbar\omega_c u_c e^{-i(\omega_4 - \omega_s)t} \\ + \hat{V} [C_a u_a + C_d u_d e^{-i\omega_4 t} + C_c u_c e^{-i(\omega_4 - \omega_s)t}]. \end{aligned} \quad (3.8.5)$$

We turn this result into three separate equations by the usual procedure of multiplying successively by u_a^* , u_d^* , and u_c^* and integrating the resulting equation over all space. Assuming the quantities u_j to be orthonormal, we obtain

$$\begin{aligned} i\hbar\dot{C}_a &= \hbar\omega_a C_a + V_{ad}C_d e^{-i\omega_4 t}, \\ i\hbar[\dot{C}_d e^{-i\omega_4 t} - i\omega_4 C_d e^{-i\omega_4 t}] &= \hbar\omega_d C_d e^{-i\omega_4 t} + V_{da}C_a + V_{dc}C_c e^{-i(\omega_4 - \omega_s)t}, \\ i\hbar[\dot{C}_c e^{-i(\omega_4 - \omega_s)t} - i(\omega_4 - \omega_s)C_c e^{-i(\omega_4 - \omega_s)t}] &= \hbar\omega_c C_c e^{-i(\omega_4 - \omega_s)t} + V_{cd}C_d e^{-i\omega_4 t}. \end{aligned} \quad (3.8.6)$$

We next introduce the explicit forms of the matrix elements of V :

$$\begin{aligned} V_{ad}^* &= V_{da} = -\mu_{da}E_4 e^{-i\omega_4 t}, \\ V_{dc}^* &= V_{cd} = -\mu_{cd}E_s^* e^{i\omega_s t}. \end{aligned} \quad (3.8.7)$$

Also, we measure energies relative to that of the ground state a so that

$$\hbar\omega_a \rightarrow \hbar\omega_{aa} = 0, \quad \hbar\omega_d \rightarrow \hbar\omega_{da}, \quad \hbar\omega_c \rightarrow \hbar\omega_{ca}. \quad (3.8.8)$$

In addition, we introduce the Rabi frequencies

$$\Omega = \mu_{da}E_4/\hbar \quad \text{and} \quad \Omega_s^* = \mu_{cd}E_s^*/\hbar. \quad (3.8.9)$$

Eqs. (3.8.6) thus become

$$\begin{aligned} \dot{C}_a &= iC_d\Omega^*, \\ \dot{C}_d - i\delta C_d &= iC_a\Omega + iC_c\Omega_s, \\ \dot{C}_c - i(\delta - \Delta)C_c &= iC_d\Omega_s^*, \end{aligned} \quad (3.8.10)$$

where

$$\delta \equiv \omega_4 - \omega_{da} \quad \text{and} \quad \Delta \equiv \omega_s - \omega_{dc}. \quad (3.8.11)$$

We want to solve these equations correct to all orders in Ω_s and to lowest order in Ω . One might guess that one can do so by ignoring the first equation and replacing C_a by unity in the second equation. But to proceed more rigorously, we perform a formal perturbation expansion in the field amplitude Ω . We introduce a strength parameter λ , which we assume to be real, and we replace Ω by $\lambda\Omega$. We also expand C_j as a power series in λ as

$$C_j = C_j^{(0)} + \lambda C_j^{(1)} + \lambda^2 C_j^{(2)} + \dots \quad (3.8.12)$$

where $j = a, c$, or d . By introducing these forms into each of the three equations of expression (3.8.10), we obtain

$$\begin{aligned}\dot{C}_a^{(0)} + \lambda \dot{C}_a^{(1)} &= iC_d^{(0)}\lambda\Omega^* + iC_d^{(1)}\lambda^2\Omega^*, \\ (\dot{C}_d^{(0)} - i\delta C_d^{(0)}) + \lambda(\dot{C}_d^{(1)} - i\delta C_d^{(1)}) &= iC_a^{(0)}\Omega\lambda + iC_a^{(1)}\Omega\lambda^2 + iC_c^{(0)}\Omega_s\lambda + iC_c^{(1)}\Omega_s\lambda^2, \\ [\dot{C}_c^{(0)} - i(\delta - \Delta)C_c^{(0)}] + \lambda[\dot{C}_c^{(1)} - i(\delta - \Delta)C_c^{(1)}] &= iC_d^{(0)}\lambda\Omega_s^* + iC_d^{(1)}\lambda^2\Omega_s^*.\end{aligned}\tag{3.8.13}$$

We next note that because these equations must be valid for arbitrary values of the parameter λ , the coefficients of each power of λ must satisfy the equations separately. In particular, the portions of Eqs. (3.8.13) that are independent of λ are given by:

$$\begin{aligned}\dot{C}_a^{(0)} &= 0, \\ \dot{C}_d^{(0)} - i\delta C_d^{(0)} &= iC_a^{(0)}\Omega + iC_c^{(0)}\Omega_s, \\ \dot{C}_c^{(0)} - i(\delta - \Delta)C_c^{(0)} &= iC_d^{(0)}\Omega_s^*.\end{aligned}\tag{3.8.14}$$

We take the solution to these equations to be the one corresponding to the assumed initial conditions—that is,

$$C_a^{(0)} = 1 \quad \text{and} \quad C_d^{(0)} = C_c^{(0)} = 0,\tag{3.8.15}$$

for all times. Next, we note that the portions of Eqs. (3.8.13) that are linear in λ are given by:

$$\begin{aligned}\dot{C}_a^{(1)} &= 0, \\ \dot{C}_d^{(1)} - i\delta C_d^{(1)} &= i\Omega + iC_c^{(0)}\Omega_s, \\ \dot{C}_c^{(1)} - i(\delta - \Delta)C_c^{(1)} &= iC_d^{(0)}\Omega_s^*.\end{aligned}\tag{3.8.16}$$

We take the solution to the first equation as $C_a^{(1)} = 0$ for all times. We now drop the superscript (1) on the remaining equations for notational simplicity. We thus need to solve the equations

$$\begin{aligned}\dot{C}_d - i\delta C_d &= i\Omega + i\Omega_s C_c, \\ \dot{C}_c - i(\delta - \Delta)C_c &= i\Omega_s^* C_d.\end{aligned}\tag{3.8.17}$$

Note that these equations are consistent with the “guess” that we made earlier in connection with Eqs. (3.8.10). Note also that there are no time-dependent coefficients on the right-hand sides of Eqs. (3.8.17). (This is in fact why we chose to work in the interaction picture.) We can thus find the steady state solution to these equations by setting the time derivatives to zero:

$$\begin{aligned}0 &= \Omega + \delta C_d + \Omega_s C_c, \\ 0 &= \Omega_s^* C_d + (\delta - \Delta)C_c.\end{aligned}\tag{3.8.18}$$

We solve these equations algebraically to find that

$$C_d = \frac{\Omega(\delta - \Delta)}{|\Omega_s|^2 - \delta(\delta - \Delta)}. \quad (3.8.19)$$

The physical quantity of primary interest is the induced dipole moment, which can be determined as follows:

$$\begin{aligned} \tilde{p} &= \langle \psi | \hat{\mu} | \psi \rangle = \langle \psi^{(0)} | \hat{\mu} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{\mu} | \psi^{(0)} \rangle \\ &= \langle a | \hat{\mu} | d \rangle C_d e^{-i\omega_d t} + \text{c.c.} = \mu_{ad} C_d e^{-i\omega_d t} + \text{c.c.} \end{aligned} \quad (3.8.20)$$

We thus find that the dipole moment amplitude is given by

$$p = \frac{\mu_{ad} \Omega(\delta + \Delta)}{|\Omega_s|^2 - (\delta + \Delta)\delta} \quad (3.8.21)$$

and consequently that the polarization is given by

$$P = Np \equiv \epsilon_0 \chi_{\text{eff}}^{(1)} E, \quad (3.8.22)$$

which implies that

$$\chi_{\text{eff}}^{(1)} = \frac{N |\mu_{da}|^2}{\epsilon_0 \hbar} \frac{(\delta + \Delta)}{|\Omega_s|^2 - (\delta + \Delta)\delta}. \quad (3.8.23)$$

Note that we have called $\chi_{\text{eff}}^{(1)}$ an effective linear susceptibility because it depends on the intensity of the ω_s field.

Next, we add damping, using a phenomenological description. We let γ_d and γ_c be the decay rates of the probability amplitudes to be in levels d and e respectively. By examination of Eqs. (3.8.17) we see that we can model the effects of damping by replacing δ by $\delta + i\gamma_d$ and Δ by $\Delta + i(\gamma_c - \gamma_d)$. We thus find that Eq. (3.8.21) becomes

$$p = \frac{\mu_{ad} \Omega(\delta + \Delta + i\gamma_c)}{|\Omega_s|^2 - (\delta + i\gamma_d)(\delta + \Delta + i\gamma_c)} \quad (3.8.24)$$

and that the form of $\chi_{\text{eff}}^{(1)}$ is given by

$$\chi_{\text{eff}}^{(1)} = \frac{N}{\epsilon_0 \hbar} \frac{|\mu_{da}|^2 (\delta + \Delta + i\gamma_c)}{|\Omega_s|^2 - (\delta + i\gamma_d)(\delta + \Delta + i\gamma_c)}. \quad (3.8.25)$$

Note that when both fields are turned to the exact resonance ($\delta = \Delta = 0$), the susceptibility becomes simply

$$\chi_{\text{eff}}^{(1)} = \frac{N}{\epsilon_0 \hbar} \frac{|\mu_{da}|^2 i\gamma_c}{|\Omega_s|^2 + \gamma_c \gamma_d}, \quad (3.8.26)$$

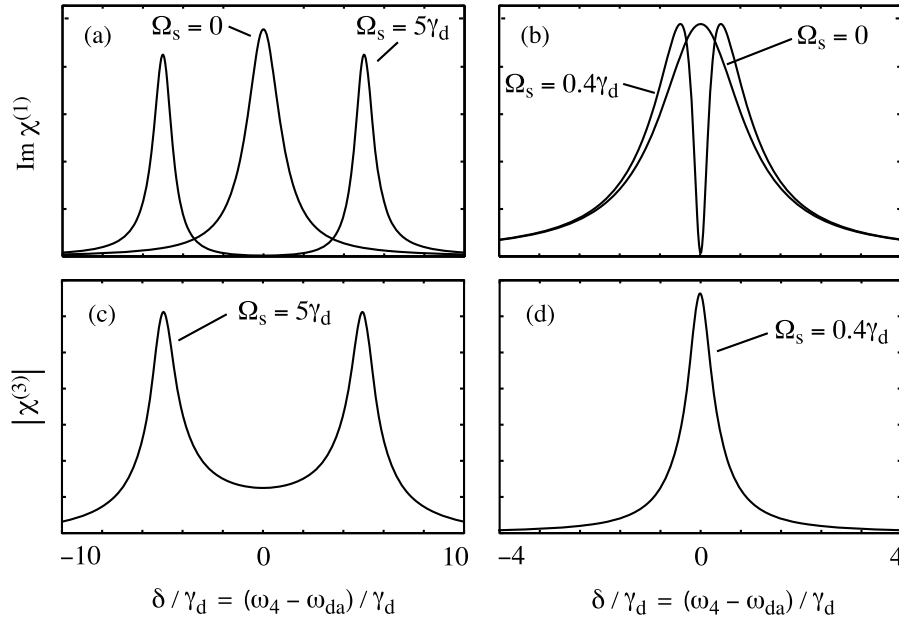


FIGURE 3.8.2: (a) and (b) Illustration of reduced optical absorption based on EIT. In the examples shown, $\Delta = \omega_s - \omega_{dc}$ is set equal to 0 and the ratio γ_c/γ_d is set equal to 0.01. The absorption spectrum is shown in the presence of a strongly saturating field (a) and a weakly saturating field (b). In each case the absorption nearly vanishes at line center, and the absorption spectrum in the complete absence of the saturating field (labeled $\Omega_s = 0$) is shown for comparison. (c) and (d) The magnitude of the nonlinear response leading to sum-frequency generation is shown. In each case the nonlinear response remains appreciable at the frequency of nearly complete transparency.

which is purely imaginary. In this case, the absorption experienced by the field at frequency ω_4 can be rendered arbitrarily small by choosing the field Ω_s to be saturating. The nature of the modification of the absorption spectrum is illustrated in parts (a) and (b) of Fig. 3.8.2. In part (a), we see that in the presence of a strongly saturating field the absorption feature splits into two components, with each component separated from the center of the feature by the Rabi frequency $|\Omega_s|$ associated with the strong field. In part (b), we see that in the presence of a weakly saturating field a pronounced dip is induced in the absorption profile. In each case the absorption drops to nearly zero at the position of the resonance.

We now calculate the response leading to sum-frequency generation. We express the wavefunction in the interaction picture as

$$\begin{aligned} \psi(\mathbf{r}, t) = & C_a(t)u_a(\mathbf{r}) + C_b(t)u_b(\mathbf{r})e^{-i\omega t} \\ & + C_c(t)u_c(\mathbf{r})e^{-i2\omega t} + C_d(t)u_d(\mathbf{r})e^{-i(2\omega+\omega_c)t}. \end{aligned} \quad (3.8.27)$$

As before, this wavefunction must satisfy the Schrödinger equation (3.8.3). We thereby find that

$$\begin{aligned}
& i\hbar[\dot{C}_a u_a + \dot{C}_b u_b e^{-i\omega t} - i\omega C_b u_b e^{-i\omega t} + \dot{C}_c u_c e^{-i2\omega t} - 2i\omega C_c u_c e^{-i2\omega t} \\
& \quad + \dot{C}_d u_d e^{-i(2\omega+\omega_c)t} - i(2\omega+\omega_c)C_d u_d e^{-i(2\omega+\omega_c)t}] \\
& = \hbar\omega_{ba} C_b u_b e^{-i\omega t} + \hbar\omega_{ca} C_c u_c e^{-i2\omega t} + \hbar\omega_{da} C_d u_d e^{-i(2\omega+\omega_c)t} \\
& \quad + \hat{V}[C_a u_a + C_b u_b e^{-i\omega t} + C_c u_c e^{-i2\omega t} + C_d u_d e^{-i(2\omega+\omega_c)t}]. \tag{3.8.28}
\end{aligned}$$

We now separate this expression into four equations by the usual method of multiplying successively by u_a^* , u_b^* , u_c^* , and u_d^* and integrating over all space. Recalling from Eq. (3.8.8) that $\hbar\omega_{aa} = 0$, we find that

$$\begin{aligned}
& i\hbar\dot{C}_a = V_{ab}C_b e^{-i\omega t}, \\
& i\hbar(\dot{C}_b - i\omega C_b)e^{-i\omega t} = \hbar\omega_{ba}C_b e^{-i\omega t} + V_{ba}C_a + V_{bc}C_c e^{-i2\omega t}, \\
& i\hbar(\dot{C}_c - i2\omega C_c)e^{-i2\omega t} = \hbar\omega_{ca}C_c e^{-i2\omega t} + V_{cb}C_b e^{-i\omega t} + V_{cd}C_d e^{-i(2\omega+\omega_s)t}, \\
& i\hbar[\dot{C}_d - i(2\omega+\omega_c)C_d]e^{-(2\omega+\omega_s)t} = \hbar\omega_{da}C_d e^{-(2\omega+\omega_s)t} + V_{dc}C_c e^{-i2\omega t}. \tag{3.8.29}
\end{aligned}$$

We next represent the matrix elements of the interaction Hamiltonian as

$$\begin{aligned}
V_{ba} &= V_{ab}^* = -\mu_{ba}E e^{-i\omega t} = -\hbar\Omega_{ba}e^{-i\omega t}, \\
V_{cb} &= V_{bc}^* = -\mu_{cb}E e^{-i\omega t} = -\hbar\Omega_{cb}e^{-i\omega t}, \\
V_{dc} &= V_{cd}^* = -\mu_{dc}E_s e^{-i\omega_s t} = -\hbar\Omega_{dc}e^{-i\omega_s t}, \tag{3.8.30}
\end{aligned}$$

and introduce the detuning factors as

$$\delta_1 = \omega - \omega_{ba}, \quad \delta_2 = 2\omega - \omega_{ca} \quad \text{and} \quad \Delta = \omega_s - \omega_{dc}. \tag{3.8.31}$$

We thus find that

$$\dot{C}_a = iC_b\Omega_{ba}^*, \tag{3.8.32a}$$

$$\dot{C}_b - iC_b\delta_1 = iC_a\Omega_{ba} + iC_c\Omega_{cb}^*, \tag{3.8.32b}$$

$$\dot{C}_c - iC_c\delta_2 = iC_b\Omega_{cb} + iC_d\Omega_{dc}^*, \tag{3.8.32c}$$

$$\dot{C}_d - iC_d(\delta_2 + \Delta) = iC_c\Omega_{dc}. \tag{3.8.32d}$$

We wish to solve these equations perturbatively in Ω_{ba} and Ω_{cb} but to all orders in Ω_{dc} . We first note that consistent with this assumption we can ignore Eq. (3.8.32a) altogether, as $|C_b| \ll |C_a|$ and therefore $C_a \approx 1$. In solving Eq. (3.8.32b), we can drop the last term because $|C_c| \ll |C_b|$. Then setting $C_a = 1$ and taking $\dot{C}_b = 0$ for the steady-state solution, we find that

$$C_b = -\Omega_{ba}/\delta_1. \tag{3.8.33}$$

We next need to find the simultaneous, steady-state solutions to Eqs. (3.8.32c) and (3.8.32d). We set the time derivatives to zero to obtain

$$\begin{aligned} -C_c &= \frac{C_b \Omega_{cb}}{\delta_2} + \frac{C_d \Omega_{dc}^*}{\delta_2}, \\ C_d &= \frac{-C_c \Omega_{dc}}{(\delta_2 + \Delta)}. \end{aligned} \quad (3.8.34)$$

We now introduce the first of these equations into the second and make use of Eq. (3.8.33) to obtain

$$C_d = \frac{-\Omega_{ba} \Omega_{cb} \Omega_{dc}}{\delta_1 \delta_2 (\delta_2 + \Delta)} + C_d \frac{|\Omega_{dc}|^2}{(\delta_2 + \Delta) \delta_2} \quad (3.8.35)$$

and thus to find that

$$C_d = -\frac{\Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 \delta_2 (\delta_2 + \Delta)} \left[1 - \frac{|\Omega_{dc}|^2}{\delta_2 (\delta_2 + \Delta)} \right]^{-1} \quad (3.8.36)$$

$$= -\frac{\Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]}. \quad (3.8.37)$$

The induced electric dipole moment at the sum frequency is now calculated as

$$\tilde{p} = \langle \psi | \hat{\mu} | \psi \rangle = \langle u_a | \hat{\mu} | C_d u_d \rangle + \text{c.c.} = \mu_{ad} C_d + \text{c.c.} \quad (3.8.38)$$

We thus find that the complex amplitude of the induced dipole moment is given by

$$p = \frac{-\mu_{ad} \Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]} = \frac{-\mu_{ad} \mu_{dc} \mu_{cb} \mu_{ba} E^2 E_s}{\hbar^3 \delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]} \equiv \frac{3\epsilon_0 \chi^{(3)} E^2 E_c}{N}. \quad (3.8.39)$$

We thus find that

$$\chi^{(3)} = \frac{-N \mu_{ad} \mu_{dc} \mu_{cb} \mu_{ba}}{3\epsilon_0 \hbar \delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]}. \quad (3.8.40)$$

As in Eq. (3.8.25), we can add the effects of damping to this result by replacing δ_2 with $\delta_2 + i\gamma_c$ and replacing $\delta_2 + \Delta$ with $\delta_2 + \Delta + i\gamma_d$. We thus find that

$$\chi^{(3)} = \frac{-N \mu_{ad} \mu_{dc} \mu_{cb} \mu_{ba}}{3\epsilon_0 \hbar \delta_1 [(\delta_2 + i\gamma_c)(\delta_2 + \Delta + i\gamma_d) - |\Omega_{dc}|^2]}. \quad (3.8.41)$$

Note that in the limit $|\Omega_{dc}| \rightarrow 0$ this result reduces to the usual expression for the resonant contribution to the third-order susceptibility. Some of the numerical predictions given by Eq. (3.8.41) are shown in Fig. 3.8.2(c) and (d). We see that in each case the nonlinear response remains appreciable at the position of the initial resonance, and even shows a peak for the conditions of panel (d).

3.9 Local-Field Effects in the Nonlinear Optics

The treatment of the nonlinear optical susceptibility presented thus far has made the implicit assumption that the electric field acting on each atom or molecule is the macroscopic electric field that appears in Maxwell's equations. In general, one has to distinguish between the macroscopic electric field and the effective electric field that each atom experiences, which is also known as the Lorentz local field. The distinction between these two fields is important except for the case of a medium that is so dilute that its linear dielectric constant is nearly equal to unity.

3.9.1 Local-Field Effects in Linear Optics

Let us first review the theory of local field effects in linear optics. The electric field $\tilde{\mathbf{E}}$ that appears in Maxwell's equations in the form of Eqs. (2.1.1) through (2.1.8) is known as the macroscopic or Maxwell field. This field is obtained by performing a spatial average of the actual (that is, microscopic) electric field over a region of space whose linear dimensions are of the order of at least several atomic diameters. It is useful to perform such an average to smooth out the wild variations in the electric field that occur in the immediate vicinity of the atomic nuclei and electrons. The macroscopic electric field thus has contributions from sources external to the material system and from the charges of all of the molecules that constitute the system.

Let us now see how to calculate the dipole moment induced in a representative molecule contained within the material system. We assume for simplicity that the medium is lossless and dispersionless, so that we can conveniently represent the fields as time-varying quantities. We let $\tilde{\mathbf{E}}$ represent the macroscopic field and $\tilde{\mathbf{P}}$ the polarization within the bulk of the material. Furthermore, we represent the electric-dipole moment induced in a typical molecule as

$$\tilde{\mathbf{p}} = \epsilon_0 \gamma^{(1)} \tilde{\mathbf{E}}_{\text{loc}}, \quad (3.9.1)$$

where $\gamma^{(1)}$ is the usual linear polarizability* and where $\tilde{\mathbf{E}}_{\text{loc}}$ is the local field—that is, the effective electric field that acts on the molecule. The local field is the field resulting from all external sources and from all molecules within the sample *except* the one under consideration.

We calculate this field through use of a procedure described by Lorentz (1952). We imagine drawing a small sphere centered on the molecule under consideration, as shown in Fig. 3.9.1. This sphere is assumed to be sufficiently large that it contains many molecules. The electric field produced at the center of the sphere by molecules contained within the sphere (not including the molecule at the center) will tend to cancel, and for the case of a liquid, gas, or cubic crystal, this

* Many authors use the symbol α to represent the linear polarizability. We use the symbol $\gamma^{(1)}$ to avoid confusion over the use of α for the absorption coefficient.

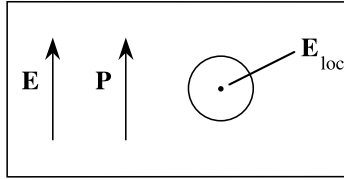


FIGURE 3.9.1: Calculation of the Lorentz local field.

cancellation can be shown to be exact. We can then imagine removing these molecules from the sphere, leaving only the molecule under consideration, which is then located at the center of an evacuated sphere within an otherwise uniformly polarized medium. It is then a simple problem in electrostatics to calculate the value of the field at the center of the sphere. The field, which we identify as the Lorentz local field, is given by (see also Born and Wolf, 1975, Section 2.3, or Jackson, 1975, Section 4.5)

$$\tilde{\mathbf{E}}_{\text{loc}} = \tilde{\mathbf{E}} + \frac{1}{3\epsilon_0} \tilde{\mathbf{P}}. \quad (3.9.2)$$

By definition, the polarization of the material is given by

$$\tilde{\mathbf{P}} = N\tilde{\mathbf{p}}, \quad (3.9.3)$$

where N is the number density of molecules and $\tilde{\mathbf{p}}$ is the dipole moment per molecule, which under the present circumstances is given by Eq. (3.9.1). By combining Eqs. (3.9.1) through (3.9.3), we find that the polarization and macroscopic field are related by

$$\tilde{\mathbf{P}} = N\epsilon_0\gamma^{(1)} \left(\tilde{\mathbf{E}} + \frac{1}{3\epsilon_0} \tilde{\mathbf{P}} \right). \quad (3.9.4)$$

It is useful to express this result in terms of the linear susceptibility $\chi^{(1)}$, defined by

$$\tilde{\mathbf{P}} = \epsilon_0\chi^{(1)}\tilde{\mathbf{E}}. \quad (3.9.5)$$

If we substitute this expression for $\tilde{\mathbf{P}}$ into Eq. (3.9.4) and solve the resulting equation for $\chi^{(1)}$, we find that

$$\chi^{(1)} = \frac{N\gamma^{(1)}}{1 - \frac{1}{3}N\gamma^{(1)}}. \quad (3.9.6)$$

For the usual case in which the polarizability $\gamma^{(1)}$ is positive, we see that the susceptibility is larger than the value $N\gamma^{(1)}$ predicted if we ignore local-field effects. We also see that the susceptibility increases with N more rapidly than linearly.

Alternatively, we can express the result given by Eq. (3.9.6) in terms of the linear dielectric constant

$$\epsilon^{(1)} = 1 + \chi^{(1)}. \quad (3.9.7)$$

If the left-hand side of Eq. (3.9.6) is replaced by $\chi^{(1)} = (\epsilon^{(1)} - 1)$ and the resulting equation is rearranged so that its right-hand side is linear in $\gamma^{(1)}$, we find that the dielectric constant is given by the expression

$$\frac{\epsilon^{(1)} - 1}{\epsilon^{(1)} + 2} = \frac{1}{3} N \gamma^{(1)}. \quad (3.9.8a)$$

This equation (often with $\epsilon^{(1)}$ replaced by n^2) is known as the Lorentz–Lorenz law. Note that, through rearrangement, Eq. (3.9.8a) can be written as

$$\frac{\epsilon^{(1)} + 2}{3} = \frac{1}{1 - \frac{1}{3} N \gamma^{(1)}}. \quad (3.9.8b)$$

Eq. (3.9.6) can thus be expressed as

$$\chi^{(1)} = \frac{\epsilon^{(1)} + 2}{3} N \gamma^{(1)}. \quad (3.9.8c)$$

This result shows that $\chi^{(1)}$ is larger than $N \gamma^{(1)}$ by the factor $(\epsilon^{(1)} + 2)/3$. The factor $(\epsilon^{(1)} + 2)/3$ can thus be interpreted as the local-field enhancement factor for the linear susceptibility.

3.9.2 Local-Field Effects in Nonlinear Optics

In the nonlinear-optical case, the Lorentz local field is still given by Eq. (3.9.2), but the polarization now has both linear and nonlinear contributions:

$$\tilde{\mathbf{P}} = \tilde{\mathbf{P}}^L + \tilde{\mathbf{P}}^{\text{NL}}. \quad (3.9.9)$$

We represent the linear contribution as

$$\tilde{\mathbf{P}}^L = N \epsilon_0 \gamma^{(1)} \tilde{\mathbf{E}}_{\text{loc}}. \quad (3.9.10)$$

Note that this contribution is “linear” in the sense that it is linear in the strength of the local field. In general it is not linear in the strength of the macroscopic field. We next introduce Eqs. (3.9.2) and (3.9.9) into this equation to obtain

$$\tilde{\mathbf{P}}^L = N \epsilon_0 \gamma^{(1)} \left(\tilde{\mathbf{E}} + \frac{1}{3 \epsilon_0} \tilde{\mathbf{P}}^L + \frac{1}{3 \epsilon_0} \tilde{\mathbf{P}}^{\text{NL}} \right). \quad (3.9.11)$$

We now solve this equation for $\tilde{\mathbf{P}}^L$ and use Eqs. (3.9.6) and (3.9.7) to express the factor $N\gamma^{(1)}$ that appears in the resulting expression in terms of the linear dielectric constant. We thereby obtain

$$\tilde{\mathbf{P}}^L = [\epsilon^{(1)} - 1](\epsilon_0 \tilde{\mathbf{E}} + \frac{1}{3} \tilde{\mathbf{P}}^{\text{NL}}). \quad (3.9.12)$$

Next we consider the displacement vector

$$\tilde{\mathbf{D}} = \epsilon_0 \tilde{\mathbf{E}} + \tilde{\mathbf{P}} = \epsilon_0 \tilde{\mathbf{E}} + \tilde{\mathbf{P}}^L + \tilde{\mathbf{P}}^{\text{NL}}. \quad (3.9.13)$$

If the expression (3.9.12) for the linear polarization is substituted into this expression, we obtain

$$\tilde{\mathbf{D}} = \epsilon_0 \epsilon^{(1)} \tilde{\mathbf{E}} + \left(\frac{\epsilon^{(1)} + 2}{3} \right) \tilde{\mathbf{P}}^{\text{NL}}. \quad (3.9.14)$$

We see that the second term is not simply $\tilde{\mathbf{P}}^{\text{NL}}$, as might have been expected, but rather that the nonlinear polarization appears multiplied by the factor $(\epsilon^{(1)} + 2)/3$. We recall that in the derivation of the polarization-driven wave equation of nonlinear optics, a nonlinear source term appears when the second time derivative of $\tilde{\mathbf{D}}$ is calculated (see, for example, Eq. (2.1.9a)). As a consequence of Eq. (3.9.14), we see that the nonlinear source term is actually the nonlinear polarization $\tilde{\mathbf{P}}^{\text{NL}}$ multiplied by the factor $(\epsilon^{(1)} + 2)/3$. To emphasize this point, Bloembergen (1965) introduces the *nonlinear source polarization* defined by

$$\tilde{\mathbf{P}}^{\text{NLS}} = \left(\frac{\epsilon^{(1)} + 2}{3} \right) \tilde{\mathbf{P}}^{\text{NL}} \quad (3.9.15)$$

so that Eq. (3.9.14) can be expressed as

$$\tilde{\mathbf{D}} = \epsilon_0 \epsilon^{(1)} \tilde{\mathbf{E}} + \tilde{\mathbf{P}}^{\text{NLS}}. \quad (3.9.16)$$

When the derivation of the wave equation is carried out as in Section 2.1 using this expression for $\tilde{\mathbf{D}}$, we obtain the result

$$\nabla \times \nabla \times \tilde{\mathbf{E}} + \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \tilde{\mathbf{E}}}{\partial t^2} = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{\mathbf{P}}^{\text{NLS}}}{\partial t^2}. \quad (3.9.17)$$

This result shows how local-field effects are incorporated into the wave equation.

The distinction between the local and macroscopic fields also arises in that the field that induces a dipole moment in each atom is the local field, whereas by definition the nonlinear susceptibility relates the nonlinear source polarization to the macroscopic field. To good approximation, we can relate the local and macroscopic fields by replacing $\tilde{\mathbf{P}}$ by $\tilde{\mathbf{P}}^L$ in Eq. (3.9.2) to obtain

$$\tilde{\mathbf{E}}_{\text{loc}} = \tilde{\mathbf{E}} + \frac{1}{3} \chi^{(1)} \tilde{\mathbf{E}} = \left[1 + \frac{1}{3} (\epsilon^{(1)} - 1) \right] \tilde{\mathbf{E}},$$

or

$$\tilde{\mathbf{E}}_{\text{loc}} = \left(\frac{\epsilon^{(1)} + 2}{3} \right) \tilde{\mathbf{E}}. \quad (3.9.18)$$

We now apply the results given by Eqs. (3.9.17) and (3.9.18) to the case of second-order nonlinear interactions. We define the nonlinear susceptibility by means of the equation (see also Eq. (1.3.13))

$$P_i^{\text{NLS}}(\omega_m + \omega_n) = \epsilon_0 \sum_{jk} \sum_{(mn)} \chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) E_j(\omega_m) E_k(\omega_n), \quad (3.9.19)$$

where

$$P_i^{\text{NLS}}(\omega_m + \omega_n) = \left(\frac{\epsilon^{(1)}(\omega_m + \omega_n) + 2}{3} \right) P_i^{\text{NL}}(\omega_m + \omega_n) \quad (3.9.20)$$

and where the quantities $E_j(\omega_m)$ represent macroscopic fields. The nonlinear polarization (i.e., the second-order contribution to the dipole moment per unit volume) can be represented as

$$P_i^{\text{NL}}(\omega_m + \omega_n) = N \epsilon_0 \sum_{jk} \sum_{(mn)} \beta_{ijk}(\omega_m + \omega_n, \omega_m, \omega_n) E_j^{\text{loc}}(\omega_m) E_k^{\text{loc}}(\omega_n), \quad (3.9.21)$$

where the proportionality constant β_{ijk} is known as the second-order hyperpolarizability. The local fields appearing in this expression are related to the macroscopic fields according to Eq. (3.9.18), which we now rewrite as

$$E_j^{\text{loc}}(\omega_m) = \left(\frac{\epsilon^{(1)}(\omega_m) + 2}{3} \right) E_j(\omega_m). \quad (3.9.22)$$

By combining Eqs. (3.9.19) through (3.9.22), we find that the nonlinear susceptibility can be represented as

$$\begin{aligned} & \chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) \\ &= \mathcal{L}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) N \beta_{ijk}(\omega_m + \omega_n, \omega_m, \omega_n), \end{aligned} \quad (3.9.23)$$

where

$$\begin{aligned} & \mathcal{L}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) \\ &= \left(\frac{\epsilon^{(1)}(\omega_m + \omega_n) + 2}{3} \right) \left(\frac{\epsilon^{(1)}(\omega_m) + 2}{3} \right) \left(\frac{\epsilon^{(1)}(\omega_n) + 2}{3} \right) \end{aligned} \quad (3.9.24)$$

gives the local-field enhancement factor for the second-order susceptibility. For example, Eq. (3.6.18) for $\chi^{(2)}$ should be multiplied by this factor to obtain the correct expression including local-field effects.

This result is readily generalized to higher-order nonlinear interaction. For example, the expression for $\chi^{(3)}$ obtained ignoring local-field effects should be multiplied by the factor

$$\begin{aligned} & \mathcal{L}^{(3)}(\omega_l + \omega_m + \omega_n, \omega_l, \omega_m, \omega_n) \\ &= \left(\frac{\epsilon^{(1)}(\omega_l + \omega_m + \omega_n) + 2}{3} \right) \left(\frac{\epsilon^{(1)}(\omega_l) + 2}{3} \right) \\ & \quad \times \left(\frac{\epsilon^{(1)}(\omega_m) + 2}{3} \right) \left(\frac{\epsilon^{(1)}(\omega_n) + 2}{3} \right). \end{aligned} \quad (3.9.25)$$

Our derivation of the form of the local-field enhancement factor has essentially followed the procedure of Bloembergen (1965). The nature of local-field effects in nonlinear optics can be understood from a very different point of view introduced by Mizrahi and Sipe (1986). This method has the desirable feature that, unlike the procedure just described, it does not require that we introduce the somewhat arbitrary distinction between the nonlinear polarization and the nonlinear source polarization. For simplicity, we describe this procedure only for the case of third-harmonic generation in the scalar field approximation. We assume that the total polarization (including both linear and nonlinear contributions) at the third-harmonic frequency is given by

$$P(3\omega) = N\epsilon_0 \gamma^{(1)}(3\omega) E_{\text{loc}}(3\omega) + N\epsilon_0 \gamma^{(3)}(3\omega, \omega, \omega, \omega) E_{\text{loc}}^3(\omega), \quad (3.9.26)$$

where $\gamma^{(1)}(3\omega)$ is the linear polarizability for radiation at frequency 3ω and where $\gamma^{(3)}(3\omega, \omega, \omega, \omega)$ is the hyperpolarizability leading to third-harmonic generation. We next use Eqs. (3.9.2) and (3.9.18) to rewrite Eq. (3.9.26) as

$$\begin{aligned} P(3\omega) &= N\epsilon_0 \gamma^{(1)}(3\omega) \left[E(3\omega) + \frac{1}{3\epsilon_0} P(3\omega) \right] \\ & \quad + N\epsilon_0 \gamma^{(3)}(3\omega, \omega, \omega, \omega) \left(\frac{\epsilon^{(1)}(\omega) + 2}{3} \right)^3 E(\omega)^3. \end{aligned} \quad (3.9.27)$$

This equation is now solved algebraically for $P(3\omega)$ to obtain

$$P(3\omega) = \frac{N\gamma^{(1)}(3\omega)E(3\omega)}{1 - \frac{1}{3}N\gamma^{(1)}(3\omega)} + \frac{N\gamma^{(3)}(3\omega, \omega, \omega, \omega)}{1 - \frac{1}{3}N\gamma^{(1)}(3\omega)} \left(\frac{\epsilon^{(1)}(\omega) + 2}{3} \right)^3 E(\omega)^3. \quad (3.9.28)$$

We can identify the first and second terms of this expression as the linear and third-order polarizations, which we represent as

$$P(3\omega) = \epsilon_0 \chi^{(1)}(3\omega) E(3\omega) + \epsilon_0 \chi^{(3)}(3\omega, \omega, \omega, \omega) E(\omega)^3, \quad (3.9.29)$$

where (in agreement with the unusual Lorentz–Lorenz law) the linear susceptibility is given by

$$\chi^{(1)}(3\omega) = \frac{N\gamma^{(1)}(3\omega)}{1 - \frac{1}{3}N\gamma^{(1)}(3\omega)}, \quad (3.9.30)$$

and where the third-order susceptibility is given by

$$\chi^{(3)}(3\omega, \omega, \omega, \omega) = \left(\frac{\epsilon^{(1)}(\omega) + 2}{3} \right)^3 \left(\frac{\epsilon^{(1)}(3\omega) + 2}{3} \right) N\gamma^{(3)}(3\omega, \omega, \omega, \omega). \quad (3.9.31)$$

We have made use of Eq. (3.9.8b) in writing Eq. (3.9.31) in the form shown. Note that the result (3.9.31) agrees with the previous result described by Eq. (3.9.25). Experimental results demonstrating the influence of local-field effects on the linear and nonlinear optical response have been presented by Maki et al. (1991).

Throughout this section, we have made the implicit assumption that the material under consideration is chemically homogeneous. Different considerations come into play for the case of molecules of one chemical species embedded in a host material of a different species. This situation has been treated by Glauber and Lewenstein (1991). They find that in this case the local field factor is given by $3\epsilon^{(1)}/(2\epsilon^{(1)} + 1)$ rather than by $(\epsilon^{(1)} + 2)/3$ as given in Eq. (3.9.8c). Dolgaleva et al. (2007) verified this type of dependence for the radiative lifetime of emitting nanoparticles embedded in a host material. The analysis of local-field effects in composite materials comprised of two or more constituents is an area of active current research. In a composite material, the local electric field can vary considerably in space, and this effect can lead to an overall enhancement of the nonlinear optical response. These effects have been described by Fischer et al. (1995) and by Nelson and Boyd (1999).

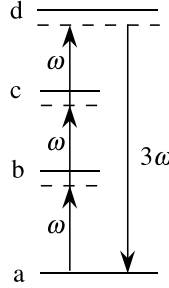
Problems

1. *Estimate of the refractive index of an atomic vapor.* Starting (for instance) from Eq. (3.5.20), perform an estimate of the magnitude of the on-resonance absorption coefficient of a dense atomic vapor assuming that the atomic number density is $N = 10^{17} \text{ cm}^{-3}$, that $\mu = 2.5ea_0$, that the transition vacuum wavelength is $0.6 \mu\text{m}$, and that the transition is homogeneously broadened with a linewidth (FWHM) of 10 GHz . Under the same conditions, calculate the maximum value of the real part of the refractive index near the peak of the absorption line. (These values are realistic under laboratory conditions. See for instance Maki et al., 1991.)

$$[\text{Ans.: } \alpha = 8 \times 10^4 \text{ cm}^{-1}, \quad n^{(\text{max})} = 1.2.]$$

2. *Estimate of the refractive index of glass.* Starting (for instance) from Eq. (3.5.20), perform an estimate of the magnitude of the real part of the refractive index of glass at visible wavelengths. Choose realistic values for the atomic number density, dipole transition moment, and detuning from resonance.

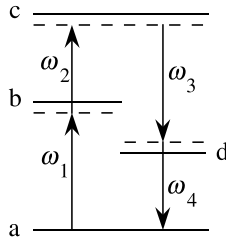
3. *Maximum value of the on-resonance cross section.* Verify Eq. (3.5.42).
4. *Permutation symmetry of the nonlinear susceptibility.* Show that Eq. (3.6.24) possesses full permutation symmetry.
5. *Resonant nonlinear optical response.* Derive, using the density matrix formalism, an expression for the resonant contribution to the third-order susceptibility $\chi^{(3)}$ describing third-harmonic generation as illustrated below.



Assume that, in thermal equilibrium, all of the population resides in the ground state. Note that since all input frequencies are equal and since only the resonant contribution is required, the answer will consist of one term and not 48 terms, which occur for the most general case of $\chi^{(3)}$. Work this problem by starting with the perturbation expansion (3.4.16) derived in the text and specializing the ensuing derivation to the interaction shown in the figure.

$$\begin{aligned}
 & [\text{Ans.: } \chi_{kjih}^{(3)}(3\omega, \omega, \omega, \omega) \\
 &= \frac{N}{\epsilon_0 \hbar^3} \frac{\mu_{ad}^k \mu_{dc}^j \mu_{cb}^i \mu_{ba}^h}{[(\omega_{da} - 3\omega) - i\gamma_{da}][(\omega_{ca} - 2\omega) - i\gamma_{ca}][(\omega_{ba} - \omega) - i\gamma_{ba}]}.]
 \end{aligned}$$

6. *Model calculation of the nonlinear susceptibility.* Consider the mutual interaction of four optical fields as illustrated in the following figure. Assume that all of the fields have the same linear polarization and that in thermal equilibrium all of the population is contained in level a . Assume that the waves are tuned sufficiently closely to the indicated resonances that only these contributions to the nonlinear interaction need be taken into account.



You may work this problem either by specializing the general result of Eq. (3.7.11) to the interaction shown in the figure or by repeating the derivation given in the text and specializing at each step to this interaction.

(a) Calculate the four nonlinear susceptibilities

$$\begin{aligned}\chi^{(3)}(\omega_4 = \omega_1 + \omega_2 - \omega_3), & \quad \chi^{(3)}(\omega_3 = \omega_1 + \omega_2 - \omega_4), \\ \chi^{(3)}(\omega_1 = \omega_3 + \omega_4 - \omega_2), & \quad \chi^{(3)}(\omega_2 = \omega_3 + \omega_4 - \omega_1)\end{aligned}$$

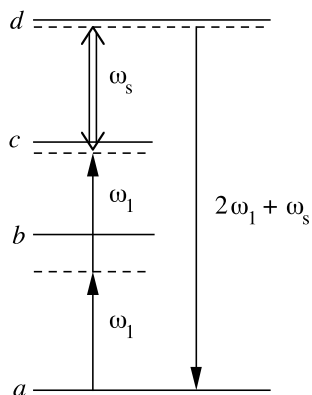
that describe the four-wave mixing process, and determine the conditions under which these quantities are equal.

(b) In addition, calculate the nonlinear susceptibilities

$$\chi^{(3)}(\omega_1 = \omega_1 + \omega_2 - \omega_2), \quad \chi^{(3)}(\omega_2 = \omega_2 + \omega - \omega_1)$$

that describe two-photon absorption of the ω_1 and ω_2 fields, and determine the conditions under which they are equal. [Experimental investigation of some of the effects described by these quantities is reported by Malcuit et al., 1985.]

7. *Generalization of Problems 4 and 5.* Repeat the calculation of the resonant contributions to $\chi^{(3)}$ for the cases studied in Problems 4 and 5 for the more general situation in which each of the levels can contain population in thermal equilibrium. Interpret your results. [Note: The solution to this problem is very lengthy.]
8. *Pressure-induced resonances in nonlinear optics.* Verify the statement made in the text that Eq. (3.7.11) reduces to Eq. (3.2.33) in the limit in which damping effects are negligible. Show also that, even when damping is not negligible, the general 48-term expression for $\chi^{(3)}$ can be cast into an expression containing 24 terms, 12 of which contain “pressure-induced” resonances.
9. *Electromagnetically induced transparency.* The goal of this problem is to determine how the linear susceptibility $\chi^{(1)}(2\omega_1 + \omega_s)$ and the nonlinear optical susceptibility $\chi^{(3)}(\omega_{\text{sum}} = \omega_1 + \omega_1 + \omega_s)$ are modified when the field at frequency ω_s is a strong saturating field. We shall find that under appropriate circumstances the presence of the strong field can significantly decrease the (unwanted) linear absorption experienced by the sum frequency field while leaving the magnitude of the nonlinear response relatively unaffected. This problem was worked out in the body of the text using the wavefunction formalism. For this problem, you are to treat this problem using the density-matrix formalism, using the coupling scheme shown in the accompanying figure. Note that level b is appreciably detuned from a one-photon resonance but that all other excited states are excited at a near resonance frequency.



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