1 Introduction

Classical Theory of Electric Dipole Radiative Interactions

1.1 Introduction

The classical theory of the interaction of light with the electron clouds of atoms and molecules will be discussed in this chapter. The discussion will begin with the interaction of a steady electric field with a collection of point charges, leading to the development of terms describing the electric dipole and quadrupole moments. The classical Lorentz model is then introduced to describe the interaction of an oscillating electric field with the electron cloud of an atom, and the concepts of absorption and emission are introduced. The propagation of a light wave through a medium with electric dipoles is then discussed. Finally, the classical theory of radiation from an oscillating dipole is discussed.

1.2 Interaction of a Collection of Charges with a Steady Electric Field

Before beginning a discussion of the interaction of atoms and molecules with the oscillating electric field associated with a light wave, we will first consider the interaction of a collection of point charges with a steady electric field. The result of this analysis will be the separation of the contributions of the electric dipole and quadrupole moments to the energy of a system of point charges in a steady electric field. The point charges in an atom or molecule are associated with the electrons $(-e)$ and the nuclei $(+Ze)$ (C), where Z is the number of protons in each nucleus. Now consider a point charge q located at position r (m) in a steady electric field $\boldsymbol{E}(\boldsymbol{r})$ (V/m or J/C-m), where

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla\Phi(\boldsymbol{r}) \tag{1.1}$$

and $\Phi(\boldsymbol{r})$ (J/C) is the scalar potential. The potential energy of the point charge q(C) is given by

$$V = q\Phi(\boldsymbol{r}). \tag{1.2}$$

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Following Struve (1988), the scalar potential can be expanded in a Taylor series about $\boldsymbol{r} = 0$:

$$\begin{aligned}\Phi(\boldsymbol{r}) = \Phi(\mathbf{0}) &+ x\left[\frac{\partial\Phi}{\partial x}(\mathbf{0})\right] + y\left[\frac{\partial\Phi}{\partial y}(\mathbf{0})\right] + z\left[\frac{\partial\Phi}{\partial z}(\mathbf{0})\right] \\ &+ \frac{1}{2}\left\{x^2\left[\frac{\partial^2\Phi}{\partial x^2}(\mathbf{0})\right] + y^2\left[\frac{\partial^2\Phi}{\partial y^2}(\mathbf{0})\right] + z^2\left[\frac{\partial^2\Phi}{\partial z^2}(\mathbf{0})\right]\right. \\ &\left. + 2xy\left[\frac{\partial^2\Phi}{\partial x\partial y}(\mathbf{0})\right] + 2yz\left[\frac{\partial^2\Phi}{\partial y\partial z}(\mathbf{0})\right] + 2zx\left[\frac{\partial^2\Phi}{\partial z\partial x}(\mathbf{0})\right]\right\} + \cdots.\end{aligned} \tag{1.3}$$

Equation (1.3) can be written in more compact form as

$$\Phi(\boldsymbol{r}) = \Phi(\mathbf{0}) + \boldsymbol{r}\bullet[\nabla\Phi(\mathbf{0})] + \frac{1}{2}\sum_i\sum_j x_i x_j \frac{\partial}{\partial x_i}\left[\frac{\partial\Phi}{\partial x_j}(\mathbf{0})\right] + \cdots. \tag{1.4}$$

The electric field is calculated from the gradient of the potential,

$$\boldsymbol{E}(\mathbf{0}) = -\nabla\Phi(\mathbf{0}) \tag{1.5}$$

and

$$E_i(\mathbf{0}) = -\frac{\partial\Phi}{\partial x_i}(\mathbf{0}). \tag{1.6}$$

Substituting Eqs. (1.5) and (1.6) into (1.4), we obtain

$$\Phi(\boldsymbol{r}) = \Phi(\mathbf{0}) - \boldsymbol{r}\bullet\boldsymbol{E}(\mathbf{0}) - \frac{1}{2}\sum_i\sum_j x_i x_j \frac{\partial E_j}{\partial x_i}(\mathbf{0}) + \cdots. \tag{1.7}$$

For a point charge q, the interaction energy is thus given by

$$V = q\Phi(\mathbf{0}) - q\boldsymbol{r}\bullet\boldsymbol{E}(\mathbf{0}) - \frac{q}{2}\sum_i\sum_j x_i x_j \frac{\partial E_j}{\partial x_i}(\mathbf{0}) + \cdots. \tag{1.8}$$

For a collection of N point charges q_n with associated position vectors $\boldsymbol{r}_n$, the energy due to the interaction with the potential $\Phi(\boldsymbol{r})$ is given by

$$V = \Phi(\mathbf{0})\sum_{n=1}^{N} q_n - \left(\sum_{n=1}^{N} q_n\boldsymbol{r}_n\right)\bullet\boldsymbol{E}(\mathbf{0}) - \sum_{n=1}^{N}\frac{q_n}{2}\sum_i\sum_j x_{ni}x_{nj}\frac{\partial E_j}{\partial x_{ni}}(\mathbf{0}) + \cdots, \tag{1.9}$$

where

$$\boldsymbol{r}_n = x_n\hat{\boldsymbol{x}} + y_n\hat{\boldsymbol{y}} + \boldsymbol{z}_n\hat{\boldsymbol{z}} = x_{n1}\hat{\boldsymbol{x}}_1 + x_{n2}\hat{\boldsymbol{x}}_2 + x_{n3}\hat{\boldsymbol{x}}_3. \tag{1.10}$$

The electric dipole moment is given by

$$\boldsymbol{\mu} = \sum_{n=1}^{N} q_n\boldsymbol{r}_n. \tag{1.11}$$

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The components of the electric quadrupole moment tensor for a given charge n can be written as (Struve, 1988)

$$Q_{ij}^{(n)} = \frac{q_n}{2}\left(3x_{ni}x_{nj} - \boldsymbol{r}_n^2\delta_{ij}\right). \tag{1.12}$$

Substituting Eqs. (1.11) and (1.12) into Eq. (1.9), we obtain

$$V = \Phi(\mathbf{0})\sum_{n=1}^{N} q_n - \boldsymbol{\mu}\cdot\boldsymbol{E}(\mathbf{0}) - \frac{1}{6}\sum_{n=1}^{N}\sum_{i}\sum_{j} Q_{ij}^{(n)}\frac{\partial E_j}{\partial x_{ni}}(\mathbf{0}) + \cdots. \tag{1.13}$$

The first term in Eq. (1.13) is the product of the sum of the charges and the scalar potential at $\boldsymbol{r} = \mathbf{0}$, the second term is the dot product of the dipole moment of the charge distribution with the electric field, and the third term describes the interaction of the quadrupole moment of the electric field with the gradients of the electric field.

1.3 The Lorentz Classical Electron Oscillator Model

For an atom or molecule interacting with an electric field oscillating at the very high frequencies associated with visible radiation, the electric dipole moment term is dominant compared to the quadrupole term, except for transitions where electric dipole transitions are forbidden. We begin our discussion of the electric dipole interaction of laser radiation with atoms and molecules by considering the classical electron oscillator model originally developed by Lorentz (2011). The Lorentz classical electron oscillator (CEO) model was developed before the advent of quantum mechanics and our modern picture of the atom consisting of negatively charged electrons orbiting a massive and positively charged nucleus. The CEO model is schematically illustrated in Figure 1.1. In the absence of an external electric field, the center of the electron charge cloud coincides with the positively charged nucleus of the atom, and the electric dipole moment $\boldsymbol{\mu}$ (C-m) of the atom is zero. When a high-frequency oscillating electric field is applied, it is assumed that the electron cloud can respond to the applied force $-eE_x(t)$ but that the position of the massive nucleus is

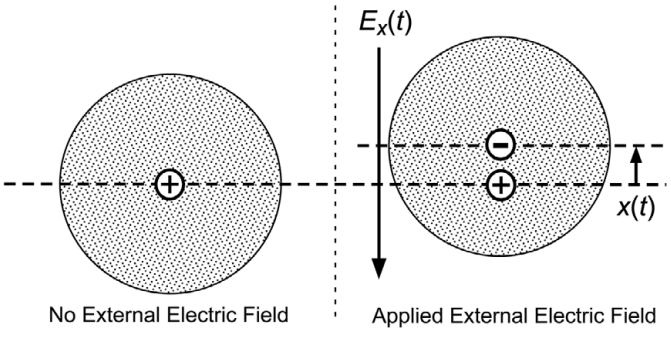

Figure 1.1 Schematic illustration of the CEO model.

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essentially unchanged by the interaction. It is further assumed that the restoring force between the electron cloud and the nucleus is linearly proportional to the displacement of the electron cloud from its equilibrium position. The response of the electron cloud to the oscillating electric field is given by

$$m_e \frac{d^2x(t)}{dt^2} = -Kx(t) - eE_x(t), \tag{1.14}$$

where m_e (kg) is the electron mass, x(m) the electron displacement, $K\,(\mathrm{N/m})$ the magnitude of the restoring force, $e\,(\mathrm{C})$ the magnitude of the electron charge, and $E_x(t)$ $(\mathrm{J/C\text{-}m})$ the electric field amplitude in the x-direction. Equation (1.14) can be rewritten as

$$\frac{d^2x(t)}{dt^2} + \omega_a^2 x(t) = -\left(\frac{e}{m_e}\right)E_x(t). \tag{1.15}$$

The term $\omega_a = \sqrt{K/m_e}\ (\mathrm{s}^{-1})$ is identified as the resonant frequency of the CEO. The motion of the electron cloud is damped by processes such as spontaneous emission, and we therefore introduce a damping constant $\Gamma\,(\mathrm{s}^{-1})$:

$$\frac{d^2x(t)}{dt^2} + \Gamma\frac{dx(t)}{dt} + \omega_a^2 x(t) = -\left(\frac{e}{m_e}\right)E_x(t). \tag{1.16}$$

Before discussing the solution of Eq. (1.16) in the presence of an applied electric field, we consider the solution of the equation given a nonzero initial displacement $x(0)$ and zero applied electric field. The solution to Eq. (1.16) under these conditions is given by

$$x(t) = x(0)\exp\left[-\frac{\Gamma t}{2}\right][\exp(-i\omega_{a1}t) + \exp(+i\omega_{a1}t)]. \tag{1.17}$$

The electron amplitude given by Eq. (1.17) contains an oscillating term with frequency ω_{a1} given by

$$\omega_{a1} = \sqrt{\omega_a^2 - \left(\frac{\gamma}{2}\right)^2}. \tag{1.18}$$

For optical transitions, $\omega_{a1} \cong \omega_a$. The amplitude of the initial displacement decays with a time constant of $2/\Gamma$. In the absence of collisions, the decay rate Γ is associated with the rate of spontaneous emission for the CEO. The amplitude of the initial displacement can also decay as a result of inelastic collisions.

Usually we are concerned not with the interaction of laser radiation with a single atom but with a collection of atoms in a small volume element. Rewriting Eq. (1.16) in terms of the electric dipole moment $\mu_x(t) = -ex(t)$, we obtain

$$\frac{d^2\mu_x(t)}{dt^2} + \Gamma\frac{d\mu_x(t)}{dt} + \omega_a^2\mu_x(t) = \left(\frac{e^2}{m_e}\right)E_x(t). \tag{1.19}$$

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The macroscopic polarization per unit volume $p_x(t)$ (C-m/m^3) is given by summing over all the atoms in a small volume element and then dividing by the volume,

$$p_x(t) = \frac{1}{\forall}\sum_{i=1}^{N}\mu_{xi}(t). \tag{1.20}$$

The decay rate of the macroscopic polarization is in general greater than the decay rate of the dipole moments for the individual molecules because of elastic pure dephasing collisions. Consider a group of three atoms with electron clouds oscillating in phase at time zero. The amplitude of the macroscopic polarization will be a maximum at time zero. At time t_1, one of the atoms undergoes an elastic pure dephasing collision. As a result of the collision, it is assumed that the phase of the electron cloud oscillation is randomized. On average, the individual dipole moment of the atom that undergoes the collision no longer contributes to the macroscopic polarization, and the amplitude of the macroscopic polarization decreases. This is illustrated in Figure 1.2, where the results of pure dephasing collisions at times t_2 and t_3 are also shown.

Consider N_0 atoms with dipole moments oscillating in phase at time t_0. At time $t - t_0$, $N_0 - \tilde{N}(t)$ of these atoms will have undergone pure dephasing collisions, where $\tilde{N}(t)$ is given by

$$\tilde{N}(t) = N_0 \exp\left(-\frac{t - t_0}{T_2}\right) = N_0\left[-Q_{pd}(t - t_0)\right]. \tag{1.21}$$

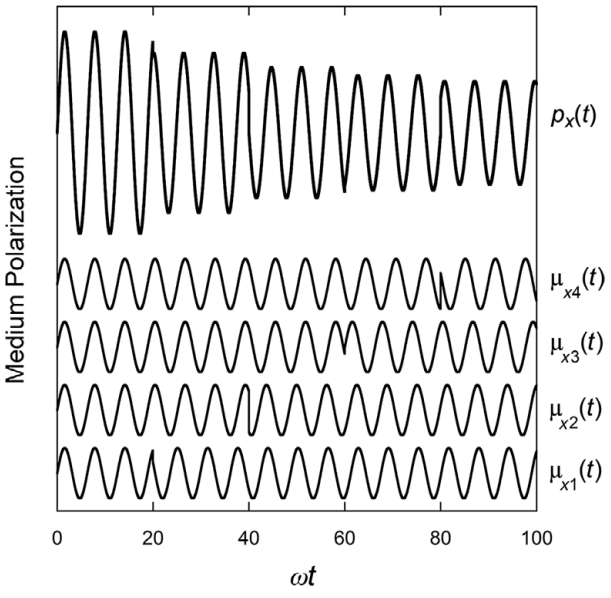

Figure 1.2 Effect of dephasing collisions on the macroscopic dipole polarization of the medium.

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The parameters T_2 (s) and Q_{pd} (s^{-1}) are the characteristic time and rate coefficient, respectively, for pure dephasing collisions. After time t, the macroscopic polarization of the medium will be given by

$$\begin{aligned} p_x(t) &= \tilde{n}(t)\mu_x(t) \\ &= n_0\mu_x(t_0)\exp\left[-\left(\frac{\gamma}{2}+Q_{pd}\right)(t-t_0)+i\omega_a(t-t_0)+i\varphi_0\right]+\text{c.c.}, \end{aligned} \tag{1.22}$$

where the number densities $\tilde{n}(t)$ and n_0 (m^{-3}) are given by $\tilde{N}(t)/\forall$ and $N_0/\forall$, respectively, and the abbreviation c.c. denotes the complex conjugate of the preceding term. The initial phase of the oscillators at time t_0 is φ_0. Comparing Eqs. (1.17) and (1.22), it is apparent that the macroscopic polarization decays with a rate coefficient of $\frac{\Gamma}{2}+Q_{pd}$ as compared to a rate coefficient of $\frac{\Gamma}{2}$ for a single atomic dipole.

Incorporating the effects of the pure dephasing collisions, we rewrite Eq. (1.19) as

$$\frac{d^2p_x(t)}{dt^2}+\left(\Gamma+2Q_{pd}\right)\frac{dp_x(t)}{dt}+\omega_a^2p_x(t)=\left(\frac{ne^2}{m_e}\right)E_x(t). \tag{1.23}$$

Consider the response of the medium to an oscillating electric field given by

$$E_x(t)=\frac{1}{2}\left[E_{0x}\exp(+i\omega t)+E_{0x}^*\exp(-i\omega t)\right]. \tag{1.24}$$

Assume that the applied electric field at angular frequency ω induces a polarization at the same frequency,

$$p_x(t)=\frac{1}{2}\left[P_{0x}\exp(+i\omega t)+P_{0x}^*\exp(-i\omega t)\right]. \tag{1.25}$$

The steady-state response of the medium is determined by substituting Eqs. (1.24) and (1.25) into Eq. (1.23). Rearranging and equating terms that contain $\exp(+i\omega t)$, we solve for the steady-state polarization amplitude,

$$P_{0x}=\frac{ne^2}{m_e}E_{0x}\frac{1}{\omega_a^2-\omega^2+i\omega\left(\Gamma+2Q_{pd}\right)}. \tag{1.26}$$

The resonant susceptibility $\chi_{res}(\omega)$ is given by

$$\chi_{res}(\omega)=\frac{P_{0x}}{\varepsilon_0E_{0x}}=\left(\frac{ne^2}{m_e}\right)\frac{1}{\omega_a^2-\omega^2+i\omega\left(\Gamma+2Q_{pd}\right)}, \tag{1.27}$$

where ε_0 is the dielectric permittivity and has a value of 8.854187×10^{-12} C^2/J m for free space. The resonant susceptibility is a complex quantity. Following Siegman (1986), the atomic linewidth $\Delta\omega_a$ (s^{-1}) is defined as

$$\Delta\omega_a=\Gamma+2Q_{pd}. \tag{1.28}$$

Further, it is assumed that the laser frequency ω is close to the resonant frequency ω_a and the following approximation is assumed to be valid:

$$\omega_a^2-\omega^2=(\omega_a+\omega)(\omega_a-\omega)\cong2\omega_a(\omega_a-\omega)\quad\text{for}\ \ \omega_a\cong\omega. \tag{1.29}$$

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Using Eqs. (1.28) and (1.29), we rewrite Eq. (1.27) as

$$\chi_{res}(\omega) = \frac{ne^2}{\varepsilon_0 m_e}\left[\frac{1}{2\omega_a(\omega_a - \omega) + i\omega_a\Delta\omega_a}\right] = -i\frac{ne^2}{\varepsilon_0 m_e \omega_a \Delta\omega_a}\frac{1}{1 + i\Delta x}, \tag{1.30}$$

where the normalized detuning Δx is given by

$$\Delta x = 2\frac{\omega - \omega_a}{\Delta\omega_a}. \tag{1.31}$$

The real and imaginary components of the susceptibility are given by

$$\chi_{res}(\omega) = \chi'(\omega) + i\chi''(\omega) = -\chi_0''\left[\frac{\Delta x}{1 + (\Delta x)^2} + i\frac{1}{1 + (\Delta x)^2}\right], \tag{1.32}$$

where

$$\chi_0'' = \frac{ne^2}{\varepsilon_0 m_e \omega_a \Delta\omega_a}. \tag{1.33}$$

The real or dispersive component of the susceptibility is given by

$$\chi'(\omega) = -\chi_0''\frac{\Delta x}{1 + (\Delta x)^2} \tag{1.34}$$

and the imaginary or absorbing component of the susceptibility is given by

$$\chi''(\omega) = -\chi_0''\frac{1}{1 + (\Delta x)^2}. \tag{1.35}$$

The normalized line shapes for the real and imaginary components of the resonant susceptibility are plotted in Figure 1.3. The real part of the susceptibility oscillates in phase with the applied electric field, and the imaginary part of the susceptibility oscillates 90° out of phase with the applied electric field. The real part of the susceptibility is much greater than the imaginary part of the susceptibility when the laser field is far from resonance ($\Delta x \gg 1$). Because the real part of the susceptibility oscillates in phase with the applied field, the integral of $\boldsymbol{F}\cdot\mathbf{v} = -e\boldsymbol{E}\cdot\mathbf{v}$ over a complete cycle of the electric field is zero, and there is no energy exchange with the applied field. For a laser field in exact resonance ($\Delta x = 0$), the response is purely imaginary, and the integral of $-e\boldsymbol{E}\cdot\mathbf{v}$ over a complete cycle of the applied field is nonzero.

As discussed in detail by Siegman (1986), at this point some quantum mechanical results can be incorporated into this purely classical picture of the interaction of the electron cloud with the applied field. The resonant frequency ω_a in Eq. (1.33) can be written as

$$\omega_a = \frac{(\varepsilon_e - \varepsilon_g)}{\hbar}, \tag{1.36}$$

where ε_e and ε_g are the energies (J) of the upper (excited) and lower (ground) quantum states for an allowed radiative transition. Furthermore, the number density n in Eq. (1.33) is replaced by the number density difference $(n_g - n_e)$. We can rewrite Eq. (1.33) as

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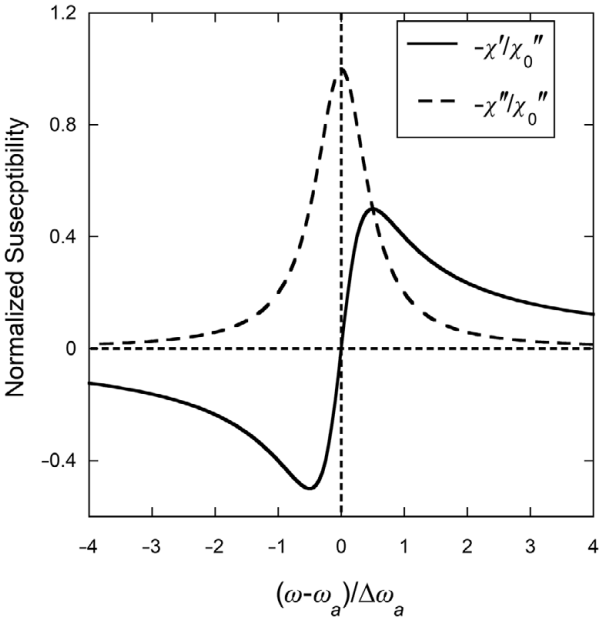

Figure 1.3 Normalized real and imaginary components of the complex resonant susceptibility.

$$\chi_0'' = \frac{(n_g - n_e)e^2}{\varepsilon_0 m_e \omega_a \Delta\omega_a}. \tag{1.37}$$

Whether the electron cloud gains or loses energy will depend on the relative phase of the applied field and the electron motion. The electron cloud gains energy by absorption from the field when the population of the lower energy level of the transition is greater than the population of the upper energy level of the transition; it loses energy by stimulated emission when the population of the upper energy level of the transition is greater than the population of the lower energy level of the transition.

To illustrate the energy exchange between the field and the oscillating electron cloud, consider the case of exact resonance, $\omega = \omega_a, \Delta x = 0$. If the incident plane wave electric field is given by

$$\boldsymbol{E}(t) = E_{0x}\cos(\omega t)\hat{\boldsymbol{x}}, \tag{1.38}$$

where E_{0x} is a real and constant, then from Eqs. (1.27) and (1.32) we obtain

$$P_{0x} = -i\varepsilon_0 \chi_0'' E_{0x}. \tag{1.39}$$

From Eq. (1.25), the macroscopic polarization is given by

$$\begin{aligned} p_x(t) &= \frac{1}{2}\left[-i\varepsilon_0 \chi_0'' E_{0x}\exp(+i\omega t) + i\varepsilon_0 \chi_0'' E_{0x}\exp(-i\omega t)\right] \\ &= \varepsilon_0 \chi_0'' E_{0x}\sin(\omega t). \end{aligned} \tag{1.40}$$

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We can define a displacement of the electron cloud for each atom in the medium as

$$x_e(t) = -\frac{p_x(t)}{(n_g + n_e)e} = -\frac{\varepsilon_0 \chi_0'' E_{0x} \sin(\omega t)}{(n_g + n_e)e}. \tag{1.41}$$

The velocity of the electron cloud is given by

$$\mathrm{v}_e(t) = \dot{x}_e(t) = -\frac{\varepsilon_0 \chi_0'' E_{0x}}{(n_g + n_e)e} \omega \cos(\omega t). \tag{1.42}$$

Substituting for χ_0'' in Eqs. (1.41) and (1.42) using Eq. (1.37), we obtain

$$x_e(t) = -\frac{eE_{0x}(n_g - n_e)}{m_e \omega \Delta\omega_a (n_g + n_e)} \sin(\omega t) \tag{1.43}$$

and

$$\mathrm{v}_e(t) = \dot{x}_e(t) = -\frac{eE_{0x}(n_g - n_e)}{m_e \Delta\omega_a (n_g + n_e)} \cos(\omega t). \tag{1.44}$$

Normalized values of the electric field, the position and velocity of the electron cloud, and the force acting on the electron cloud will now be plotted for the case of a "normal" population distribution $(n_g > n_e)$ and a population inversion $(n_g < n_e)$. The normalized input electric field is given by $E_x(t)/E_{0x}$. The normalized force on the electron cloud is given by

$$\tilde{F}_x(t) = \frac{F_x(t)}{eE_{0x}} = -\frac{eE_x(t)}{eE_{0x}} = -\cos(\omega t). \tag{1.45}$$

The normalized electron cloud displacement is given by

$$\tilde{x}_e(t) = \frac{1}{2} \frac{x_e(t) m_e \omega \Delta\omega_a (n_g + n_e)}{eE_{0x} |n_g - n_e|} = -\frac{(n_g - n_e)}{2|n_g - n_e|} \sin(\omega t). \tag{1.46}$$

The factor of $\frac{1}{2}$ is introduced in Eq. (1.46) to make it easier to see the difference between the electric field and the electron cloud displacement. The normalized electron cloud velocity is given by

$$\tilde{\mathrm{v}}_e(t) = \frac{1}{2} \frac{\mathrm{v}_e(t) m_e \Delta\omega_a (n_g + n_e)}{eE_{0x} |n_g - n_e|} = -\frac{(n_g - n_e)}{2|n_g - n_e|} \cos(\omega t). \tag{1.47}$$

Again, the factor of $\frac{1}{2}$ is introduced to make it easier to see the difference between the normalized force on the electron cloud and the normalized electron velocity.

The normalized position of the electron cloud is plotted as a function of the normalized electric field in Figure 1.4. The "normal" population distribution case is shown in Figure 1.4a, and the population inversion case is shown in Figure 1.4b. Note that in both cases the electron position is oscillating 90° out of phase with the driving electric field.

The normalized velocity of the electron cloud is plotted as a function of the normalized force on the electron in Figure 1.5. The "normal" population distribution

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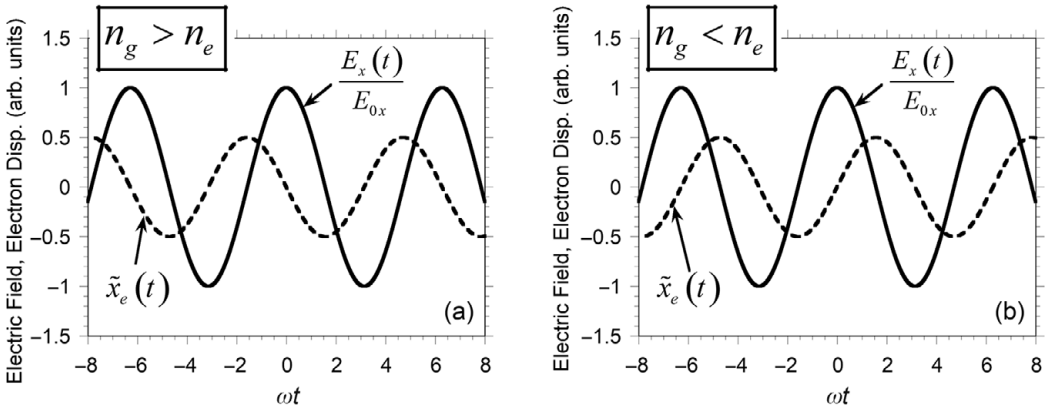

Figure 1.4 Normalized electric field and electron cloud displacement for (a) a "normal" population distribution and (b) a population inversion.

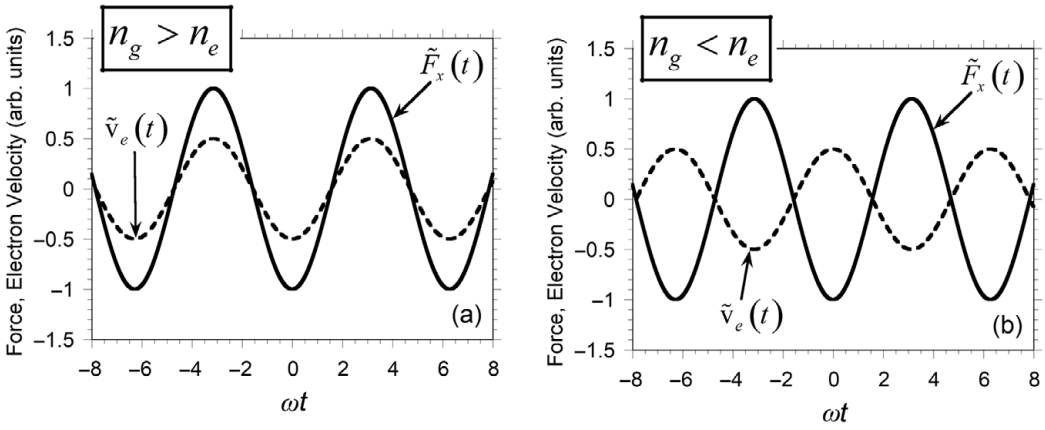

Figure 1.5 Normalized force on the electron and electron velocity for (a) a "normal" population distribution and (b) a population inversion.

case is shown in Figure 1.5a, and the population inversion case is shown in Figure 1.5b. For the "normal" population distribution case, the velocity of the electron cloud is in phase with the force imposed by the driving field. Thus, the electron cloud continually gains energy due to its interaction with the driving field, which results in a decrease of energy for the driving electric field, or in other words through stimulated absorption of the input plane wave electromagnetic field. Conversely, for the population inversion case, the velocity of the electron cloud is 180° out of phase with the driving field. The electron cloud continually loses energy, resulting in an increase of energy for the input electromagnetic field. The medium is said to exhibit "gain" in the case of a population inversion due to the phenomenon of stimulated emission.

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There are further refinements to the CEO model that would be necessary to develop a model of the resonance that is rigorously correct. Rather than incorporate these quantum mechanical details at this point, we will discuss the quantum structure of atoms and molecules in Chapters 2 and 3 and the quantum mechanical theory of resonance interactions in Chapter 4.

1.4 Propagation of an Applied Laser Field through an Absorbing or Emitting Medium

In Section 1.2 expressions for the macroscopic polarization of a medium were developed. In this section the effect of the medium's polarization on the propagation of a plane wave electromagnetic field is discussed. The equation for a plane wave propagating in free space is given by (Siegman, 1986)

$$\nabla^2 \boldsymbol{E} - \mu_0 \varepsilon_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = \frac{\partial^2 \boldsymbol{E}}{\partial z^2} - \mu_0 \varepsilon_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = 0, \tag{1.48}$$

where the magnetic permeability μ_0 has a value of $4\pi \times 10^{-7}$ J s^2/C^2 m for free space. The speed of light in free space is given by

$$c = c_0 = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}. \tag{1.49}$$

For a plane wave polarized in the x-direction and propagating in the z-direction, the solution to the wave equation is given by

$$\boldsymbol{E}(z,t) = \hat{\boldsymbol{x}} \left\{ \frac{1}{2} E_0 \exp[+i(kz - \omega t)] + \frac{1}{2} E_0^* \exp[-i(kz - \omega t)] \right\}, \tag{1.50}$$

where the propagation constant k (m^{-1}) is given by

$$k = \frac{2\pi}{\lambda}, \tag{1.51}$$

where λ(m) is the wavelength of the plane wave. The angular frequency ω is given by

$$\omega = \frac{2\pi c}{\lambda} = 2\pi \nu, \tag{1.52}$$

where ν (Hz) is the optical frequency of the plane wave.

For propagation in a dielectric medium containing atoms or molecules with electric dipole resonance transitions, the wave equation becomes

$$\frac{\partial^2 \boldsymbol{E}}{\partial z^2} - \mu_0 \varepsilon_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \boldsymbol{P}}{\partial t^2}, \tag{1.53}$$

where

$$\boldsymbol{P} = \chi_{res}(\omega) \varepsilon_0 \boldsymbol{E}. \tag{1.54}$$

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We will assume that a plane wave defined by Eq. (1.50) enters the dielectric medium at $z = 0$, i.e.,

$$\boldsymbol{E}(0,t) = \hat{\boldsymbol{x}}\left[\frac{1}{2}E_0 \exp(-i\omega t) + \text{c.c.}\right]. \tag{1.55}$$

The solution for the wave equation in the dielectric medium is

$$\boldsymbol{E}(z,t) = \frac{1}{2}\hat{\boldsymbol{x}}E_0 \exp\{+i[(k + \Delta k_{res})z - \omega t]\} \exp(+\alpha_{res} z) + \text{c.c.}, \tag{1.56}$$

where

$$\Delta k_{res} = \left(\frac{k}{2}\right)\chi'(\omega) \tag{1.57}$$

and

$$\alpha_{res} = \left(\frac{k}{2}\right)\chi''(\omega). \tag{1.58}$$

The effect of the medium's polarization is thus to induce both a phase shift and an amplitude change in the propagating EM wave. The phase shift is due to the real part of the resonant susceptibility, and the amplitude change is due to the imaginary part of the susceptibility.

1.5 Emission of Electromagnetic Radiation by the Classical Electron Oscillator

In this section the electromagnetic field radiated by the classical electron oscillator is discussed. For an arbitrary distribution of charge and current, the scalar and vector potentials, $\Phi(\boldsymbol{r},t)$ and $\boldsymbol{A}(\boldsymbol{r},t)$, respectively, are given by (Becker 1964; Marion and Heald 1980)

$$\Phi(\boldsymbol{r},t) = \frac{1}{4\pi\varepsilon_0}\iiint \frac{\rho(\boldsymbol{r}',\tau)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,dx'dy'dz' = \frac{1}{4\pi\varepsilon_0}\int_{\forall}\frac{\rho(\boldsymbol{r}',\tau)}{|\boldsymbol{r}-\boldsymbol{r}'|}d\forall', \tag{1.59}$$

$$\boldsymbol{A}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi}\int_{\forall}\frac{\boldsymbol{J}(\boldsymbol{r}',\tau)}{|\boldsymbol{r}-\boldsymbol{r}'|}d\forall', \tag{1.60}$$

where ρ is the charge density (C/m^3), $\boldsymbol{J}$ is the current density (A/m^2), and the variable $\tau(\text{s})$ is the retarded time,

$$\tau = t - \frac{|\boldsymbol{r}-\boldsymbol{r}'|}{c}. \tag{1.61}$$

For the calculation of the radiation field from the oscillating dipole, we assume that the dipole is confined to a volume element at the origin with a characteristic dimension d that is very small compared to our region of interest $(d \ll r = |\boldsymbol{r}|)$. The coordinate

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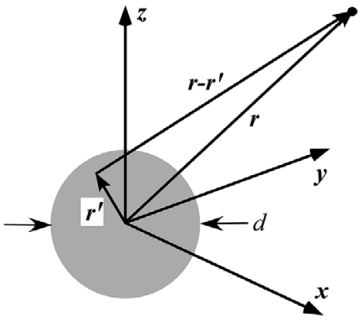

Figure 1.6 Geometry for the calculation of the electromagnetic radiation emitted by a distribution of current confined within a region with a characteristic dimension d.

system for the calculations is shown in Figure 1.6. The dipole is located the origin of the coordinate system so that

$$r = |\boldsymbol{r}| = \sqrt{x^2 + y^2 + z^2}. \tag{1.62}$$

With this assumption we can rewrite Eq. (1.60) as

$$\boldsymbol{A}(\boldsymbol{r}, t) = \frac{\mu_0}{4\pi r} \int_{\forall} \boldsymbol{J}(\boldsymbol{r}', \tau) d\forall'. \tag{1.63}$$

The current density is the product of charge density and velocity,

$$\boldsymbol{J}(\boldsymbol{r}', \tau) = \rho(\boldsymbol{r}', \tau)\mathbf{v}(\boldsymbol{r}', \tau). \tag{1.64}$$

For a collection of discrete charges within the volume element, the integral in Eq. (1.63) reduces to

$$\boldsymbol{A}(\boldsymbol{r}, t) = \frac{\mu_0}{4\pi r} \int_{\forall} \rho(\boldsymbol{r}', \tau)\mathbf{v}(\boldsymbol{r}', \tau) d\forall' = \frac{\mu_0}{4\pi r} \sum_i q_i \mathbf{v}_i(\boldsymbol{r}', \tau). \tag{1.65}$$

Specializing to the case where an electron (cloud) is executing harmonic motion about an atomic nucleus, we obtain

$$\boldsymbol{A}(\boldsymbol{r}, t) = \frac{\mu_0}{4\pi r} [-e\mathbf{v}_e(\boldsymbol{r}', \tau)] = \frac{\mu_0}{4\pi r} \left[-e \frac{d\boldsymbol{r}_e(\boldsymbol{r}', \tau)}{d\tau}\right] = \frac{\mu_0}{4\pi r} \frac{d\boldsymbol{\mu}(\boldsymbol{r}', \tau)}{d\tau}. \tag{1.66}$$

The magnetic field of the emitted radiation is given by

$$\begin{aligned} \boldsymbol{B}(\boldsymbol{r}, t) &= \nabla \times \boldsymbol{A}(\boldsymbol{r}, t) = \frac{\mu_0}{4\pi} \nabla \times \left[\frac{1}{r} \frac{d\boldsymbol{\mu}(\tau)}{d\tau}\right] \\ &= \frac{\mu_0}{4\pi} \nabla\left(\frac{1}{r}\right) \times \frac{d\boldsymbol{\mu}(\tau)}{d\tau} + \frac{\mu_0}{4\pi r} \nabla \times \left(\frac{d\boldsymbol{\mu}(\tau)}{d\tau}\right) \\ &= -\frac{\mu_0}{4\pi r^3} \boldsymbol{r} \times \dot{\boldsymbol{\mu}}(\tau) + \frac{\mu_0}{4\pi r} \nabla \times \dot{\boldsymbol{\mu}}(\tau). \end{aligned} \tag{1.67}$$

In the far field, the first term on the right-hand side is negligible compared to the second term. Eliminating the first term, we obtain

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$$\boldsymbol{B}(\boldsymbol{r},t)=\frac{\mu_0}{4\pi r}\nabla\times\dot{\boldsymbol{\mu}}(\tau). \tag{1.68}$$

At this point we solve for the x-component of the magnetic field. Using Eq. (1.62) we obtain

$$\begin{aligned}B_x(\boldsymbol{r},t)&=\frac{\mu_0}{4\pi r}\left[\frac{\partial\dot{\mu}_z(\tau)}{\partial y}-\frac{\partial\dot{\mu}_y(\tau)}{\partial z}\right]=\frac{\mu_0}{4\pi r}\left[\frac{\partial\dot{\mu}_z(\tau)}{\partial\tau}\frac{\partial\tau}{\partial y}-\frac{\partial\dot{\mu}_y(\tau)}{\partial\tau}\frac{\partial\tau}{\partial z}\right]\\&=\frac{\mu_0}{4\pi r}\left[\ddot{\mu}_z(\tau)\frac{\partial\tau}{\partial y}-\ddot{\mu}_y(\tau)\frac{\partial\tau}{\partial z}\right]=\frac{\mu_0}{4\pi r}\left[\ddot{\mu}_z(\tau)\left(-\frac{y}{cr}\right)-\ddot{\mu}_y(\tau)\left(-\frac{z}{cr}\right)\right]\\&=\frac{\mu_0}{4\pi cr^2}\left[\ddot{\mu}_y(\tau)z-\ddot{\mu}_z(\tau)y\right].\end{aligned} \tag{1.69}$$

A similar analysis for the y- and z-components of the magnetic field results in

$$\begin{aligned}B_y(\boldsymbol{r},t)&=\frac{\mu_0}{4\pi cr^2}\left[\ddot{\mu}_z(\tau)x-\ddot{\mu}_x(\tau)z\right]\\B_z(\boldsymbol{r},t)&=\frac{\mu_0}{4\pi cr^2}\left[\ddot{\mu}_x(\tau)y-\ddot{\mu}_y(\tau)x\right].\end{aligned} \tag{1.70}$$

Generalizing, we obtain

$$\boldsymbol{B}(\boldsymbol{r},t)=\frac{\mu_0}{4\pi cr^2}\ddot{\boldsymbol{\mu}}(\tau)\times\boldsymbol{r}. \tag{1.71}$$

The electric field due to the dipole is given by

$$\boldsymbol{E}(\boldsymbol{r},t)=\boldsymbol{B}(\boldsymbol{r},t)\times\frac{\boldsymbol{r}}{r}=\frac{\mu_0}{4\pi cr^3}(\ddot{\boldsymbol{\mu}}(\tau)\times\boldsymbol{r})\times\boldsymbol{r}. \tag{1.72}$$

Now consider an electron cloud executing harmonic motion along the z-axis. The polarization and the second derivative of the polarization are given by

$$\boldsymbol{\mu}(\tau)=a\cos(\omega\tau)\hat{\boldsymbol{z}}\quad\ddot{\boldsymbol{\mu}}(\tau)=-\omega^2a\cos(\omega\tau)\hat{\boldsymbol{z}}, \tag{1.73}$$

where $a(\mathrm{m})$ is the amplitude of the harmonic motion of the electron cloud (the symbol μ_0 would have been more appropriate for the amplitude but would be too easy to confuse with the magnetic permeability). The magnetic and electric fields due to the harmonic motion of the dipole are given by

$$\boldsymbol{B}(\boldsymbol{r},t)=\frac{\mu_0}{4\pi cr^3}\left[-\omega^2a\cos(\omega\tau)\hat{\boldsymbol{z}}\times\boldsymbol{r}\right]=-\frac{\mu_0\omega^2a\cos(\omega\tau)}{4\pi cr}\sin\theta\hat{\boldsymbol{\varphi}}, \tag{1.74}$$

$$\boldsymbol{E}(\boldsymbol{r},t)=\frac{\mu_0}{4\pi cr^3}\left[-\omega^2a\cos(\omega\tau)\hat{\boldsymbol{z}}\times\boldsymbol{r}\right]\times\boldsymbol{r}=-\frac{\mu_0\omega^2a\cos(\omega\tau)}{4\pi cr}\sin\theta\hat{\boldsymbol{\theta}}, \tag{1.75}$$

The Poynting vector for the dipole is given by

$$\boldsymbol{S}(\boldsymbol{r},t)=\boldsymbol{E}(\boldsymbol{r},t)\times\boldsymbol{H}(\boldsymbol{r},t)=\frac{\mu_0^2\omega^4a^2\cos^2(\omega\tau)}{16\pi^2c^2r^2}\sin^2\theta. \tag{1.76}$$

We calculate the total power W radiated by the dipole oscillator by integrating over all solid angles and averaging over a single cycle of the oscillator. The result is

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$$W = \frac{d\varepsilon_d}{dt} = -\frac{\omega^4 a^2}{12\pi\varepsilon_0 c^3}. \tag{1.77}$$

The energy associated with the harmonic oscillation of the electron cloud is given by

$$\varepsilon_d = \frac{1}{2}Ka^2 = \frac{1}{2}m_e\omega^2 a^2. \tag{1.78}$$

Substituting Eq. (1.78) into Eq. (1.77) and rearranging, we obtain

$$W = \frac{d\varepsilon_d}{dt} = -\frac{e^2\omega^2\varepsilon_d}{6\pi m_e\varepsilon_0 c^3}. \tag{1.79}$$

If an oscillator has an initial energy ε_{d0} in the absence of an applied field, the time dependence of the dipole energy is given by

$$\varepsilon_d = \varepsilon_{d0}\exp\left(-\gamma_{rad,ceo}\,t\right), \tag{1.80}$$

where

$$\gamma_{rad,ceo} = \frac{e^2\omega^2}{6\pi m_e\varepsilon_0 c^3}. \tag{1.81}$$

The radiative decay rate $\gamma_{rad,ceo}$ (s^{-1}) is proportional to the square of the angular frequency of the electric dipole operator. For electric dipole transitions in atoms and molecules, spontaneous emission is responsible for the decay of the induced electric dipole, and the spontaneous emission rate coefficient Γ_{spe} (s^{-1}) is analogous to the radiative decay rate. The radiative decay rate of the classical electron oscillator is an upper limit on the decay rate Γ_{spe} (s^{-1}) for an actual atomic or molecular electric dipole transition.

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