

Four Wave Mixing

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Abstract

In this essay we will be exploring the process arising from the interaction of coherent waves in optical fields through the third order nonlinear susceptibility. Effects from this interaction include the Raman- enhanced four wave mixing , sum frequency generation, difference frequency generation and third harmonic generation. We will be mainly concerned with the case of third harmonic generation in the nonlinear medium in which case our nonlinear medium is a gaseous mixture of a metal vapour and an inert gas in a heat pipe.

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1. Concepts

1.1 Introduction

The field of nonlinear optics was ushered in with the development of the first laser by Maiman in 1960. Though nonlinear effects had been known as early as the nineteenth century (The Pockels and Kerr effects), only DC fields were produced with high enough intensity to produce nonlinear optical response. The lack of high intensity fields meant that nonlinear responses could not be observed. However, nonlinear response was demonstrated by Franken and co-workers in 1961 in which second harmonic generation was demonstrated in quartz with the use of a ruby laser. As more sources of coherent optical radiation were discovered, some nonlinear optical phenomena were then observed. Some of these observed effects were two-photon absorption by Kaiser and Garrett, stimulated Raman scattering by Ng and Woodbury, third harmonic generation by Maker and co-workers, and anti-Stokes frequency mixing by Terhune and co-workers. After the observations of optical nonlinearities were made, a theoretical explanation of these observations were provided based on nonlinear response of electron oscillation in the atomic Coulomb field.[1]

In this chapter we shall give an introduction to linear optics and in subsequent chapters we shall extend our discussion to nonlinear optics.

1.2 Maxwell's Equations

Maxwell's equations predict the propagation of transversely oscillating electromagnetic waves. The equations predict the velocity of light, c , in a vacuum as $c = (\mu_0\epsilon_0)^{\frac{1}{2}}$, and this is in agreement with independent measurements of the velocity of light[2]. The velocity of light that is obtained is based on the permeability μ_0 and the permittivity ϵ_0 of vacuum. The Maxwell's equations, in differential forms, are[3]:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (1.1)$$

$$\nabla \times \mathbf{B} = \mu \left(\mathbf{J} + \epsilon \frac{\partial \mathbf{E}}{\partial t} \right), \quad (1.2)$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon}, \quad (1.3)$$

$$\nabla \cdot \mathbf{B} = 0. \quad (1.4)$$

1.3 Linear Polarisation and Harmonic Oscillator

The electromagnetic wave has no perpendicular electric field in the direction of propagation. The electric field, \mathbf{E} , associated with the plane wave is transverse. For a linearly polarised wave,

the orientation of the electric field is constant. Let us consider an isotropic medium (a medium in which the physical properties are independent of direction) made up of dipoles (a system of two oppositely charged particles separated by a distance). The charged particles in this case are the electrons and the protons. The protons form the nucleus of the atom. The application of an electric field to the medium causes the charges to be displaced and the negative charge distribution bound to the nuclei is displaced in a direction opposite to the electric field while the positive end of the dipole is displaced in the direction of the electric field. This shift of the electron cloud relative to the nucleus results in an induced dipole and hence we define the dipole moment \mathbf{p} due to each atom as the product of the displacement charge e and the effective separation, \mathbf{r} , of the negative charge in the atomic dipole. This can be written as

$$\mathbf{p} = -e\mathbf{r}. \quad (1.5)$$

The direction of the dipole moment is from the negative toward the positive charge and its magnitude depends on the ease with which the charge is displaced under the influence of an applied field. With the above definition of the dipole moment, we can then define the polarisation \mathbf{P} of the medium as the dipole moment per unit volume, written as

$$\mathbf{P} = -Ner, \quad (1.6)$$

where N is the number of elementary dipoles per unit volume or the number density, and e is the magnitude of the electronic charge. If electrons behave as though they are connected by springs, then the forces binding them can be described by Hooke's law, where the restoring force is proportional to the displacement of the electron cloud and oppositely directed to the displacement. Thus we consider for our case, a simple model where electrons are held by a spring-like force. The elastic potential energy function, V , is given by

$$V = \frac{1}{2}K\mathbf{r}^2, \quad (1.7)$$

where K is the force constant of the spring. The potential energy varies quadratically with \mathbf{r} as in (1.7). Ideally, springs do not follow (1.7) exactly and neither does the molecular oscillator[4]. The effective potential energy can be written as a power series in \mathbf{r} but for small oscillations the terms higher than the quadratic terms have negligible effect on the potential energy. The terms of orders higher than \mathbf{r}^2 are responsible for the nonlinear optical effects as will be discussed in the proceeding chapters. The force on the electrons due to an electromagnetic field is the Lorentz force[4] which is given by

$$\mathbf{F} = q\mathbf{E} + e\mathbf{v} \times \mathbf{B}, \quad (1.8)$$

where \mathbf{E} is the electric field, \mathbf{B} the magnetic field and \mathbf{v} is the velocity of the electron. The velocity of the electron is small compared to the velocity of light in vacuum and hence the magnetic force ($e\mathbf{v} \times \mathbf{B}$) on the electron is negligible compared to the force due to the electric field. This model of the oscillating electron is that of a damped harmonic oscillator and the frictional force is proportional to the velocity. Applying Newton's second law to this model, we obtain the equation of motion as

$$-K\mathbf{r} - m\gamma\frac{d\mathbf{r}}{dt} - e\mathbf{E} = m\frac{d^2\mathbf{r}}{dt^2} \quad (1.9)$$

where m is the electronic mass, and γ is the frictional constant with dimensions of reciprocal time. For static fields, the dipoles are assumed not to be oscillating and the velocity in this case is taken to be zero. Thus, (1.9) then becomes

$$-K\mathbf{r} = e\mathbf{E}, \quad (1.10)$$

and using the substitution for \mathbf{r} in (1.10) we then obtain the static polarisation as

$$\mathbf{P} = \frac{Ne^2\mathbf{E}}{K}. \quad (1.11)$$

Suppose that \mathbf{E} is a field of harmonic wave with a time dependence given by $\mathbf{E} = \mathbf{E}_0e^{-i\omega t}$ and the time dependence of the electron oscillation is $\mathbf{r} = \mathbf{r}_0e^{-i\omega t}$ [2], we then write (1.9) as

$$\mathbf{r} = \frac{-e\mathbf{E}}{-m\omega^2 - im\omega\gamma + K}, \quad (1.12)$$

which is the relative displacement between the negative and positive nucleus. Substituting the above equation into (1.6) and solving for \mathbf{P} , we obtain the polarisation as

$$\mathbf{P} = \left(\frac{Ne^2}{-m\omega^2 - im\omega\gamma + K} \right) \mathbf{E}, \quad (1.13)$$

and this is in good agreement with the polarisation for a static field given by (1.11) where $\omega = \gamma = 0$. For all other cases the polarisation is a function of the radiation frequency ω and the imaginary part leads to a phase shift in the response under certain conditions. Let us define the resonance or absorption frequency ω_0 as

$$\omega_0 = \left(\frac{K}{m} \right)^{\frac{1}{2}}, \quad (1.14)$$

and then substituting (1.14) into the expression for the polarisation (1.13), we obtain the relation

$$\mathbf{P} = \frac{\frac{Ne^2}{m}}{\omega_0^2 - \omega^2 - i\omega\gamma} \mathbf{E}, \quad (1.15)$$

which is of the form of a driven harmonic oscillator with damping. With the driving frequency close to the resonance frequency ω_0 , the amplitude of the vibrations becomes large and subsides again as the frequency increases beyond the resonance frequency.

1.4 Linear Polarisation and Refractive Index

In a dielectric the free charge and current densities ρ_f and \mathbf{J}_f are zero respectively and with these restrictions we can write Maxwell's equation in a dielectric as[3]

$$\nabla \cdot \mathbf{E} = \frac{-\nabla \cdot \mathbf{P}}{\epsilon_0}, \quad (1.16)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (1.17)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1.18)$$

$$c^2 \nabla \times \mathbf{B} = \frac{\partial \mathbf{E}}{\partial t} + \frac{1}{\epsilon} \frac{\partial \mathbf{P}}{\partial t}. \quad (1.19)$$

We then take the curl of (1.17) and making use of Maxwell's equations, we then obtain

$$c^2 \nabla^2 \mathbf{E} = \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{1}{\epsilon_0} \frac{\partial^2 \mathbf{P}}{\partial t^2}. \quad (1.20)$$

Substituting (1.15) into (1.20), and making use of a trial solution of the form [2] $\mathbf{E} = \mathbf{E}_0 e^{i(kz - \omega t)}$, where k is the complex propagation constant, we can write the propagation constant k^2 as

$$k^2 = \frac{\omega^2}{c^2} \left[1 + \frac{Ne^2}{m\epsilon_0} \frac{1}{(\omega_0^2 - \omega^2 - i\omega\gamma)} \right]. \quad (1.21)$$

Let us express k in terms of its real and imaginary parts as

$$k = k_R + ik_I. \quad (1.22)$$

Substituting this in the expression for the harmonic wave, we obtain

$$\mathbf{E} = \mathbf{E}_0 e^{-k_I z} e^{i(k_R z - \omega t)}. \quad (1.23)$$

The exponential term in k_I is the extinction index and this represents an exponential decay of the electric field \mathbf{E} with distance z into the medium[2]. The energy absorption or flux density I is proportional to $|\mathbf{E}|^2$. Therefore we can write the energy density as, $I = \mathbf{E}^* \mathbf{E} = I_0 e^{-\delta z}$, where δ is the absorption coefficient of the medium. From the above equation for the intensity, it can be seen that the intensity of the wave decreases as the wave traverses through the medium. Given that the propagation constant is complex, consequently, the refractive index is complex as well and the propagation constant in terms of the refractive index can be written as[2]

$$k = \frac{2\pi}{\lambda} = \left(\frac{\omega}{c} \right) \eta. \quad (1.24)$$

The refractive index η , can be expressed in terms of its real and imaginary parts as

$$\tilde{\eta} = \eta_R + i\eta_I, \quad (1.25)$$

where η_R and η_I are the usual refractive index and extinction coefficient respectively. Making use of (1.24) and (1.25) we then have the expression

$$(\eta_R + i\eta_I)^2 = \left(\frac{ck}{\omega} \right)^2. \quad (1.26)$$

Substituting the expression in (1.21) for k^2 , we obtain the relation

$$(\eta_R + i\eta_I)^2 = 1 + \left(\frac{Ne^2}{m\epsilon_0} \right) \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma}. \quad (1.27)$$

which can be simplified to obtain the respective the real and complex parts as

$$(\eta_R^2 - \eta_I^2) = 1 + \left(\frac{Ne^2}{m\epsilon_0} \right) \left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2} \right), \quad (1.28)$$

$$(2\eta_R\eta_I) = \frac{Ne^2}{m\epsilon_0} \left[\frac{\omega\gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2} \right]. \quad (1.29)$$

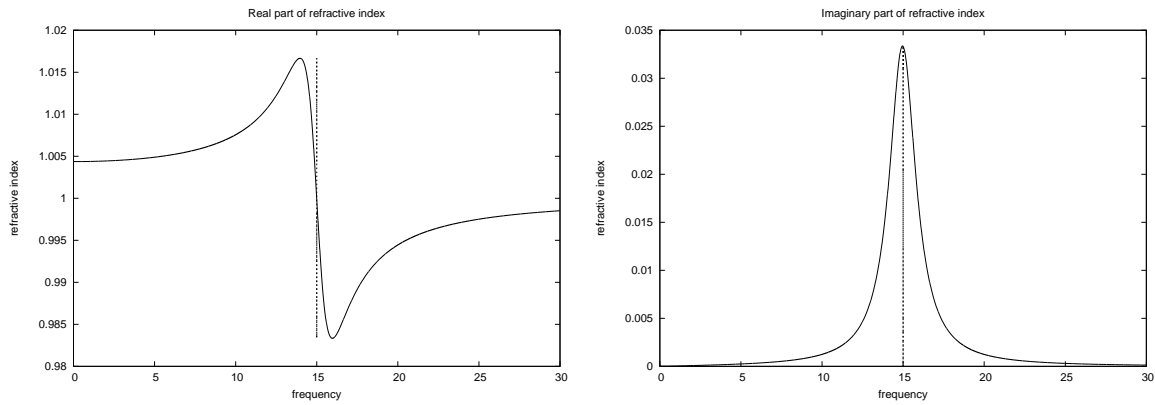


Figure 1.1: The Real and Imaginary parts of the refractive index

A plot of the real part of the refractive index versus frequency and the imaginary part of the refractive index versus frequency reveals some interesting features about the behaviour of the field in the material. The plots are shown in figure (1.1). From the plot it is observed that the imaginary part of the refractive index goes through a maximum at the resonance frequency ω_0 . The resonance frequency for this plot was taken to be $\omega_0 = 15Hz$. From figure(1.1) it seen that the refractive index rises sharply and then falls as ω increases towards and passes the resonance frequency after which it rises again, approaching the value $\eta_R = 1$ at high frequency. The region where $\frac{d\eta}{d\omega} > 0$ is the region of normal dispersion while the region where $\frac{d\eta_R}{d\omega} < 0$ is called the region of anomalous dispersion. The absorption is very high at values of the frequency ω , where anomalous dispersion occurs. The region immediately surrounding ω_0 are the absorption bands. There is high absorption of the incident photons at resonance frequency which is the frequency at which the incident electric field induces an electron in the material to make a transition from one bound state to a higher bound state and the energy of this transition corresponds to $E = \hbar\omega_0$, where \hbar is the reduced Planck's constant. Other resonance frequencies are obtained by varying ω and if resonance occurs in the visible range of frequencies, a portion of the spectrum is absorbed and the material appears coloured, while the remainder is transmitted. The number of resonance frequencies encountered is as a result of the different degrees of freedom of the dielectric in response to the applied field and is accounted for by generalising the refractive index as

$$\eta^2 = 1 + \frac{Ne^2}{m\epsilon_0} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega} \quad (1.30)$$

where f_j , called the oscillator strength, represents the fraction of dipoles having resonance frequency ω_j . For negligible damping coefficient γ , the relation above is known as Sellmeir's formula[2].

2. Polarisation

2.1 Introduction

In this chapter we shall discuss the origin of nonlinear polarisation and also consider the field corrections as they affect the linear and nonlinear polarisations.

2.2 Origin of Nonlinear Optics

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of high intensity light. Lasers have an intensity high enough to modify the optical properties of a material system[5]. The response of the material to the applied field is dependent in a nonlinear way on the strength of the field. Because of the high intensity of the field, nonlinear effects such as second harmonic and third harmonic generation could result as the atoms respond to the strength of the applied field. The polarisation \mathbf{P} is related to the applied electric field, when compared to (1.13), as

$$\mathbf{P} = \chi\epsilon_0\mathbf{E}, \quad (2.1)$$

where χ is the susceptibility of the material. For symmetric materials (such as glass), χ is a simple scalar quantity. For anisotropic materials χ is a tensor so as to account for the polarisation responses of the material to different applied electric field with respect to the crystal axis. When the electric field intensity is significantly high, nonlinear interactions begin to occur within the material and the polarisation is expressed as a power series of the electric field components as

$$\mathbf{P} = \epsilon_0 (\chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots) \quad (2.2)$$

where $\chi^{(1)}$ is the linear susceptibility of the dielectric, and $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order nonlinear optical susceptibilities respectively. The polarisation results from charges that are oscillating within the medium which are produced by the incident oscillating electric field and re-radiate, thus adding to the field. In treating nonlinear optical susceptibility, the electric field acting on each atom or molecule has been assumed to be the macroscopic electric field that appears in the Maxwell's equations (1.1) to (1.4). The atom experiences two fields, namely the macroscopic field and the effective electric field, otherwise known also as the Lorentz local field[6].

2.3 Local Field Effects in Linear Optics

The electric field \mathbf{E} in Maxwell's equations (1.1) to (1.4) is known as the macroscopic or Maxwell field. To obtain this field, a spatial average of the actual (or microscopic) electric field over a region of space whose linear dimensions are of the order of several atomic diameters is performed[6].

Such averaging smoothens out wild variations in electric field that occur in the immediate vicinity of the atomic nuclei and electrons. The macroscopic electric field has contributions due to sources external to the material and due to the dipole moments of all the dipoles that make up the system. Let us assume for simplicity that the medium is lossless, then the fields can be represented as time-varying quantities. Then the dipole moment induced in a molecule is

$$\mathbf{p} = \alpha \mathbf{E}_{loc}, \quad (2.3)$$

where α is the linear polarisability and \mathbf{E}_{loc} is the local field or the effective electric field that acts on the molecule. The field due to all the external sources and to all molecules within the sample except the one under consideration is the local field[6]. Let us represent the macroscopic field by \mathbf{E} and the polarisation within the bulk of the material by \mathbf{P} . Then, the Lorentz local field is given as [7]

$$\mathbf{E}_{loc} = \mathbf{E} + \frac{4\pi}{3} \mathbf{P}, \quad (2.4)$$

where \mathbf{P} is the polarisation of the material. We can, with the use of (2.3), (2.4) and (2.5), write the polarisation as

$$\mathbf{P} = N\alpha \left(\mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right). \quad (2.5)$$

However, the polarisation can be expressed in terms of the linear susceptibility $\chi^{(1)}$ as

$$\mathbf{P} = \chi^{(1)} \mathbf{E}. \quad (2.6)$$

From (2.5), the polarisation follows as

$$\mathbf{P} \left(1 - \frac{4}{3} \pi N \alpha \right) = N \alpha \mathbf{E}, \quad (2.7)$$

and from (2.6) and (2.7), we can write the linear susceptibility as

$$\chi^{(1)} = \frac{N\alpha}{1 - \frac{4}{3} \pi N \alpha}. \quad (2.8)$$

For the case where α is positive, it can be seen that the susceptibility $\chi^{(1)}$, is larger than the value of $N\alpha$ as predicted by the theories that ignore local field correction[6]. The dielectric linear constant $\epsilon^{(1)}$ is related to the susceptibility [7] as

$$\epsilon^{(1)} = 1 + 4\pi \chi^{(1)}, \quad (2.9)$$

and from the above equation the susceptibility can be written as

$$\chi^{(1)} = \frac{\epsilon^{(1)} - 1}{4\pi}. \quad (2.10)$$

To obtain an expression for the dielectric constant in terms of the linear polarisability we make use of (2.10) and (2.8) and we obtain

$$\frac{\epsilon^{(1)} - 1}{4\pi} = \frac{1 + \frac{8\pi N\alpha}{3}}{1 - \frac{4\pi N\alpha}{3}}. \quad (2.11)$$

The equation (2.11) gives the dependence of the polarisability on N . The polarisability α can be expressed in terms of the dielectric susceptibility $\epsilon^{(1)}$ from (2.11). Thus,

$$\frac{\epsilon^{(1)} - 1}{\epsilon^{(1)} + 2} = \frac{4\pi N\alpha}{3}. \quad (2.12)$$

From (2.12), we can obtain the linear polarisability α as

$$\alpha = \frac{3}{4\pi N} \frac{\epsilon^{(1)} - 1}{\epsilon^{(1)} + 2}, \quad (2.13)$$

and this relation, discovered by Lorentz and Lorenz, is known as the Lorentz-Lorenz formula. Using Maxwell's relation, we can replace $\epsilon^{(1)}$ with n^2 [7] in (2.12) to obtain

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}. \quad (2.14)$$

We can rearrange (2.12) to obtain

$$\frac{\epsilon^{(1)} + 2}{3} = \frac{\epsilon^{(1)} - 1}{4\pi N\alpha},$$

and using (2.8) and (2.9), the above equation could be written as

$$\frac{\epsilon^{(1)} + 2}{3} = \frac{1}{1 - \frac{4}{3}\pi N\alpha}, \quad (2.15)$$

and from (2.15), we can express the linear susceptibility $\chi^{(1)}$ as

$$\chi^{(1)} = \frac{\epsilon^{(1)} + 2}{3} N\alpha. \quad (2.16)$$

From (2.16) it is seen that $\chi^{(1)}$ is larger than α by the factor $\frac{\epsilon^{(1)} + 2}{3}$. The factor $\frac{\epsilon^{(1)} + 2}{3}$ is the local-field correction factor for the linear susceptibility.[6]

2.4 Local Field Corrections in Nonlinear Optics

The Lorentz local field for the nonlinear-optical situation is given by equation (2.4). Due to the nonlinear contribution, the polarisation can be written as a

$$\mathbf{P} = \mathbf{P}^L + \mathbf{P}^{NL}, \quad (2.17)$$

where \mathbf{P}^{L} and \mathbf{P}^{NL} is the respective linear and nonlinear contributions to the polarisation. The linear contribution can be represented as[6]

$$\mathbf{P}^{\text{L}} = N\alpha\mathbf{E}_{loc}. \quad (2.18)$$

The above equation is linear in the field strength of the local field though not linear in the macroscopic field[6]. Using (2.17) in (2.4), we can then write the local field as

$$\mathbf{E}_{loc} = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}^{\text{L}} + \frac{4\pi}{3}\mathbf{P}^{\text{NL}}. \quad (2.19)$$

Substituting (2.19) in (2.18), we obtain the expression for the linear polarisation as

$$\mathbf{P}^{\text{L}} = \frac{N\alpha \left(\mathbf{E} + \frac{4\pi}{3}\mathbf{P}^{\text{NL}} \right)}{\left(1 - \frac{4\pi}{3}N\alpha \right)}, \quad (2.20)$$

and from (2.8) and (2.9), we can write

$$1 - \frac{4\pi}{3}N\alpha = \frac{N\alpha}{\chi^{(1)}} = \frac{4\pi N\alpha}{\epsilon^{(1)} - 1}.$$

The above expression is substituted into (2.20) to obtain the nonlinear polarisation as

$$\mathbf{P}^{\text{L}} = \frac{\epsilon^{(1)} - 1}{4\pi} \left(\mathbf{E} + \frac{4\pi}{3}\mathbf{P}^{\text{NL}} \right). \quad (2.21)$$

According to Maxwell's equations, the displacement vector \mathbf{D} can be written as [3]

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}^{\text{L}} + \mathbf{P}^{\text{NL}}. \quad (2.22)$$

Substituting (2.21) in (2.22) and the displacement vector follows as

$$\mathbf{D} = \epsilon^{(1)}\mathbf{E} + 4\pi\mathbf{P}^{\text{NL}} \left(\frac{\epsilon^{(1)} + 2}{3} \right). \quad (2.23)$$

From (2.23), we see that the second term or the nonlinear source term is the product of the nonlinear polarisation and the factor $\left(\frac{\epsilon^{(1)} + 2}{3} \right)$. The nonlinear source polarisation can be written as[6]

$$\mathbf{P}^{\text{NLS}} = \frac{\epsilon^{(1)} + 2}{3}\mathbf{P}^{\text{NL}}, \quad (2.24)$$

so that (2.23) becomes

$$\mathbf{D} = \epsilon^{(1)}\mathbf{E} + 4\pi\mathbf{P}^{\text{NLS}}. \quad (2.25)$$

Using (2.25), we can write the wave equation as

$$\begin{aligned} \nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2} &= 0, \\ \nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} (\epsilon^{(1)}\mathbf{E} + 4\pi\mathbf{P}^{\text{NLS}}) &= 0, \\ \nabla \times \nabla \times \mathbf{E} + \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} &= -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}^{\text{NLS}}}{\partial t^2}. \end{aligned} \quad (2.26)$$

The local and macroscopic fields are different because the local field induces a dipole moment in the atom whereas the nonlinear susceptibility relates the nonlinear source polarisation to the macroscopic field[6]. We make an approximation by replacing \mathbf{P} by \mathbf{P}^L in (2.4)[6] and the local field follows as

$$\mathbf{E}_{loc} = \mathbf{E} \left(1 + \frac{4}{3} \pi \chi^{(1)} \right). \quad (2.27)$$

Using the expression for the susceptibility in (2.9) and that for $\epsilon^{(1)} - 1$ from (2.12), we can write b.27 as

$$\mathbf{E}_{loc} = \mathbf{E} \left(\frac{3 + \frac{4\pi N\alpha}{3} (\epsilon^{(1)} + 2)}{3} \right). \quad (2.28)$$

From (2.12), we obtain the expression

$$\frac{4\pi N\alpha}{3} = \frac{(\epsilon^{(1)} + 2) - 3}{\epsilon^{(1)} + 2}. \quad (2.29)$$

Substituting the expression in (2.29) into (2.28), the local field in terms of the dielectric constant and the macroscopic field can then be written as

$$\mathbf{E}_{loc} = \mathbf{E} \left(\frac{\epsilon^{(1)} + 2}{3} \right). \quad (2.30)$$

We can also express the mean polarisability α in terms of another quantity, A , called the molar refractivity. The molar refractivity is defined as the total polarisability of a mole of the substance[7] and is given by

$$A = \frac{4\pi N_m \alpha}{3}, \quad (2.31)$$

where N_m is the Avogadro number which is the number of molecules in a mole [7]. If W is the molecular weight, ρ the density, p the pressure and T the absolute temperature of the gas, then using Boyles's law we can express the molar volume of the gas as

$$\frac{N_m}{N} = \frac{W}{\rho} = \frac{RT}{p}, \quad (2.32)$$

where R is the ideal gas constant. To express A in terms of the refractive index we make use of (2.12) and (2.13) and we have

$$A = \frac{4\pi}{3} \left(\frac{W}{\rho} N \right) \alpha = \frac{RT}{p} \frac{n^2 - 1}{n^2 + 2}, \quad (2.33)$$

and the above equation has the dimensions of molar volume.

2.4.1 Molar Refractivity of Gas

The equation (2.14) gives the explicit dependence of the refractive index of light, of any particular colour, on the density provided that isotropy is preserved [7]. For gases, $n^2 - 1$ and ρ are very nearly proportional to each other. With $n^2 \approx 1$, the Lorentz-Lorenz formula (2.14) reduces to

$$\alpha \approx \frac{n^2 - 1}{4\pi N},$$

and also with the approximation $n^2 \approx 1$, (2.33) becomes

$$A = \frac{W}{\rho} \frac{n^2 - 1}{3}. \quad (2.34)$$

At high pressure $n^2 - 1$ differs appreciably from unity.

2.5 Dispersion in Gases

In this section we shall obtain the dispersion relation for gases and also study how dispersion occurs in gases. The variation of the refractive index with frequency results in a phenomena known as dispersion. For polar molecules, the centre of the positive and negative charges do not coincide while for non-polar molecules the centre of the positive and negative charges coincide. The electrons and nuclei of non-polar molecules are displaced when subjected to an electric field. The polarisation vector \mathbf{P} is the vector sum of all the dipole moments of the molecules in the unit of volume. As was seen earlier in chapter 1, the particles have a displacement \mathbf{r} from its equilibrium position, and the force on the particle is given, approximately, by

$$\mathbf{F} \approx e\mathbf{E}',$$

where we have neglected the contribution due to the magnetic force when compared to the electric force. Assuming there is one electron with resonance frequency ω_0 , the polarisation \mathbf{P} , as obtained in chapter 1 could be written as

$$\mathbf{P} = N\mathbf{p} = \frac{Ne^2}{m} \frac{\mathbf{E}'}{(\omega_0^2 - \omega^2)},$$

and comparing the above equation with the expression for the polarisation from (2.2), we have

$$N\alpha = \frac{Ne^2}{m} \frac{1}{(\omega_0^2 - \omega^2)}. \quad (2.35)$$

Equation (2.35) expresses the 'density of polarisability' in terms of atomic parameters. Using Maxwell's relation, we introduce a frequency-dependent dielectric constant $\epsilon(\omega)$ [7] as $\epsilon = n^2$, where the refractive index n is a function of frequency, $n(\omega)$. For a static dielectric constant, $\epsilon(0) = n^2(0)$ and hence (2.35) becomes

$$N\alpha(0) = \frac{Ne^2}{m\omega_0^2},$$

and the static constant $\epsilon(0)$ follows from (2.11) as

$$\epsilon(0) = \frac{1 + \frac{8\pi N^2}{3m\omega_0^2}}{1 - \frac{4\pi N^2}{3m\omega_0^2}}. \quad (2.36)$$

From (2.35) and (2.14) we then obtain

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{Ne^2}{m(\omega_0^2 - \omega^2)}. \quad (2.37)$$

For a gas, n is close to unity[7] and so we may set $n^2 + 2 \approx 3$ and the refractive index follows as

$$n^2 - 1 \approx \frac{4\pi Ne^2}{m(\omega_0^2 - \omega^2)}. \quad (2.38)$$

The vibrating electrons emit electromagnetic waves which carry away energy and this causes damping in the system. Damping (dissipation of energy) or absorption could also result due to the collisions between the atoms. A plot of the refractive index versus frequency for gas is shown in figure (2.1).

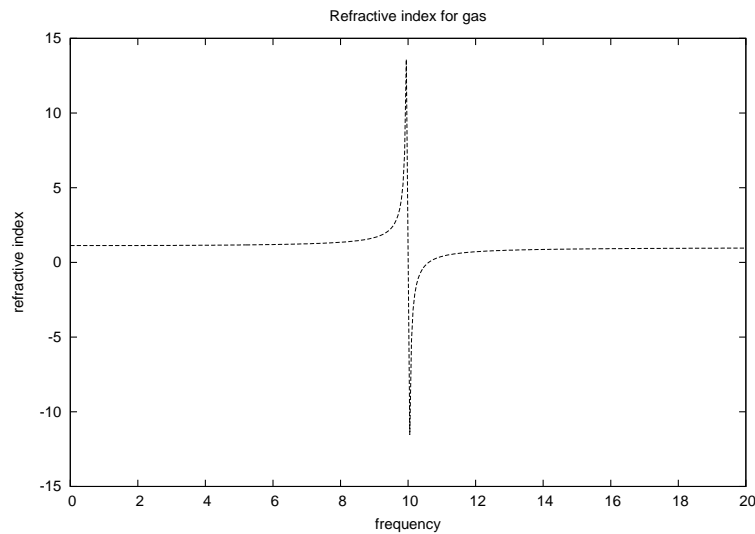


Figure 2.1: Refractive index of gas

For values of ω slightly smaller and slightly greater than the resonance frequency ω_0 , the curve has a large maximum. Between the maximum and the minimum, the function decreases as frequency increases and this is known as anomalous dispersion. The shorter wavelength (higher frequency) are refracted less than those of longer wavelength (high frequency). A consequence of this is the usual sequence of prismatic colours[7]. If there are a number of electrons N corresponding to the

resonance frequency ω_j , we can write (2.14) in terms of the oscillator strength f_k as [7]

$$\begin{aligned}\frac{4\pi N\alpha}{3} &= \frac{n^2 - 1}{n^2 + 2} \\ &= \frac{4\pi N}{3} \frac{e^2}{m} \sum \frac{f_k}{(\omega_0^2 - \omega^2)}.\end{aligned}\quad (2.39)$$

With the approximation that $n \sim 1$ for gases[7], (2.39) becomes

$$n^2 - 1 = 4\pi N \frac{e^2}{m} \sum_k \frac{f_k}{(\omega_0^2 - \omega^2)}.\quad (2.40)$$

We may write (2.40) in terms of the frequency by using $\omega = 2\pi\nu$ and $\omega_k = 2\pi\nu_k$, and substituting this for the respective frequencies in (2.40), we have that

$$\begin{aligned}n^2 - 1 &= 4\pi N \frac{e^2}{m} \sum_k \frac{f_k}{4\pi^2\nu_k^2 - 4\pi^2\nu^2} \\ &= \frac{Ne^2}{m\pi} \sum \frac{f_k}{\nu_k^2 - \nu^2}.\end{aligned}\quad (2.41)$$

We can express the frequencies in terms of the wavelengths as $\nu_k = \frac{c}{\lambda_k}$ and $\nu = \frac{c}{\lambda}$, and setting $\rho_k = \frac{Ne^2}{m\pi}$, and then substituting in (2.41) to obtain the expression

$$\begin{aligned}n^2 - 1 &= \sum_k \frac{\rho_k}{\nu_k^2 - \nu^2} \\ &= \sum_k \frac{\rho_k}{c^2} \frac{\lambda_k^2 \lambda^2}{\lambda^2 - \lambda_k^2}.\end{aligned}\quad (2.42)$$

Using the identity $\frac{\lambda^2}{\lambda^2 - \lambda_k^2} = 1 + \frac{\lambda_k^2}{\lambda^2 - \lambda_k^2}$, we can write (2.42) as

$$\begin{aligned}n^2 - 1 &= \sum_k \frac{\rho_k}{c^2} \cdot \lambda_k^2 \left[1 + \frac{\lambda_k^2}{\lambda^2 - \lambda_k^2} \right] \\ &= a + \sum_k \frac{b_k}{\lambda^2 - \lambda_k^2},\end{aligned}\quad (2.43)$$

where $a = \sum_k \frac{\rho_k}{\nu_k^2} = \frac{1}{c^2} \sum_k \frac{\rho_k}{\lambda_k^2}$ and $b = \frac{\rho_k \lambda_k^2}{c^2} = \frac{c^2 \rho_k}{\nu_k^4}$.

It was found by KOCH that (2.43) holds for hydrogen, oxygen and air for λ between the range of 0.436μ to 8.68μ [7]. Within some spectral range, there are no resonance frequencies and some substances appear transparent to the eye. For these substances, the visible domain is in such a range. For substances of higher densities such as liquids or solids, n can no longer be replaced by unity in the denominator of the second term in the (2.39).

3. Nonlinear Polarisation

3.1 Introduction

In this section we shall discuss some nonlinear optical interactions such as second harmonic generation, sum-frequency generation, difference frequency generation and third harmonic generation.

3.2 Nonlinear Optical Interactions

The nonlinear optical response is generalised by expressing $\tilde{\mathbf{P}}$ as a power series in the field strength $\tilde{\mathbf{E}}$ as[2]

$$\tilde{\mathbf{P}} = \chi^{(1)}\tilde{\mathbf{E}} + \chi^{(2)}\tilde{\mathbf{E}}^2 + \chi^{(3)}\tilde{\mathbf{E}}^3 + \dots, \quad (3.1)$$

where $\chi^{(2)}$ and $\chi^{(3)}$ are the respective second and third order nonlinear optical susceptibilities. The nonlinear susceptibilities depends on the frequency of the applied field. Second order nonlinear optical interactions can only occur in noncentrosymmetric crystals, that is, crystals that do not display inversion symmetry. Liquids, gases, amorphous solids (such as glasses) and some crystals do display inversion symmetry and $\chi^{(2)}$ vanishes identically for such media and hence they do not produce second order nonlinear optical interactions. The third order nonlinear optical interactions can occur in both centrosymmetric and noncentrosymmetric media. A common procedure for describing nonlinear optical phenomena is by expressing the polarisation, $\tilde{\mathbf{P}}$, in terms of the applied electrical field strength $\tilde{\mathbf{E}}$ as in (3.1), since a time varying polarisation can act as a source of new components of the electromagnetic field.

3.2.1 Second Harmonic Generation (SHG)

When a beam of light is incident on a material, generation of light at twice the frequency of the incident light can occur in the material. This effect can be ignored for conventional sources of light; however, this is not the case when a high intensity source, such as a laser, is used. An important application of second harmonic generation is in the studying of surface phenomena such as molecular adsorption, aggregation and orientation. An illustration of second harmonic generation is shown in figure (3.1). A laser beam with electric field strength is incident on a crystal with $\chi^{(2)}$ nonzero, given by

$$\tilde{\mathbf{E}} = \mathbf{E}e^{-i\omega t} + c.c.,$$

where *c.c.* denotes complex conjugate. The nonlinear polarisation follows from (3.1) as

$$\begin{aligned} \tilde{\mathbf{P}}_{(t)}^{(2)} &= \chi^{(2)}\tilde{\mathbf{E}}_{(t)}^2 \\ &= 2\chi^{(2)}\mathbf{E}\mathbf{E}^* + (\chi^{(2)}\mathbf{E}^2e^{-2i\omega t} + c.c.). \end{aligned} \quad (3.2)$$

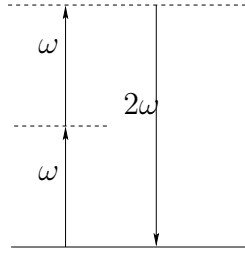


Figure 3.1: Energy level description of second harmonic generation

There is a contribution at zero frequency from the first term and a contribution at frequency 2ω from the second term. The first contribution in (3.2) does not lead to the generation of electromagnetic radiation since it has no time dependence and thus a process known as optical rectification results in which a static electric field is created within the nonlinear crystal.

Second harmonic generation can also be seen as an exchange of photons between the various frequency components of the electric field as shown in figure (3.1) above. Two photons of frequency ω and a photon of frequency 2ω is simultaneously created in a single-quantum mechanical process. The atomic ground state is represented by the solid line and the dashed lines are known as the virtual levels which represents the combined energy of one of the energy eigenstates of the atom and of or more of photons in the radiation level. Let us consider the case in which an optical field incident upon the nonlinear optical material medium consists of two distinct frequency components ω_1 and ω_2 , represented as

$$\tilde{\mathbf{E}}_{(t)} = \mathbf{E}_1 e^{-i\omega_1 t} + \mathbf{E}_2 e^{-i\omega_2 t} + c.c..$$

With the above expression for electric field, the second order contribution to the nonlinear polarisation can be written as

$$\begin{aligned} \tilde{\mathbf{P}}_{(t)}^{(2)} = & \chi^{(2)} [\mathbf{E}_1^2 e^{-2i\omega_1 t} + \mathbf{E}_2^2 e^{-2i\omega_2 t} + 2\mathbf{E}_1 \mathbf{E}_2 e^{-i(\omega_1 + \omega_2)t} + 2\mathbf{E}_1 \mathbf{E}_2^* e^{-i(\omega_1 - \omega_2)t} + c.c.] \\ & + 2\chi^{(2)} [\mathbf{E}_1 \mathbf{E}_1^* + \mathbf{E}_2 \mathbf{E}_2^*]. \end{aligned}$$

To simplify the above equation we group each term of the expansion with its complex conjugate. We then have the following set of equations for the polarisation, with the corresponding frequencies, as

$$\begin{aligned} \mathbf{P}(2\omega_1) &= \chi^{(2)} \mathbf{E}_1^2, \\ \mathbf{P}(2\omega_2) &= \chi^{(2)} \mathbf{E}_2^2, \\ \mathbf{P}(\omega_1 + \omega_2) &= 2\chi^{(2)} \mathbf{E}_1 \mathbf{E}_2, \\ \mathbf{P}(\omega_1 - \omega_2) &= 2\chi^{(2)} \mathbf{E}_1 \mathbf{E}_2^*, \\ \mathbf{P}(0) &= 2\chi^{(2)} (\mathbf{E}_1 \mathbf{E}_1^* + \mathbf{E}_2 \mathbf{E}_2^*). \end{aligned} \quad (3.3)$$

There is also a response at the negative nonzero frequencies given by

$$\begin{aligned} \mathbf{P}(-2\omega_1) &= \chi^{(2)} \mathbf{E}_1^{*2}, \\ \mathbf{P}(-\omega_1 - \omega_2) &= 2\chi^{(2)} \mathbf{E}_1^* \mathbf{E}_2^*, \\ \mathbf{P}(\omega_2 - \omega_1) &= 2\chi^{(2)} \mathbf{E}_2 \mathbf{E}_1^*. \end{aligned} \quad (3.4)$$

Equation (3.4) is a complex conjugate of (3.3) and hence there is no need in taking both the positive and negative frequency components[6]. From (3.3), we find that there are four nonzero components in the nonlinear polarisation and no more than one of these frequency components will be present in any appreciable intensity in the radiation generated by the nonlinear optical interaction. This is because the nonlinear polarisation can efficiently produce an output signal only if the phasematching conditions are satisfied, and this condition is not satisfied for more than one frequency component of the nonlinear polarisation. Phase matching will be discussed in Chapter 4. Practically, we choose frequency components which will be reradiated by properly selecting the polarisation of the input signal radiation and orientation of the nonlinear crystal.

3.2.2 Sum Frequency Generation (SFG)

The complex amplitude of the nonlinear polarisation for this process, from (3.3), is given by

$$\mathbf{P}(\omega_1 + \omega_2) = 2\chi^{(2)}\mathbf{E}_1\mathbf{E}_2.$$

This is similar to the case of the second harmonic generation described in the preceding section. However, in this case, the two input waves are at different frequencies ω_1 and ω_2 . An application of this is in the tunable radiation in the ultraviolet spectral region by choosing one of the input waves to be the output of a fixed-frequency visible laser and the other to be the output of a frequency-tunable visible laser.

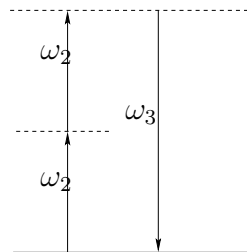


Figure 3.2: Energy level description of sum frequency generation

3.2.3 Difference Frequency Generation (DFG)

This process is described by the nonlinear polarisation given by

$$\mathbf{P}(\omega_1 - \omega_2) = 2\chi^{(2)}\mathbf{E}_1\mathbf{E}_2^*.$$

The frequency of the generated wave is the difference of that of the applied fields. For every photon that is created at the difference frequency $\omega_3 = \omega_1 - \omega_2$, a photon at the higher input frequency ω_1 must be destroyed and a photon at the lower input frequency ω_2 must be created, thus there is an amplification of the lower frequency input field and this is known as optical parametric amplification. The atom absorbs a photon of frequency ω_1 and jumps to the highest virtual energy level, and the level decays by a two-photon emission process that is stimulated by

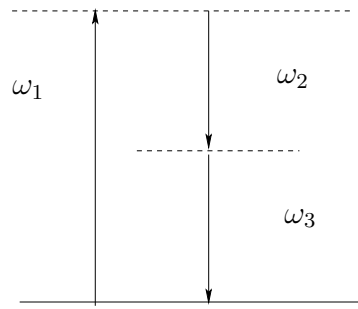


Figure 3.3: Energy level description of difference frequency generation

the presence of the ω_2 field. The generated fields are much weaker because they are created by spontaneous two-photon emission from a virtual level and this is known as parametric fluorescence. An application of this is in the generation of tunable radiation.

3.3 Third Order Polarisation

The third order contribution to the polarisation is given by

$$\tilde{\mathbf{P}}_{(t)}^{(3)} = \chi^{(3)} \tilde{\mathbf{E}}_{(t)}^3, \quad (3.5)$$

where the applied field, which consists of three frequency components, is given by[6]

$$\tilde{\mathbf{E}} = \mathbf{E}_1 e^{-i\omega_1 t} + \mathbf{E}_2 e^{-i\omega_2 t} + \mathbf{E}_3 e^{-i\omega_3 t} + c.c. .$$

To obtain the different frequency components for the third order susceptibility, we substitute for the field in (3.5) using the above expression for the field. Carrying out the expansion and collecting terms of the same frequency, we obtain 44 different frequency components given below as

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

An illustration of this process is seen in figure (3.4). More about third order polarisation will be discussed in chapter four.

3.4 Nonlinear Susceptibility of an Anharmonic Oscillator

3.4.1 Introduction

The Lorentz model of the atom treats the atom as a harmonic oscillator and this provides a good description of the linear optical properties of atomic vapours and of nonmetallic solids[6]. We

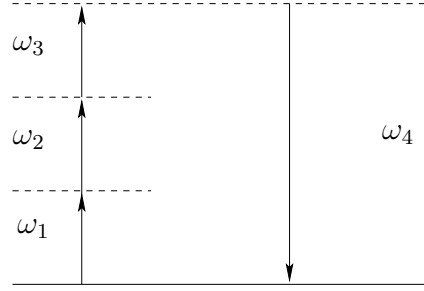


Figure 3.4: Energy level description of a third order process

are going to allow nonlinearity in the restoring force exerted on the electron and also consider the symmetry in the material. Noncentrosymmetric medium can give rise to second-order optical nonlinearity. For a medium with a centre of symmetry we find that the lowest-order nonlinearity is a third-order nonlinear susceptibility[6].

3.4.2 Noncentrosymmetric Media

The equation of motion of the electron with coordinate \tilde{x} , as obtained from the Lorentz model, is of the form[6]

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -\frac{e\tilde{\mathbf{E}}(t)}{m}, \quad (3.6)$$

where $\tilde{\mathbf{E}}(t)$ is the applied electric field, $-e$ the charge of the electron, $-2m\gamma\dot{\tilde{x}}$ is the restoring force given by

$$\tilde{F}_r = -m\omega_0^2\tilde{x} - ma\tilde{x}^2, \quad (3.7)$$

and a is a parameter that characterises the nonlinearity of the response. We have assumed that the restoring force is a nonlinear function of the displacement of the electron from its equilibrium position and retains the linear and quadratic terms in the Taylor series expansion of the restoring force in the displacement \tilde{x} . The restoring force is given in terms of the potential energy as

$$F_r = -\frac{dV}{dx},$$

and from which the potential follows as

$$V = \frac{1}{2}m\omega_0^2\tilde{x}^2 + \frac{1}{3}ma\tilde{x}^3. \quad (3.8)$$

The first term corresponds to a harmonic potential and the second term corresponds to an anharmonic correction term. Physically, this model is more realistic because the actual potential

well that the atomic electron feels is not perfectly parabolic[6]. This model can describe only noncentrosymmetric media because of the assumption that the potential energy function V in (3.8) contains both even and odd powers of \tilde{x} ; for a centrosymmetric medium only even powers of \tilde{x} appear, because the potential function $V(\tilde{x})$ possesses the symmetry $V(\tilde{x}) = V(-\tilde{x})$. Let us assume that the applied field is of the form

$$\tilde{\mathbf{E}}(t) = \mathbf{E}_1 e^{-i\omega_1 t} + \mathbf{E}_2 e^{-i\omega_2 t} + c.c.. \quad (3.9)$$

There is no known general solution of (3.6) for an applied field of the form (3.9)[6]. For a sufficiently weak field, the nonlinear term $a\tilde{x}^2$ is much smaller than the linear term ω_0^2 or ($a\tilde{x}^2 \ll \omega_0^2$) for any displacement \tilde{x} of the field and then we can solve (3.6) by means of a perturbation expansion. Let us replace $\tilde{\mathbf{E}}(t)$ in (3.6) by $\lambda\tilde{\mathbf{E}}(t)$, where λ is a parameter that ranges continuously between zero and one and that will be set equal to one at the end of the calculation[6]. The expansion parameter characterises the strength of the perturbation. We can write (3.6) as

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -\frac{\lambda e\tilde{\mathbf{E}}(t)}{m}. \quad (3.10)$$

Now, let us seek a solution to (3.10) in the form of a power series expansion in the strength λ of the perturbation, that is, a solution of the form

$$\tilde{x} = \lambda\tilde{x}^{(1)} + \lambda^2\tilde{x}^{(2)} + \lambda^3\tilde{x}^{(3)} + \dots \quad (3.11)$$

We require that the terms proportional to $\lambda, \lambda^2, \lambda^3, \dots$ each satisfy the equation separately. Differentiating (3.11) twice with respect to t we obtain the respective time derivatives as

$$\dot{\tilde{x}} = \lambda\dot{\tilde{x}}^{(1)} + \lambda^2\dot{\tilde{x}}^{(2)} + \lambda^3\dot{\tilde{x}}^{(3)} + \dots \quad (3.12)$$

$$\ddot{\tilde{x}} = \lambda\ddot{\tilde{x}}^{(1)} + \lambda^2\ddot{\tilde{x}}^{(2)} + \lambda^3\ddot{\tilde{x}}^{(3)} + \dots \quad (3.13)$$

We substitute (3.12) and (3.13) into (3.10) and we have

$$\begin{aligned} \frac{-\lambda e\tilde{\mathbf{E}}(t)}{m} &= (\lambda\ddot{\tilde{x}}^{(1)} + \lambda^2\ddot{\tilde{x}}^{(2)} + \lambda^3\ddot{\tilde{x}}^{(3)} + \dots) + 2\gamma(\lambda\dot{\tilde{x}}^{(1)} + \lambda^2\dot{\tilde{x}}^{(2)} + \lambda^3\dot{\tilde{x}}^{(3)} + \dots) \\ &\quad + \omega_0^2(\lambda\tilde{x}^{(1)} + \lambda^2\tilde{x}^{(2)} + \lambda^3\tilde{x}^{(3)} + \dots) + a(\lambda^2\tilde{x}^{(1)2} + 2\lambda^3\tilde{x}^{(1)}\tilde{x}^{(2)} + \dots) \end{aligned} \quad (3.14)$$

We then compare the respective coefficients of $\lambda, \lambda^2, \lambda^3$ in (3.14) to have the corresponding equations as

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x}^{(1)} = -\frac{e\tilde{\mathbf{E}}(t)}{m}, \quad (3.15)$$

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} + a\tilde{x}^{(1)2} = 0, \quad (3.16)$$

$$\ddot{\tilde{x}}^{(3)} + 2\gamma\dot{\tilde{x}}^{(3)} + \omega_0^2\tilde{x}^{(3)} + 2a\tilde{x}^{(1)}\tilde{x}^{(2)} = 0. \quad (3.17)$$

The linear Lorentz model is of the form of (3.15) and the steady state solution is given by

$$\tilde{x}_{(t)}^{(1)} = \tilde{x}_{(\omega_1)}^{(1)} e^{-i\omega_1 t} + \tilde{x}_{(\omega_2)}^{(1)} e^{-i\omega_2 t} + c.c.. \quad (3.18)$$

Thus using the above equations, (3.14) can be written as

$$\begin{aligned}
& [-\omega_1^2 x^{(1)}(\omega_1) e^{-i\omega_1 t} - \omega_2^2 x^{(1)}(\omega_2) e^{-i\omega_2 t} + c.c..] \\
& + 2\gamma [-i\omega_1 x^{(1)}(\omega_1) e^{-i\omega_1 t} + -i\omega_2 x^{(1)}(\omega_2) e^{-i\omega_2 t} + c.c..] \\
& + \omega_0^2 [x(\omega_1)^{(1)} e^{-i\omega_1 t} + x(\omega_2)^{(1)} e^{-i\omega_2 t} + c.c..] \\
& = \frac{-e}{m} [\mathbf{E}_1 e^{-i\omega_1 t} + \mathbf{E}_2 e^{-i\omega_2 t} + c.c.],
\end{aligned}$$

and comparing terms in ω_1 for the LHS and RHS from the above equation, we obtain an expression in $x^{(1)}(\omega_1)$ which we can solve to obtain $x^{(1)}(\omega_1)$ as follows

$$\begin{aligned}
(-\omega_1^2 - 2i\gamma\omega_1 + \omega_0^2) x^{(1)}(\omega_1) e^{-i\omega_1 t} &= \frac{-e}{m} \mathbf{E}_1 e^{-i\omega_1 t} \\
x^{(1)}(\omega_1) &= \frac{-e}{m} \frac{\mathbf{E}_1}{D(\omega_1)},
\end{aligned}$$

where $D(\omega_1) = \omega_0^2 - \omega_1^2 - 2i\gamma\omega_1$. Following a similar argument for the frequency ω_2 , we likewise obtain

$$x^{(1)}(\omega_2) = \frac{-e}{m} \frac{\mathbf{E}_2}{D(\omega_2)},$$

and in general, we could write

$$x^{(1)}(\omega_j) = \frac{-e}{m} \frac{\mathbf{E}_j}{D(\omega_j)}, \quad (3.19)$$

where

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\gamma\omega_j. \quad (3.20)$$

There are frequency responses corresponding to second harmonic generation, sum frequency and difference frequency respectively. To determine the response at frequency $2\omega_1$, we substitute (3.18) into (3.16) and then solve the resulting equation. We can substitute the expression for $\tilde{x}^{(1)2}(t)$ and that for $\tilde{\mathbf{E}}(t)^2$ from (3.9) into (3.16). From the resulting equation, we can then obtain the frequency term corresponding to the second harmonic generation, sum frequency, difference frequency and so on. To obtain the second harmonic generation at $2\omega_1$, we compare terms with frequency $2\omega_1$ and we have

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2 \tilde{x}^{(2)} = a \frac{e^2}{m^2} \frac{E_1^2}{D^2(\omega_1)} e^{-2i\omega_1 t}. \quad (3.21)$$

We seek a steady state solution of the form

$$\tilde{x}^{(2)}(t) = x^{(2)}(2\omega_1) e^{-2i\omega_1 t}. \quad (3.22)$$

Substituting (3.22) into (3.21), we have

$$\begin{aligned}
-4\omega_1^2 x^{(2)}(2\omega_1) e^{-2i\omega_1 t} - 4i\gamma\omega_1 x^{(2)}(2\omega_1) e^{-2i\omega_1 t} + \omega_0^2 x^{(2)}(2\omega_1) e^{-2i\omega_1 t} \\
= \frac{-a \left(\frac{eE_1}{m}\right)^2}{D^2(\omega_1)} e^{-2i\omega_1 t},
\end{aligned}$$

and simplifying the above equation, we can express $x^{(2)}(2\omega_1)$ as

$$x^{(2)}(2\omega_1) = \frac{-a \left(\frac{e}{m}\right)^2 E_1^2}{D(2\omega_1) D^2(\omega_1)}. \quad (3.23)$$

where $D(2\omega_1) = -4\omega_1^2 - 4i\gamma\omega_1 + \omega_0^2$. Likewise, for frequency $2\omega_2$, we follow a similar analogy as used in obtaining to obtain

$$x^{(2)}(2\omega_2) = \frac{-a \left(\frac{e}{m}\right)^2 E_2^2}{D(2\omega_2) D^2(\omega_2)}. \quad (3.24)$$

For the sum frequency $(\omega_1 + \omega_2)$, we use the expansion of (3.9) and (3.16) and we substitute the corresponding expression for the electric field at the sum frequency $(\omega_1 + \omega_2)$ and we obtain the equation

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} = \frac{-2ae^2}{m^2 D(\omega_1) D(\omega_2)} E_1 E_2 e^{-i(\omega_1 + \omega_2)t}. \quad (3.25)$$

As before, we seek a solution of the form

$$\tilde{x}^{(2)}(t) = x^{(2)}(\omega_1 + \omega_2) e^{-i(\omega_1 + \omega_2)t}.$$

Substituting the respective derivatives of the above solution in (3.25), we then have

$$\begin{aligned} & \left(-(\omega_1 + \omega_2)^2 - 2i\gamma(\omega_1 + \omega_2) + \omega_0^2 \right) x^{(2)}(\omega_1 + \omega_2) e^{i(\omega_1 + \omega_2)t} \\ & = \frac{-2ae^2}{m^2 D(\omega_1) D(\omega_2)} E_1 E_2 e^{-i(\omega_1 + \omega_2)t}, \end{aligned}$$

and solving the above equation for $x^{(2)}(\omega_1 + \omega_2)$ we obtain

$$x^{(2)}(\omega_1 + \omega_2) = \frac{-2ae^2}{m^2 D(\omega_1 + \omega_2)} \frac{E_1}{D(\omega_1)} \frac{E_2}{D(\omega_2)}, \quad (3.26)$$

where $D(\omega_1 + \omega_2) = [\omega_0^2 - (\omega_1 + \omega_2)^2 - 2i\gamma(\omega_1 + \omega_2)]$. Likewise, we obtain the susceptibility $x^{(2)}(\omega_1 - \omega_2)$ for the difference frequency generation $(\omega_1 - \omega_2)$ as

$$x^{(2)}(\omega_1 - \omega_2) = \frac{-2ae^2}{m^2 D(\omega_1 - \omega_2)} \frac{E_1}{D(\omega_1)} \frac{E_2^*}{D(-\omega_2)}. \quad (3.27)$$

For the case of the zero frequency, we seek a solution of the form

$$\tilde{x}^{(2)}(t) = x^{(2)}(0),$$

Substituting the respective derivatives of the above equation in (3.17), we have

$$\omega_0^2 \tilde{x}^{(2)}(0) = -2a \frac{e^2}{m^2} \left[\frac{E_1 E_1^*}{D(\omega_1) D(-\omega_1)} + \frac{E_2 E_2^*}{D(\omega_2) D(-\omega_2)} \right],$$

and solving the above equation for $\tilde{x}^{(2)}(0)$, we have

$$\tilde{x}^{(2)}(0) = -2a \frac{e^2}{m^2} \frac{E_1 E_1^*}{D(0) D(\omega_1) D(-\omega_1)} + -2a \frac{e^2}{m^2} \frac{E_2 E_2^*}{D(0) D(\omega_2) D(-\omega_2)}. \quad (3.28)$$

We can express the susceptibilities $\chi^{(1)}$ and $\chi^{(2)}$ using (3.25) - (3.28). The linear susceptibility is defined through the relation

$$P^{(1)}(\omega_i) = \chi^{(1)}(\omega_i) E(\omega_i). \quad (3.29)$$

The linear contribution to the polarisation is given as

$$P^{(1)}(\omega_i) = -N e \tilde{x}^{(1)}(\omega_i). \quad (3.30)$$

From (3.29) and (3.30) and the expression for $E(\omega_i)$ given by (3.19), we can then write the susceptibility, $\chi^{(1)}(\omega_i)$, as

$$\chi^{(1)}(\omega_i) = \frac{N \frac{e^2}{m}}{D(\omega_i)}. \quad (3.31)$$

Let us also write the expressions for the second order nonlinear susceptibility $\chi^{(2)}$ for the second harmonic, sum frequency, difference frequency and optical rectification. The nonlinear susceptibility for the second harmonic generation at the frequency ($2\omega_1$) is defined by the relation

$$P^{(2)}(2\omega_1) = \chi^{(2)}(2\omega_1, \omega_1, \omega_1) E(\omega_1)^2 = -N e x^{(2)}(2\omega_1). \quad (3.32)$$

where $P^{(2)}(2\omega_1)$ is the amplitude of the component of the nonlinear polarisation oscillating at frequency $2\omega_1$. To obtain the expression for the second order nonlinear susceptibility in terms of the number density, we make use of (3.23) and (3.32), we then have

$$\chi^{(2)}(2\omega_1, \omega_1, \omega_1) \left[\frac{x^{(2)}(2\omega_1) D(2\omega_1) D^2(\omega_1)}{-a \left(\frac{e}{m}\right)^2} \right] = -N e x^{(2)}(2\omega_1)$$

$$\chi^{(2)}(2\omega_1, \omega_1, \omega_1) = \frac{N \frac{e^3}{m^2} a}{D(2\omega_1) D^2(\omega_1)}. \quad (3.33)$$

Using (3.31), we can express (3.33) in terms of the linear susceptibility as

$$\chi^{(2)}(2\omega_1, \omega_1, \omega_1) = N \left(\frac{e^3}{m^2}\right) a \cdot \frac{\chi^{(1)}(2\omega_1)}{N \left(\frac{e^2}{m}\right)} \cdot \frac{[\chi^{(1)}(\omega_1)]^2}{N^2 \left(\frac{e^4}{m^2}\right)}$$

$$= \frac{m a}{N^2 e^3} \chi^{(1)}(2\omega_1) [\chi^{(1)}(\omega_1)]^2. \quad (3.34)$$

Likewise, we obtain the nonlinear susceptibility for the second harmonic generation at $2\omega_2$, which is trivial from (3.33) and (3.34) by replacing ω_1 by ω_2 .

For the sum frequency generation, the nonlinear susceptibility is obtained, using the definition

$$P^{(2)}(\omega_1 + \omega_2) = 2\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) E(\omega_1) E(\omega_2), \quad (3.35)$$

and

$$P^{(2)}(\omega_1 + \omega_2) = -Nex^{(2)}(\omega_1 + \omega_2), \quad (3.36)$$

and we can then write the susceptibility as

$$\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{N \left(\frac{e^3}{m^2} \right) a}{D(\omega_1 + \omega_2) D(\omega_1) D(\omega_2)}. \quad (3.37)$$

Proceeding in a similar manner as for the second harmonic generation, we can also express the susceptibility of the sum frequency generation, $(\omega_1 + \omega_2)$, in term of the linear susceptibilities and the number density as

$$\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{ma}{N^2 e^3} \chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2). \quad (3.38)$$

The susceptibility for the difference frequency generator is trivial and follows as

$$\begin{aligned} \chi^{(2)}(\omega_1 - \omega_2, \omega_1, -\omega_2) &= \frac{N \left(\frac{e^3}{m^2} \right) a}{D(\omega_1 - \omega_2) D(\omega_1) D(-\omega_2)} \\ &= \frac{ma}{N^2 e^3} \chi^{(1)}(\omega_1 - \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_2). \end{aligned} \quad (3.39)$$

For optical rectification the susceptibility is also trivial and is given by

$$\begin{aligned} \chi^{(2)}(0, \omega_1, -\omega_1) &= \frac{N \left(\frac{e^3}{m^2} \right) a}{D(0) D(\omega_1) D(-\omega_1)} \\ &= \frac{ma}{N^2 e^3} \chi^{(1)}(0) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_1). \end{aligned} \quad (3.40)$$

This is the case of resonant enhancement, where $\omega_1 \Rightarrow \omega_2$. More discussions on this will be done in Chapter 4.

4. Four Wave Mixing

4.1 Introduction

The interaction of electromagnetic fields to produce a fourth field is the basic concept behind the description of all four wave mixing processes. The process can be considered as individual interaction of the fields within a dielectric medium. The first input field causes an oscillating polarisation in the dielectric which reradiates with some phase shift which is determined by the damping of the individual dipoles. The application of a second field will also drive the polarisation of the dielectric and the two waves can interfere. The interference of the two waves can cause harmonics in the polarisation at the sum and difference frequencies. The application of a third field will also drive the polarisation. This can beat with both the input fields and the sum and difference frequencies. The beating with the sum and difference frequencies results in a fourth wave and the process is known as four wave mixing.[1] In this chapter we shall discuss some of the most common four wave mixing processes used in experimental science[1]. These are processes that take place in any media that is centrosymmetric or in isotropic materials. A feature of this is the nonlinear coupling between four monochromatic optical waves and therefore called four wave mixing. It is also known as four-photon parametric interaction. The process could give rise to induced refractive index change or certain spectroscopic responses of the nonlinear medium, as will be discussed in this chapter.

4.2 Four Wave Mixing Processes

Here we consider four wave mixing effects in a nonlinear medium. A common feature of this is the parametric interaction between four photons in third-order nonlinear media.

4.2.1 Sum Frequency Generation

Waves of different frequencies ν_1 , ν_2 , and ν_3 interact with a nonlinear medium to generate a new coherent radiation at the sum frequency ν_4 . This can be viewed as a process composed of two steps. The first is the annihilation of three incident photons while a molecule makes a transition from its initial (ground) state to an intermediate state. In the second step, the molecules return to its initial state while a new photon is created. An illustration of the process is shown in figure (4.1). The time of the molecule staying in the intermediate state is extremely short (near to the response time of electron-cloud distortion), that the two steps actually occur simultaneously. The process does not change the quantum states of the molecules and thus, energy and momentum is conserved between the annihilated photons and the created photons[8]. The conservation of energy and momentum for this process follows as

$$\begin{aligned} h\nu_4 &= h\nu_1 + h\nu_2 + h\nu_3, \\ \kappa_4 &= \kappa_1 + \kappa_2 + \kappa_3. \end{aligned} \tag{4.1}$$

For a collinear interaction ($\kappa_1, \kappa_2, \kappa_3$ and κ_4 in the same direction), the second part of (4.1) leads to the phase matching condition for the refractive indices. Making use of the expression for κ in (1.24) and the second of (4.1), we can write the phase matching condition as

$$\begin{aligned} \frac{\omega_4}{c}n_4 &= \frac{\omega_1}{c}n_1 + \frac{\omega_2}{c}n_2 + \frac{\omega_3}{c}n_3, \\ \nu_4 n(\nu_4) &= \nu_1 n(\nu_1) + \nu_2 n(\nu_2) + \nu_3 n(\nu_3), \end{aligned} \quad (4.2)$$

where $n(\nu_1)$ is the refractive index of the wave at frequency ν_1 and this applies to the other frequencies as well. This type of interaction requires three incident waves ($\nu_1 \neq \nu_2 \neq \nu_3$) or two incident waves ($\nu_1 = \nu_2$ and ν_3)[8]. The contribution to the third order polarisation comes from the mechanism of electronic cloud distortion[8].

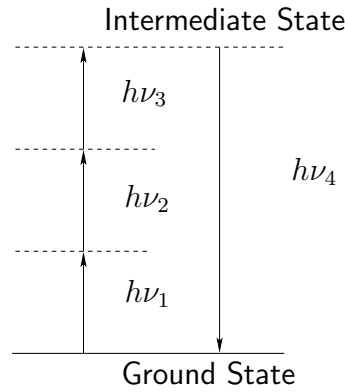


Figure 4.1: Sum frequency generation

4.2.2 Third Harmonic Generation

The first optical third harmonic generation (THG) was observed in 1962 in a calcite crystal which was centrosymmetric[8]. A single monochromatic coherent optical wave of frequency $\nu_1 = \nu$, may induce a new coherent optical wave at the frequency of $\nu_2 = 3\nu$. This involves two steps. The first is the annihilation of three photons from the fundamental wave while a molecule of the nonlinear medium makes a transition from its initial state to an intermediate state and during the second step, the molecule returns to its initial state with the creation of one photon of the third harmonic wave as shown in figure (4.2) below. The two process occur simultaneously[8]. The conservation of energy and momentum for the transition follows as

$$\begin{aligned} h\nu_2 &= 3h\nu_1, \\ \kappa_2 &= 3\kappa_1, \end{aligned} \quad (4.3)$$

where κ_1 and κ_2 are the wave vectors of the two waves. From (4.3), we obtain the refractive-index requirement for collinear interaction as

$$\frac{2\pi}{\lambda_2}n(\nu_2) = \frac{6\pi}{\lambda_1}n(\nu_1), \quad (4.4)$$

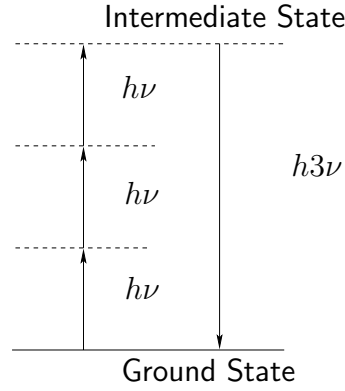


Figure 4.2: Third harmonic generation

where λ_1 and λ_2 are the wavelengths of the two waves in free space. The wavelength of the created photon of the third harmonic wave λ_3 is related to the wavelength of the incident photon λ_1 as $\lambda_3 = \lambda_1/3$ and using (4.4) we obtain the condition that

$$n(3\nu_1) = n(\nu_1), \quad (4.5)$$

which is the phase matching condition for this process. The source of the third harmonic field is the following nonlinear polarisation component[8]

$$\mathbf{P}^{(3)} = \epsilon_0 \chi^{(3)}(\omega, \omega, \omega) \mathbf{E}(\omega) \mathbf{E}(\omega) \mathbf{E}(\omega), \quad (4.6)$$

where $\mathbf{E}(\omega)$ is the incident fundamental optical field and $\chi^{(3)}(\omega, \omega, \omega)$ is the third order nonlinear susceptibility of a given nonlinear medium for third harmonic generation. Assuming that the incident fundamental field $\mathbf{E}(\omega)$ and the frequency tripled field $\mathbf{E}(3\omega)$ are linearly polarised and moving along the z axis, then they can be written as[8]

$$\begin{aligned} \mathbf{E}_1(\omega, z) &= a_1 A_1(z) e^{i\kappa_1 z}, \\ \mathbf{E}_2(3\omega, z) &= a_2 A_2(z) e^{i\kappa_2 z}, \end{aligned} \quad (4.7)$$

where $A_1(z)$ and $A_2(z)$ are the amplitude functions, and \mathbf{a}_1 and \mathbf{a}_2 are the unit vectors of the light polarisation of the fundamental wave and the third-harmonic waves respectively. The corresponding polarisation components of these two waves follows as [8]

$$\begin{aligned} \mathbf{P}^{(3)}(\omega, z) &= \epsilon_0 \chi^{(3)}(3\omega, -\omega, -\omega) \mathbf{E}_2 \mathbf{E}_1^* \mathbf{E}_1^*, \\ \mathbf{P}^{(3)}(3\omega, z) &= \epsilon_0 \chi^{(3)}(\omega, \omega, \omega) \mathbf{E}_1 \mathbf{E}_1 \mathbf{E}_1. \end{aligned} \quad (4.8)$$

Substituting (4.7) into (4.8), it then follows that

$$\begin{aligned} \mathbf{P}^{(3)}(\omega, z) &= \epsilon_0 \chi^{(3)}(3\omega, -\omega, -\omega) \mathbf{a}_2 \mathbf{a}_1 \mathbf{a}_1 A_2(z) A_1^*(z) A_1^*(z) e^{i(\kappa_2 - 2\kappa_1)z}, \\ \mathbf{P}^{(3)}(3\omega, z) &= \epsilon_0 \chi^{(3)}(\omega, \omega, \omega) \mathbf{a}_1 \mathbf{a}_1 \mathbf{a}_1 A_1(z) A_1(z) A_1(z) e^{i3\kappa_1 z}. \end{aligned} \quad (4.9)$$

The coupled wave equation is given by [8]

$$\frac{\partial A(\omega, z)}{\partial z} = \frac{i\kappa}{2\epsilon(\omega)} \left[\mathbf{a}_0 \cdot \mathbf{P}'(\omega, z) e^{-i\kappa z} \right].$$

Substituting the second of (4.9) into the coupled wave equation and we obtain the expression

$$\frac{\partial A_2(z)}{\partial z} = \frac{i\kappa_2\epsilon}{2\epsilon(3\omega)}\chi_e^{(3)}A_1^3(z)e^{i\Delta\kappa z}, \quad (4.10)$$

where

$$\chi_e^{(3)} = \mathbf{a}_2 \cdot \chi^{(3)}(\omega, \omega\omega)\mathbf{a}_1\mathbf{a}_1\mathbf{a}_1. \quad (4.11)$$

From (4.10), we can write $\Delta\kappa$ as

$$\Delta\kappa = 3\kappa_1 - \kappa_2 = \frac{6\pi}{\lambda_1}[n(\omega) - n(3\omega)], \quad (4.12)$$

which is the phase mismatch factor that is proportional to the refractive index difference at ω and 3ω . In general, $n(\omega) \neq n(3\omega)$, except for some special condition, we may have $n(\omega) = n(3\omega)$ which is the phase matching condition. Under phase mismatched condition, $\Delta\kappa \neq 0$. In this situation if we compare the expression of $\mathbf{P}^{(3)}(3\omega, z)$ in (4.9) to that of $\mathbf{E}_2(3\omega, z)$ in (4.7), it is seen that the phase velocity of the polarisation wave at 3ω is different from that of the optical wave at the same frequency. Because of this the energy of $\mathbf{E}_1(\omega, \mathbf{z})$ cannot transfer to $\mathbf{E}_2(3\omega, \mathbf{z})$ wave effectively[8]. In such a case, the signal for the fundamental wave \mathbf{E}_1 is small and thus the amplitude change along the z axis can be neglected [8] since the contribution from the fundamental wave is small compared to that at the third harmonic. We can then make the approximation

$$A_1(z) \approx A_1(0) \quad \text{and} \quad A_2(z) \approx 0,$$

where $A_1(0)$ is the initial amplitude of the fundamental wave at the incident surface of the nonlinear medium and we can then write (4.10) as

$$\begin{aligned} A_2(z) &= \frac{i\kappa_2\epsilon_0}{2\epsilon(3\omega)}\chi_e^{(3)}A_1^3(0)\int_0^z e^{i\Delta\kappa z} dz \\ &= \frac{i\kappa_2\epsilon_0}{2\epsilon(3\omega)}\chi_e^{(3)}A_1^3(0)ze^{\frac{i\Delta\kappa z}{2}}\left(\frac{\sin\frac{\Delta\kappa z}{2}}{\frac{\Delta\kappa z}{2}}\right). \end{aligned} \quad (4.13)$$

The intensity of the third harmonic wave along the z direction is proportional to the square of the amplitude and is written as

$$I_2 = A_2A_2^* = \frac{k_2^2\epsilon_0^2}{4\epsilon^2(3\omega)}|\chi_e^{(3)}|^2 I_1^3(0)z^2\left(\frac{\sin\frac{\Delta\kappa z}{2}}{\frac{\Delta\kappa z}{2}}\right)^2, \quad (4.14)$$

where $I_0(0)$ is the intensity of the incident fundamental wave. From (4.14) it follows that the intensity of the third-harmonic wave is proportional to the cube of the intensity of the fundamental wave and it varies periodically along the z axis. Therefore $I_2(z) \propto A_2A_2^*$ and hence,

$$I_2(z) \propto |\chi_e^{(3)}|^2 I_1^3(0)\left(\frac{\sin\frac{\Delta\kappa z}{2}}{\frac{\Delta\kappa z}{2}}\right)^2.$$

Let us define the coherent length, l_0 , as[6]

$$l_0 = \frac{\pi}{\Delta\kappa} = \frac{\lambda_1}{6 [n(\omega) - n(3\omega)]}. \quad (4.15)$$

The coherent length is the distance over which there is significant generation of third harmonic. For the conversion efficiency to be increased, we desire $\Delta\kappa \Rightarrow 0$ or $n(\omega) \Rightarrow n(3\omega)$. For most transparent media, the normal dispersion effect makes $n(3\omega) > n(\omega)$, but under certain circumstances, we can make the phase-matching fulfilled by special method. The third-order nonlinear susceptibility is much smaller than the second-order susceptibility even with phase matching condition of $\Delta\kappa \Rightarrow 0$.

4.3 Materials For Third Harmonic Generation

In a gaseous medium we can force the equality of $n(\omega)$ and $n(3\omega)$ by adding another gas to the vapour cell. The experimental generation of the third harmonic frequency was be done using a heat pipe.

Metal vapours are suitable materials because of low losses for ultraviolet (UV) emissions, a higher third-order nonlinearity, the achievable phase matching and applicable resonant enhancement[8]. With an anomalous dispersion of a properly chosen one photon absorption line in the near infrared (IR) of visible spectral range of metal vapours, one could find a negative dispersion for the given fundamental wave or $[n(3\omega) - n(\omega)] < 0$; and the effect is compensated for by adding a proper rare gas possessing positive dispersion or $[n(3\omega) - n(\omega)] > 0$. An allowed two-photon transition in the UV range to achieve a resonance enhancement of the nonlinearity of metal vapour system can be found. Some systems of alkali-metal vapours with rare gas added as the buffer medium are $Rb - Xe$, $Na - Xe$, $Sr - Xe$, $Mg - He$, $Mg - Kr$ and $Zn - Ar$ mixtures could be used in the experiment.

Rare gases can also be used as they have a superior transparency in the whole visible to extreme UV (XUV, $\leq 100nm$) spectral ranges, a high chemical and physical stability, and high breakdown threshold. Examples are Xe , Kr and Ar .

4.4 Phase Matching for Third Harmonic Generation

Phase matching is a primary requirement for third harmonic generation as well as other four-wave mixing processes[8]. Let us suppose that gas A is to be used for third harmonic generation and it has a normal dispersion, we can add a suitable amount of a negatively dispersive gas B . Generally $n(\omega) \neq n(3\omega)$ due to the dispersion effects, so we need to use special methods to obtain the phase-matching requirements for a given third harmonic system.

Since the system combines two components of parts A and B , with the first having a normal dispersion and the latter an anomalous dispersion at frequency ω and 3ω written as $n_a(\omega) < n_a(3\omega)$ and $n_b(\omega) > n_b(3\omega)$ respectively, where n_a and n_b are the refractive indices of these

two components when they exist separately. To achieve phase matching, we need to make $n_{a+b}(\omega) = n_{a+b}(3\omega)$ by adding a negatively dispersive gas B [4]. Let us denote the respective refractive indices of the positively and negatively dispersive gases as n_p and n_n and let their fractional concentrations be f_p and f_n respectively. The refractive indices of the mixture are [4]

$$n(\omega) = f_n n_n(\omega) + f_p n_p(\omega), \quad (4.16)$$

$$n(3\omega) = f_n n_n(3\omega) + f_p n_p(3\omega). \quad (4.17)$$

For phase matching we require that $n(\omega) = n(3\omega)$. It then follows from (4.16) and (4.17) that

$$\frac{f_n}{f_p} = \frac{n_p(3\omega) - n_p(\omega)}{n_n(\omega) - n_n(3\omega)}. \quad (4.18)$$

It is assumed that in the considered spectral range there is no resonant absorption for component A resulting in a normal dispersion behaviour. There is a strong (one-photon) absorption around the position of λ_0 for component B resulting in an anomalous dispersion behaviour. Adjusting the concentration ratio of these two components by varying the pressure, phase-matching can be realised between a given fundamental wavelength λ_1 and the corresponding third-harmonic wavelength $\lambda_2 = \frac{\lambda_1}{3}$. Practically, dispersion compensation in a mixed system can be used for liquids or gas systems involving two components.

4.5 Resonance Enhancement

The energy levels of free atoms are very sharp as opposed to those of solids and very large values of the nonlinear susceptibility can be achieved by resonance enhancement[6]. Very large values of the nonlinear susceptibility can be achieved through resonance enhancement[6]. We will illustrate resonance enhancement for the third harmonic generation by considering a two-photon transition. The real atomic levels are indicated by the solid lines while the virtual levels are indicated by the dashed lines as shown in figure (4.3(a)). If we can tune the frequency of the fundamental wave such that it is nearly coincident with the virtual level, the coupling between the radiation and the atom is particularly strong and the nonlinear optical susceptibility becomes large. By tuning the frequency ω of the fundamental wave, we can ensure that $2\omega \Rightarrow \omega_0$, where ω_0 is the resonant frequency of the two-photon absorption thereby obtaining a significant enhancement of the third-order nonlinearity[8]. The experiment was carried out for a mixture of Magnesium and Krypton vapour as the buffer gas in a heat pipe. The pressure of the mixture was varied and the data was obtained for different intensities of the field. Experimental data for the process was obtained and the plot of the data is shown figure 4.3(b). The intensity of the field was plotted against the wavelength. From the plot, it is seen that the susceptibility for the two photon resonance was highest at the wavelength of 430.91 nm. At this point there is third harmonic generation and the field intensity has a frequency three times that of the incident field.

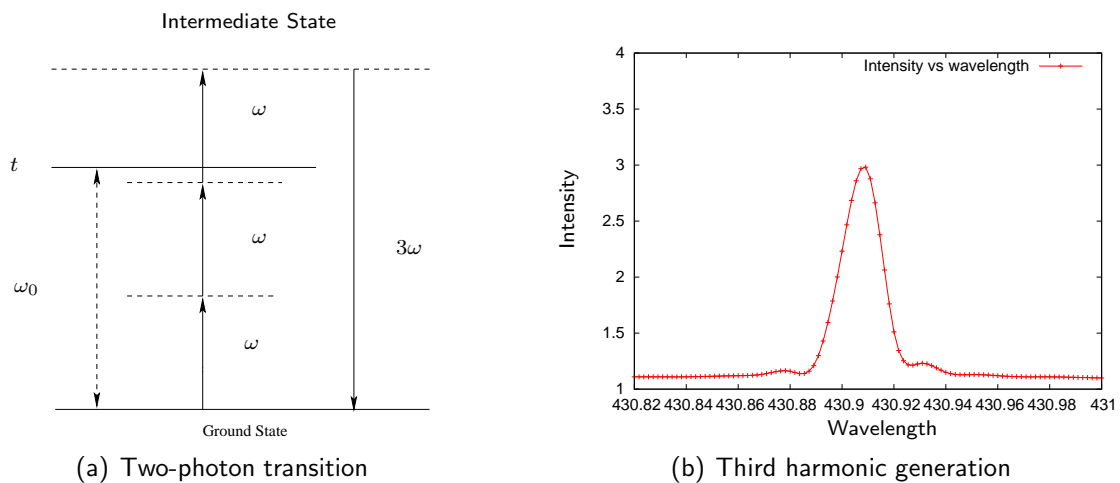


Figure 4.3: Diagrams illustrating two-photon transition and third harmonic generation

4.6 Conclusion

In this essay we have discussed nonlinear optical effects of the third order susceptibility. The nonlinear effects have been shown to occur when high intensity light sources such as lasers are used, and this was observed experimentally by Franken in 1961.

In chapter one, we discussed linear optics and the effect of a low intensity field on a material. For the low intensity fields, we saw that nonlinear effects were not observed. The material was considered as a dipole and treated as a harmonic oscillator and the linear polarisation was obtained. We then made use of Maxwell's equations and obtained the variation of refractive index with frequency in a medium.

In chapter two, we discussed the origin of nonlinear effects in relation to high intensity fields and also discussed dispersion in gases since we would be mainly concerned with gaseous materials for third harmonic generation.

In chapter three we have studied the second order nonlinear effects in a material such as sum frequency generation, difference frequency generation and second harmonic generation. We have also introduced the third order nonlinear effects which were then discussed in more detail in chapter four.

Following the discussions in chapters one, two and three, we then studied the nonlinear effects of the third order susceptibility which included sum frequency generation, difference frequency generation and third harmonic generation. However, we concentrated on third harmonic generation and we have made use of a mixture of gases consisting of metal vapours of Magnesium and Krypton. The theoretical description of the process was carried out and an experimental data of the process obtained.

Further studies on higher order susceptibilities in centrosymmetric materials such as six wave mixing and eight wave mixing can be done.

Appendix A. Codes for the Real and Imaginary Parts of the Refractive Indices

A.1 Real and Imaginary Parts of Index of Refraction with Frequency

$$(\eta_R^2 - \eta_I^2) = 1 + \left(\frac{Ne^2}{m\epsilon_0} \right) \left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2} \right) \quad (\text{A.1})$$

$$(2\eta_R\eta_I) = \frac{Ne^2}{m\epsilon_0} \left[\frac{\omega\gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2} \right] \quad (\text{A.2})$$

```
from __future__ import division
from Numeric import *
import Gnuplot
from scipy import *
from scipy.stats import *
import Gnuplot
import random
g = Gnuplot.Gnuplot(persist=1)
This code computes the real part of the refractive using the equation (A.1) above
Here for simplicity we have chosen the constant term on the right hand side as A=1.
The resonance frequency was also chosen to be w0=15.
A = 1.
w0 = 15.
gamma = 0.1
index = []
for w in arange(0,30,0.05):

    n = 1+ A*(w0**2-w**2)/((w0**2-w**2)**2 + w0**2*gamma**2)
    index.append([w,n])

data = Gnuplot.Data(index, with = 'lines lt 2')
g('set xlabel "frequency"')
g('set ylabel "refractive index"')
g.plot(data,title = 'Real part of refractive index')
g.hardcopy(filename="realindex.eps",terminal="postscript",mode = "landscape")
```

This code computes the imaginary part of the refractive using the equation (A.2) above. Here for simplicity we have chosen the constant term on the right hand side as $A=1$.

The resonance frequency was also chosen to be $w_0=15$.

```
from __future__ import division
from Numeric import *
import Gnuplot
from scipy import *
from scipy.stats import *
import Gnuplot
import random
g = Gnuplot.Gnuplot(persist=1)

A = 1.
w0 = 15.
gamma = 0.1
index = []
X = 0
for w in arange(0,30,0.05):

    I = A*((w*gamma)/((w0**2 -w**2)**2 + w**2*gamma**2))
    index.append([w,I])

data = Gnuplot.Data(index, with = 'lines lt 2')
g('set xlabel "frequency"')
g('set ylabel "refractive index"')
g.plot(data,title = 'Imaginary part of refractive index')
g.hardcopy(filename="imaginary.eps",terminal="postscript",mode = "landscape")
```

Appendix B. Codes for the Molar Refractivity of Gases

The equation (2.27) was used to obtain this plot.

n is the refractive index of the gas.

Below is the code of for the plot

```
from __future__ import division
from Numeric import *
import Gnuplot
from scipy import *
from scipy.stats import *
import Gnuplot
import random
g = Gnuplot.Gnuplot(persist=1)

A = 1.
w0 = 10.
gamma = 0.0
index = []
for w in arange(0,20,0.05):
    if w!=w0:
        n = 1+ (4*pi*A)/(w0**2-w**2 + gamma)
        index.append([w,n])

data = Gnuplot.Data(index, with = 'lines lt 2')
g('set xlabel "frequency"')
g('set ylabel "refractive index"')
g.plot(data,title = 'Refractive index for gas')
g.hardcopy(filename="gasindex.eps",terminal="postscript",mode = "landscape")
```

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