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Second-Order Nonlinear Susceptibility in Quantum Dot Structures

M. Abdullah, Farah T. Mohammed Noori, and Amin H. Al-Khursan

CONTENTS
9.1 Introduction ..........................................................................................................................307
9.2 Semiconductor Nanostructures .............................................................................................308
9.3 Quantum Dots .......................................................................................................................308
9.4 Semiconductor Nonlinearities ..............................................................................................309
9.5 Nonlinear Optical Susceptibility ..........................................................................................310
9.6 Second-Order Nonlinearity ..................................................................................................311
9.7 Quantum Dot Structure under Study ....................................................................................314
9.8 Quantum Disk Model under Applied Electric Field .............................................................315
9.9 Calculated QD Subbands under Applied Electric Field .......................................................319
9.10 Density Matrix Formulation of Optical Susceptibility ........................................................320
9.11 Results on SONS ...................................................................................................................324
9.12 SHG, SFG, DFG, and OR .....................................................................................................328
  9.12.1 Sum-Frequency Generation ......................................................................................330
  9.12.2 Difference-Frequency Generation ............................................................................330
  9.12.3 Optical Rectification .................................................................................................331
9.13 Inhomogeneity in QDs .........................................................................................................331
9.14 Results and Discussion of SHG, SFG, DFG, and OR in QDs ..............................................332
References ......................................................................................................................................339

9.1 INTRODUCTION

With the development of the fabrication technique of nanostructures, multiform semiconductor structures are fabricated [1]. The twenty-first century will see a dramatic change in lighting technologies. By 2025, fluorescent and incandescent illumination sources should be replaced by more efficient, long-lasting, and versatile light sources, offering more lumens per cm² and decreasing the consumption of energy for lighting by 29% [2]. The core of such lighting devices, in its simplest form, is a junction, a relatively simple multilayered structure formed by a semiconductor crystal between two higher bandgap semiconductors, which emits light when an electric current passes through it. The localization of carriers in all three dimensions breaks down the classical band structure of the continuous dispersion of energy as a function of momentum. Unlike quantum wells (QWs) and quantum wires (QWi’s), the energy-level structure of quantum dots (QDs) is quite discrete. This unique structure of QDs opens a new chapter both in fundamental physics in which they
can be regarded as artificial atoms and in potential applications as devices [3,4]. The density of states for a bulk material is a function of energy (−E^{1/2}), while in a zero-dimensional (QD) crystal, the density of states is described by a discrete δ-function, (δ(E)) [5], due to the quantum confinement effect.

9.2 SEMICONDUCTOR NANOSTRUCTURES

One of the important features of semiconductor nanostructures is the flexibility of controlling and designing the properties of such materials [5]. In nanostructures, normally 1–50 nm in scale, the dimensions commensurate with the de Broglie wavelength of the charge carriers so that quantum confinement effects become important and the properties of the semiconductors are significantly modified [5].

Advanced semiconductor growth techniques, such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD), allow the fabrication of various semiconductor nanostructures or low-dimensional structures. Such low-dimensional structures include (1) QWs, where the charge carriers are confined along the growth direction but are free in other two directions; (2) QWi’s, where the charge carriers are confined in two directions and allow free carrier motion in only one dimension; and (3) QDs, where the charge carriers are confined in all the three directions (see Figure 9.1). QW or QWi confinement gains the electron at some degrees of freedom, but it still gives the electron at least one direction to propagate. On the other hand, today’s technology allows us to create QD nanostructures where electron subbands were quantized in all the degrees of freedom [6]. Strong interband (IB) transitions are possible in these low-dimensional structures because there is a probability of a strong overlap between the wave functions of electrons and holes.

9.3 QUANTUM DOTS

The term “quantum dot” is usually used to describe a semiconductor nanocrystal. QDs are zero-dimensional semiconductor systems created at nanoscale. This confinement results in properties that are not found in bulk materials; see Figure 9.2. One of the main differences between QDs and traditional semiconductors is the tunability by both the dot size and composition [7].

![Figure 9.1](image-url)  
**Figure 9.1** Electronic density of states of semiconductor crystals for (a) bulk, (b) quantum well, (c) quantum wire, and (d) quantum dot.
The importance of QDs is originated from the fact that their electrical conductivity can be altered by an external stimulus such as voltage or photon flux. QDs are very sensitive to the surface properties due to a high surface to volume ratio. Surface states play a dominant role in these systems, acting as efficient traps for electrons and holes, and thus surface passivation is essential for fabricating practical semiconductor devices based on such low-dimensional structures [5].

9.4 SEMICONDUCTOR NONLINEARITIES

Semiconductor materials play an important role in nonlinear optics because they both produce a large nonlinear optical response and lend themselves to the construction of integrated devices in which electronic devices, semiconductor lasers, and nonlinear optical components are all fabricated on a single semiconductor substrate [8].

Modern technology has allowed scientists to fabricate high-precision semiconductor QD nanostructures. In these structures, the precise engineering would enable to confine the motion of charge carriers in three dimensions. So, a great deal of work has been performed in this area [10]. Electronic and optical properties of QWs with an applied external electric field are of increasing interest [11]. An analytical relation for energy subband calculations is stated earlier and gives a good result compared with experimental measurements [10–12] and numerical calculations [13,14].

By adding an additional distortion to the energy subbands through the application of an external electric field, one can tune QD nonlinear properties and change the emission spectrum of photoluminescence, both in intensity and wavelength [15]. This results in a precise control of oscillator strength, which opens the way for the development of practical devices such as optical filters and color-tunable sources [16]. Thus, studying of nonlinearity in QD nanostructures under an applied electric field is important for a large number of device applications.

Dane et al. [17] studied the effect of an electric field on the binding energy of a shallow donor impurity in a spherical QD with an infinite barrier. Xie [18] studied the second-order nonlinear susceptibility (SONS) in QDs with a quantum disk shape under an applied electric field. Baskoutas et al. [19] studied nonlinear optical rectification (OR) in semiparabolic QDs, where they found that SONS depends on the type of quantum confinement. Vaseghi et al. [20] studied OR in cubic QDs with an infinite potential barrier, where they found that both the dot size and electric field strength increase with OR. Second-harmonic generation (SHG) in cubic QDs with infinite potential under an applied electric field is considered in the work of Shao et al. [21], where they found a nonmonotonic behavior of SONS with cubic length and applied field. The aforementioned works either consider parabolic confinement or infinite potential. The parabolic confinement gives an equidistant energy subband that is far from the experiment. Also, the use of an infinite barrier limits the accuracy.
compared with experimental data. Although this type of calculations to get an overview of the physical problem is important, it is impractical to consider the finite barrier for real calculations. The accurate description of QD states requires a multiband \( k \cdot p \) calculation, which is limited by the knowledge of the exact shape and composition of QDs [22]. Beyond this tedious calculation, it is required to build a model to calculate the QD energy subbands under the applied electric field. No work deals with QDs in the shape of quantum disks with the finite potential barrier under the applied electric field. This shape of dots was considered in a large number of literatures and self-assembled QDs can be approximated to it, for example, see [22–29]. Thus, starting from the quantum disk model [12], we introduced the electric field effect on QD subbands, where the subbands are shifted to higher energies with the field.

9.5 NONLINEAR OPTICAL SUSCEPTIBILITY

Nonlinear optical properties of semiconductors have received much attention in recent years. The very large optical nonlinearities in semiconductors have offered promise for practical applications in low-power, high-speed, room-temperature optical switching, and signal processing devices [30]. Nonlinear optics has been rapidly growing as a scientific field in recent decades. It is based on the phenomena related to the interaction of intense coherent light radiation with matter. Nonlinear optics is the study of interactions of light with matter under conditions in which the nonlinear response plays an important role. During the past three decades, optics has secured a good place in application areas previously dominated by electronics. Developments in the field of nonlinear optics promise for important applications in optical information processing, telecommunications, and integrated optics. Because of the emergence of this field from solid-state physics in which inorganic semiconductors, insulators, and crystals have constituted a major part of the scientific base, the early experimental and theoretical investigations were primarily concerned with materials from these classes [31].

Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. For example, SHG occurs as a result of the part of the atomic response that scales quadratically with the strength of the applied optical field. Consequently, the intensity of light generated at the second-harmonic frequency tends to increase as the square of the intensity of the applied field [8].

Second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals, that is, in crystals that do not display inversion symmetry. Since liquids, gases, amorphous solids (such as glass), and even many crystals display inversion symmetry, SONS \( \chi^{(2)} \) vanishes identically for such media, and consequently such materials cannot produce second-order nonlinear optical interactions. On the other hand, third-order nonlinear optical interactions (i.e., those described by a third-order nonlinear susceptibility \( \chi^{(3)} \)) can occur for both centrosymmetric and noncentrosymmetric media [8].

A linear dielectric medium is characterized by the linear relation \( P = \varepsilon_0 \cdot \chi \cdot E \), between the polarization density, \( P \), and the electric field, \( E \), where \( \varepsilon_0 \) is the permittivity of free space and \( \chi \) is the optical susceptibility of the medium. A nonlinear dielectric medium, on the other hand, is characterized by a nonlinear relation between \( P \) and \( E \); see Figure 9.3. The nonlinearity may be of microscopic or macroscopic origin. The polarization density \( P = Np \) is a product of the individual dipole moment \( p \) induced by the applied electric field \( E \) and the number density of dipole moments \( N \). The nonlinear behavior may reside either in \( p \) or in \( N \). The relation between \( P \) and \( E \) is linear when \( E \) is small but becomes nonlinear when \( E \) acquires values comparable to interatomic electric fields. Since externally applied optical electric fields are small in comparison with characteristic interatomic or crystalline fields, even when focused laser light is used, the nonlinearity is usually weak. The relation between \( P \) and \( E \) is then approximately linear for small \( E \) [32].
In the regime of conventional optics, the electric polarization vector $P$ is simply assumed to be linearly proportional to the electric field strength $E$ of an applied optical wave, that is
\[ P = \varepsilon_0 \chi E \] (9.1)

where

$\varepsilon_0$ is the free-space permittivity

$\chi$ is the susceptibility of a given medium

A plot of $P$ versus $E$ is a straight line. Equation 9.1 is valid for field strengths of conventional sources. The quantity $\chi$ is a constant only in the sense of being independent of $E$; its magnitude is a function of the frequency. With sufficiently intense laser radiation, this relation does not hold good and has to be generalized to Equation 9.2, which can be written in the following vector form, as by a power series [33]:

\[ \hat{P}(t) = \varepsilon_0 \left[ \chi^{(1)} \hat{E}(t) + \chi^{(2)} \hat{E}^2(t) + \chi^{(3)} \hat{E}^3(t) + \cdots \right] \] (9.2)

The second-order nonlinear effects can occur in the noncentrosymmetrical crystals only. In the dielectric dipole approximation, isotropic media and centrosymmetrical crystals cannot be used to generate second-order nonlinear effects. Therefore, the media for SHG should be the crystals having no inversion symmetry. This requirement is the same as that for the piezoelectric effect; thus, all SHG crystals are piezoelectric crystals although the physical mechanisms for these two effects are different [33].

In SHG, the combination (addition) of two photons of the same frequency was considered to produce a single photon of twice the original frequency. Generalization of this process allows the case in which the two photons have different frequencies. SHG is a nonlinear process where a photon at frequency $2\omega$ is generated from the interaction between intense light at frequency $\omega$ and a nonlinear medium. The interaction of weak light field with matter is dominated by a linear process. With a
very intense light field, nonlinear process such as SHG becomes observable [34]. OR in anisotropic media is well known and was first observed in a potassium dihydrogen phosphate crystal [8]. The magnitude of the induced polarization was found to be proportional to the square of the optical electric field amplitude. For the effect to arise, the medium, isotropic or anisotropic, needs to be of sufficiently low symmetry such that the optically induced electric polarization does not reverse exactly with the optical field [35]. The second-order nonlinear polarization created in the crystal is given by [36]

\[ \tilde{P}^{(2)}(t) = \varepsilon_0 \chi^{(2)} \tilde{E}^2(t) = 2\chi^{(2)}E^2 + (\chi^{(2)}E^2 e^{-2i\omega t}) + \text{c.c.} \]  

(9.3)

The second-order polarization combines two parts: The first part is with zero frequency that leads to the generation of a static electric field within the nonlinear crystal and is known as OR. The second part is with \( e^{-2i\omega t} \) frequency that also leads to the generation of the radiation at the SHG [36].

Let us consider the process of SHG, which is illustrated schematically in Figure 9.4. Here, a laser beam whose electric field strength is incident upon a crystal for which the second-order susceptibility \( \chi^{(2)} \) is nonzero. The nonlinear polarization that is created in such a crystal is given according to Equation 9.3. Under proper experimental conditions, the process of SHG can be so efficient that nearly all of the power in the incident beam at frequency \( \omega \) is converted into radiation at the second-harmonic frequency \( 2\omega \). One common use of SHG is to convert the output of a fixed-frequency laser to a different spectral region. SHG can be visualized by considering the interaction in terms of the exchange of photons between the various frequency components of the field. According to this picture, which is illustrated in part (b) of Figure 9.4, two photons of frequency \( \omega \) are destroyed and a photon of frequency \( 2\omega \) is simultaneously created in a single quantum-mechanical process [8].

Let the optical field incident upon a second-order nonlinear optical medium consists of two distinct frequency components; it can be represented by

\[ \tilde{E}(t) = E_1 e^{-i\omega t} + E_2 e^{-i2\omega t} + \text{c.c.} \]  

(9.4)

The nonlinear polarization, using Equation 9.2, is given by

\[ P^2(t) = \varepsilon_0 \chi^{(2)} \left[ E_1^2 e^{-2i\omega t} + E_2^2 e^{-2i2\omega t} + 2E_1E_2 e^{-i(\omega_1 + \omega_2) t} + 2E_1\omega_1^* E_2^* e^{-i(\omega - \omega_2) t} + \text{c.c.} \right] 
\]

\[ + 2\varepsilon_0 \chi^{(2)} [E_1E_1^* + E_2E_2^*] \]  

(9.5)

FIGURE 9.4 (a) Geometry of second-harmonic generation. (b) Energy-level diagram describing second-harmonic generation.
Each expression in this equation refers to a nonlinear physical process. The first two terms with \( e^{-2i\omega t} \) dependence are related to SHG, the third term powers to \((\omega_1 + \omega_2)\) refers to sum-frequency generation (SFG), the fourth term powers to \((\omega_1 - \omega_2)\) is the difference-frequency generation (DFG), while the last two terms refer to the OR process. There is also a response to the negative of each of nonzero frequencies. It is not necessary to take explicit account of both the positive and negative frequency components [8]. SHG, SFG, DFG, and OR are four different nonzero frequency components present in the nonlinear polarization. However, typically no more than one of these frequency components will be present with any appreciable intensity in the radiation generated by the nonlinear optical interaction. The reason for this behavior is that the nonlinear polarization can efficiently produce an output signal only if a certain phase-matching condition is satisfied, and usually this condition cannot be satisfied for more than one frequency component of the nonlinear polarization. Operationally, one often chooses which frequency component will be radiated by properly selecting the polarization of the input radiation and the orientation of the nonlinear crystal [8].

The process of SFG is illustrated in Figure 9.5. In many ways, it is analogous to that of SHG, except that in SFG the two input waves are at different frequencies. The process of DFG is illustrated in Figure 9.6. Superficially, DFG and SFG appear to be a very similar process [8].

Nonlinear optics has been growing rapidly as an important scientific field in recent decades. It is based on a phenomenon related to the interaction of intense coherent light radiation with matter. Development in this field is promised for important applications in the optical information processing, telecommunications, and integrated optics. Because of the emergence of this field from solid-state physics, in which inorganic semiconductors, insulators, and crystals have constituted a major part of the scientific base, the early experimental and theoretical investigations were primarily concerned with the materials from these classes [31]. Modern technology has allowed scientists to fabricate high-precision semiconductor nanostructures, QDs. Therefore, they tremendously attract the attention due to their unique physical properties and their potential applications in micro- and nanooptoelectronic devices [9,10].
Semiconductor Nanocrystals and Metal Nanoparticles

One of the most basic nonlinear processes is the SONS. It requires a symmetry breaking. Thus, it can be explored in QWs having asymmetry results from the modulation doping or from the application of an external electric field. QDs are considered as asymmetric structures due to their inhomogeneity, and thus SONS in QDs is calculated in some articles without consideration of an applied electric field [37]. Third-order nonlinearity in QDs was studied in detail; as an example, see [23–26,38], considering zero-diagonal matrix elements (symmetry is found).

QDs are promising candidates to achieve large nonlinear susceptibilities. In nanostructures, nonlinear susceptibility increases due to two factors: (1) large dipole matrix elements associated with intersubband (ISB) transitions and (2) these ISB transitions that can be adjusted by changing the QW size [37]. Additionally, nonlinear phenomena at nanoscale are different from that at bulk (conventional structures). The conventional and second-harmonic waves must propagate in phase to fulfill the phase-matching condition to create constructive interference and, then, increase conversion efficiency. For small photonic cavities, the classical phase-matching conditions are replaced by a spatial overlap of localized modes [39].

Earlier studies of SONS in QDs depend on the asymmetrical shape of the self-assembled QDs. In [37], a lens-shaped QD with infinite barrier potential was considered by Brunhes et al. to study SONS. They predicted a giant SONS compared with the bulk and QW response due to the achievement of resonance conditions with intraband transitions. A deviation from experimental results was observed, which can be reasoned to the infinite potential considered. The research work in [37] was developed in [40] using the finite potential barrier, and a good agreement was obtained between theoretical predictions and experimental measurements of SONS.

In addition to the asymmetrical shape of spontaneously formed QDs during the growth process, most of the work dealing with SONS in QDs under applied electric field considers an infinite barrier or a simple harmonic oscillator type. This results from the complexity associated with the numerical calculations and then only small number of studies dealt with QDs under the applied electric field [15].

The purpose of this chapter is to show that a record value of SONS can be achieved using QD IB and ISB transitions. To demonstrate this effect, the chosen model system was InAs/InGaAs self-assembled QDs, which corresponds to the standard Stranski–Krastanov growth mode [37]. Although the presented results are directly connected to the shape and composition of the QDs, similar features are expected to occur for other types or shapes of QDs. The QD energy subbands are first calculated in the effective mass approximation by solving the three-dimensional Schrödinger equation. Then, SONS is computed in both the conduction and valence bands from the calculated energy dependence of the confined subbands.

Recent development in the field of nonlinear optics has been pushing nonlinear optical materials into practical applications. Nonlinear optical materials are those in which light waves can interact with each other [41]. To measure the nonlinear response of matter to electromagnetic waves in the optical region, in general, high fields are necessary, starting at about 1 kV/cm. The corresponding light intensities of some kW/cm² necessitate laser beams. As laser physics started with the ruby laser with its high pulse intensities, it took only few years after the invention of the laser [42] that many classical experiments in nonlinear optics were successfully performed.

9.7 QUANTUM DOT STRUCTURE UNDER STUDY

The QD structure simulated in this theoretical study is a 10-fold InAs QD layer grown by MBE at NanoSemiconductor GmbH in Germany [26,28]. Each QD array is covered with an InGaAs wetting layer (WL) and a 33 nm thick GaAs barrier layer. Each QD active layer is sandwiched between 1.5 μm thick AlGaAs cladding layers. An InAs QD is treated as a quantum disk with a radius of \( a \) and a height of \( h \). The corresponding material parameters used are listed in Tables 9.1 and 9.2.
Second-Order Nonlinear Susceptibility in Quantum Dot Structures

9.8 QUANTUM DISK MODEL UNDER APPLIED ELECTRIC FIELD

Dots here are considered as a quantum disk with a radius of $a$ and a height of $h$ grown on WL in the form of a QW, with a finite constant potential assumed for both quantum disk and WL. The Hamiltonian in the cylindrical coordinates ($\rho$, $\phi$, $z$) is given by

$$
H = -\frac{\hbar^2}{2m^*} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \right) + \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \right] + V
$$

(9.6)

where the effective mass is $m^* = m^*_d$ inside the disk and $m^* = m^*_b$ in the barrier. Similarly, the electric potential is $V = V_d$ inside the disk and $V = V_b$ in the barrier. For strongly confined nanostructures, the electron–hole Coulomb interaction is surpassed by the quantization energy [43]. This is used in a large number of works that deal with QDs under an applied electric field. For example, in [21], the Hamiltonian is the same, but the researchers considered infinite potential that is far from practice although it has theoretical importance in viewing the problem. In [44], the similar Hamiltonian is used, but the researchers considered a harmonic oscillator type of confinement potential that makes energy subbands as that of the simpler problem of an electron in a box where

<table>
<thead>
<tr>
<th>Table 9.1</th>
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<tr>
<td>Parameter</td>
<td>InAs (Dot)</td>
</tr>
<tr>
<td>$E_z$ (eV)</td>
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</tr>
<tr>
<td>$m^*_b$</td>
<td>0.023$m_e$</td>
</tr>
<tr>
<td>$m^*_d$</td>
<td>0.4$m_e$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>41</td>
</tr>
<tr>
<td>$N$</td>
<td>$5 \times 10^{10}$ cm$^{-2}$</td>
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</table>

<table>
<thead>
<tr>
<th>Table 9.2</th>
<th>Experimental Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
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<td>$\gamma_{31}$ (1/ps)</td>
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<tr>
<td>$\gamma_{30}$ (1/ps)</td>
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</tr>
<tr>
<td>$\gamma_{32}$ (1/ps)</td>
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<tr>
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<td>$\gamma_{30}$ (1/ps)</td>
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<tr>
<td>$\gamma_{32}$ (1/ps)</td>
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<tr>
<td>$\gamma_{33}$ (1/ps)</td>
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</tr>
<tr>
<td>$\gamma_{33}$ (1/ps)</td>
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</tr>
<tr>
<td>$\gamma_{33}$ (1/ps)</td>
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</tr>
<tr>
<td>$\gamma_{30}$ (1/ps)</td>
<td>0.25</td>
</tr>
<tr>
<td>$\Omega_s$ (eV)</td>
<td>0.1</td>
</tr>
<tr>
<td>$\Omega_p$ (eV)</td>
<td>1</td>
</tr>
</tbody>
</table>
energy subbands become multipliers of $\hbar \nu$, with the addition of the part due to the applied field. Thus, our Hamiltonian is acceptable and more practical. Solving the Schrödinger equation under the parabolic band model gives the wave function of the quantum disk. Each state can be characterized by three integral quantum numbers $(nml)$, where $nm$ and $l$ correspond to $\rho$–$\phi$ (transverse) and $z$-dependence, respectively. The wave function of the state $(nml)$ at the position $r = (\rho, \phi, z)$ is expressed as [12]

$$\phi_d(r) = C_{nm} \frac{e^{im\phi}}{\sqrt{2\pi}} \begin{cases} J_m(\rho p) \cos(kz) & \text{if } \rho \leq a \text{ and } |z| > h/2 \\ J_m(\rho p) \cos(kz/2)e^{-\alpha|z-h/2|} & \text{if } \rho > a \text{ and } |z| \leq h/2 \\ J_m(\rho p) K_m(qp) \cos(kz) & \text{Otherwise} \end{cases}$$

(9.7)

where $J_m(\rho p)$ and $K_m(qp)$ are the Bessel function of the first kind and the modified Bessel function of the second kind, respectively.

$C_{nm}$ is the normalization constant.

$p$, $q$, $k_z$, and $\alpha$ are constants that are determined from the boundary conditions at the interface between the quantum disk and the surrounding material.

If the separation of variables is assumed in the solution of the Hamiltonian, an approximate wave function of the quantum disk can be obtained [42] by solving the well-known problems of the two-dimensional circular potential well in the $\rho$–$\phi$ direction and the one-dimensional square potential well in the $z$-direction. In the $\rho$–$\phi$ direction, we have a solution of the form

$$\Psi(\rho, \phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \begin{cases} C J_m(\rho p) & \text{if } \rho \leq a \\ C K_m(qp) & \text{if } \rho > a \end{cases}$$

(9.8)

where

$$p = \sqrt{\frac{2m^* (E_p - V_d)}{\hbar}} \quad \text{and} \quad q = \sqrt{\frac{2m^* (V_b - E_p)}{\hbar}}$$

Using the boundary condition in which the wave function $\Psi$ and its first derivative are divided by the effective mass $(1/m^*) (m^* \neq m)$, this requires continuous process to obtain the eigenequation. The procedure of derivation is described well in [12]. In [27], the results of the model are compared with that obtained from tight-binding calculations and are found convenient with it. For convenience, if the potential in the disk is taken as $V_d = 0$, the transverse eigenenergy $E_p$ is obtained by [12]

$$E_p = \frac{\hbar^2}{2m^*_d} \left( \frac{(pp)^2}{a^2} \right)$$

(9.9)
Second-Order Nonlinear Susceptibility in Quantum Dot Structures

The solution for the wave function for the $z$-dependence in a finite QW of width $L$ and depth $V_0$ in the presence of a constant electric field $F$ lies along the positive direction of the well $z$ [13]. Generally, when an electric field is applied to a QW structure as schematically illustrated in Figure 9.7, the profile of the potential will be changed. The total potential is given by

$$V(z,F) = V(z,0) - e z F$$

(9.10)

where

- $V(z,0)$ is the potential profile of the QW
- $F$ is the applied electric field in (kV/cm)
- $e$ is the electronic charge
- $z$ is the associated spatial coordinate

We choose the origin to be at the center of the well.

Substituting Equation 9.10 into the Schrödinger equation, we arrive at the following formula:

$$-\frac{\hbar^2}{2m^*} \frac{d^2}{dz^2}\psi(z) + [eFz + V_0 + |eFz|]\psi(z) = E\psi(z) \quad \text{for } |z| \leq L/2$$

(9.11)

where the potential profile of the QD in the $z$-direction is given by

$$V(z) = \begin{cases} 0 & \text{for } |z| \leq L/2 \\ V_0 & \text{for } |z| \geq L/2 \end{cases}$$

(9.12)

where $V_0 = B_{\text{eff}} [E_{\text{GW}} - E_{\text{gd}}]$, in which $B_{\text{eff}}$ is the band offset and $E_{\text{gw}}$ and $E_{\text{gd}}$ are the bandgaps of WL and QD, respectively. The wave function in the well and barrier regions is described by [13]
\[
\Psi(z) = \begin{cases} 
C_1 \text{Ai}(\eta_1) & z > -L/2 \\
C_2 \text{Ai}(\eta_1) + D_2 \text{Bi}(\eta_1) & |z| \leq L/2 \\
C_3 \left[ \text{Bi}(\eta_2) + i\text{Ai}(\eta_2) \right] & z < -L/2
\end{cases}
\] (9.13)

where
\[
C_1, C_2, C_3, D_2, \text{ and } D_3 \text{ are constants}
\]

\( \text{Ai} \) and \( \text{Bi} \) are the homogeneous Airy function

From the properties of Airy function, it is clear that \( \text{Bi}(\eta_2) \) increases with increasing \( \eta_2 \) and becomes infinity when \( \eta_2 \) is at infinity. In order to make the wave function well behaved in the entire region, this part is not added in the wave function in the region \( z > -L/2 \). Note that

\[
\eta_1 = -\left[ \frac{2m^*}{(e\hbar F)^2} \right]^{1/3} (E - |e|Fz)
\] (9.14)

\[
\eta_2 = -\left[ \frac{2m^*}{(e\hbar F)^2} \right]^{1/3} (E - V_r - |e|Fz)
\]

The required boundary conditions for the coefficients are obtained from the current continuity conditions at the heterojunction as

\[
\Psi(\eta_1)|_{z=-\frac{L}{2}} = \Psi(\eta_2)|_{z=\frac{L}{2}}
\]

\[
\frac{1}{m^*_b} \frac{d\Psi(\eta_1)}{dz} \bigg|_{z=-\frac{L}{2}} = \frac{1}{m^*_d} \frac{d\Psi(\eta_2)}{dz} \bigg|_{z=\frac{L}{2}}
\] (9.15)

This results in the determinant

\[
\begin{vmatrix}
\text{Ai}(\eta_1^*) & \text{Bi}(\eta_1^*) & -\text{Ai}(\eta_2^*) & 0 \\
\text{Ai}(\eta_1^*) & \text{Bi}(\eta_1^*) & -\text{Ai}(\eta_2^*) & 0 \\
\text{Ai}(\eta_2^*) & \text{Bi}(\eta_2^*) & 0 & -\left[ \text{Bi}(\eta_2^*) + i\text{Ai}(\eta_2^*) \right] \\
\text{Ai}(\eta_2^*) & \text{Bi}(\eta_2^*) & 0 & -\left[ \text{Bi}(\eta_2^*) + i\text{Ai}(\eta_2^*) \right]
\end{vmatrix} = 0
\] (9.16)

where \( \eta_1^* \) and \( \eta_2^* \) are the values of \( \eta_1 \) and \( \eta_2 \) evaluated at \( z = L/2 \) and \( z = -L/2 \), respectively. Then, we obtain

\[
A_1 = \left[ A_1(\eta_1)B_1(\eta_2) - \left( \frac{m_b^*}{m_d^*} \right) A_1'(\eta_1)B_1(\eta_2) \right] + i \left[ A_1(\eta_1)A_1'(\eta_1) - \left( \frac{m_b^*}{m_d^*} \right) A_1'(\eta_1)A_1(\eta_1) \right]
\] (9.17)

\[
A_2 = \left[ B_1(\eta_1)B_2'(\eta_2) - \left( \frac{m_b^*}{m_d^*} \right) B_1'(\eta_1)B_2(\eta_2) \right] + i \left[ B_1(\eta_1)A_1'(\eta_1) - \left( \frac{m_b^*}{m_d^*} \right) B_1'(\eta_1)A_1(\eta_1) \right]
\] (9.18)
Second-Order Nonlinear Susceptibility in Quantum Dot Structures

\[ A_{21} = \left[ A'i(\eta_2)Ai(\eta_1) - \left( \frac{m_b^2}{m_f^2} \right) Ai(\eta_1)A'i(\eta_2) \right] \]  
(9.19)

\[ A_{22} = -\left[ A'i(\eta_2)Bi(\eta_1) - \left( \frac{m_b^2}{m_f^2} \right) Ai(\eta_1)B'i(\eta_2) \right] \]  
(9.20)

\[ a_A A_{11} + b_A A_{12} = 0 \]  
(9.21)

\[ a_A A_{21} + b_A A_{22} = 0 \]  
(9.22)

The eigenenergy \( E_z \) is obtained by solving Equation 9.22. The total eigenenergy of the quantum disk \( E_d \) is, approximately, the summation of the transverse and longitudinal eigenenergies and is expressed as

\[ E_d = E_p + E_z \]  
(9.23)

This gives the eigenenergy of the QD structure under the applied electric field.

### 9.9 CALCULATED QD SUBBANDS UNDER APPLIED ELECTRIC FIELD

Figure 9.8 shows the calculated QD ground (GS) and excited state (ES) conduction subbands under an applied electric field. The solid lines represent the GS conduction subband (\( E_{c1} \)), while the dashed lines represent the first ES conduction subband (\( E_{c2} \)). For the height \( h = 2 \text{ nm} \)

![Figure 9.8 Quantum dot energy conduction subbands versus the applied electric field for heights \( h = 2 \text{ nm} \) (the red line) and \( h = 3 \text{ nm} \) (the blue line). The disk radius \( a = 13 \text{ nm} \). The solid lines are for ground state (\( E_{c1} \)), while the dashed lines are for first excited state (\( E_{c2} \)).](image-url)
Semiconductor Nanocrystals and Metal Nanoparticles

When the field changes from 10 to 100 V/m, $E_{c1}$ changes by 35.4 meV, while $E_{c2}$ changes by 78.9 meV. This is a Stark shift for QD subbands. Thus, a nonmonotonic change was obtained with the applied field on the QD ES conduction subband. For $h = 3$ nm (the blue lines), approximately similar changes were obtained. A nonmonotonic change of energy subbands with an electric field is also shown in [45,46]. This is a practical behavior and some of this leads us to use Airy functions to describe wave functions under an applied electric field. From Figure 9.9, it is shown that subband energy becomes higher at some value of the applied electric field. This depends on the type of confinement, QD shape, and size. This result coincides with the conclusion drawn in [19,45,46]. This can be justified by a resonance that occurs between the applied field and the subband energy.

Figure 9.9 shows the change of QD GS valence subband for disk radius $a = 13$ nm and for two heights ($h = 2$ nm the red line and $h = 3$ nm the black line) when the field changes by the same range (10–100 V/m). For $h = 2$ nm, GS shifts by 89 meV. This shows that the valence subbands are more sensitive to the applied electric field.

Additionally, as it is shown in Figure 9.10, GS conduction subband was plotted for different quantum disk radii and at three field values. The subband energy decreased with increasing the disk radius and increased with increasing the electric field. Electrons and holes are separated under the applied electric field, and they are pushed apart by the field. Reducing the QD size increases the confinement of carrier wave functions. The shift of QD energy subbands by the Stark effect competes with the shift due to the quantum-size effect. Increasing the disk radius by 1 nm reduces the subband energy by ~3 meV, while increasing electric field by 1 kV/cm increases the subband energy by ~0.7 meV.

9.10 DENSITY MATRIX FORMULATION OF OPTICAL SUSCEPTIBILITY

To derive SONS relation, we use the density matrix approach. It has been proven very useful to study quantum electronic processes in different material systems [47]. The density operator $\rho$ satisfies the equation of motion

$$\frac{\partial}{\partial t} \rho = -i \frac{\hbar}{\hbar} [H, \rho]$$  \hspace{1cm} (9.24)
The Hamiltonian operator consists of three parts

$$H = H_0 + H' + H_{\text{random}}$$

(9.25)

where $H_0$ is the unperturbed Hamiltonian and $H'$ accounts for the interaction such as the electron–photon interaction, which is given by

$$H' = -\mu \cdot E(t) = \sum_{j=1}^{3} \mu^j E_j(t)$$

(9.26)

where $\mu$ is the dipole operator, $\mu = e r$, and $e = -|e|$ for electrons and $+|e|$ for holes. $E$ is the electric field. $H_{\text{random}}$ includes the relaxation effects due to incoherent scattering processes. The equation of motion, Equation 9.24, becomes

$$\frac{\partial}{\partial t} \rho = -\frac{i}{\hbar} [H_0 + H', \rho] + \left( \frac{\partial \rho}{\partial t} \right)_{\text{relax}}$$

(9.27)

where

$$\left( \frac{\partial \rho}{\partial t} \right)_{\text{relax}} = -\frac{i}{\hbar} \left[ H_{\text{random}}, \rho - \rho^{(0)} \right]$$

(9.28)

which can be written in terms of $T_1$ and $T_2$ time constants as follows:

$$\frac{\partial}{\partial t} \left( \rho_{au} - \rho_{au}^{(0)} \right)_{\text{relax}} = -\frac{\rho_{au} - \rho_{au}^{(0)}}{(T_1)_{au}}$$

(9.29)

$$\left( \frac{\partial \rho}{\partial t} \right)_{\text{relax}} = -\frac{\rho_{au}}{(T_2)_{au}} \quad \text{for} \ u = v$$

(9.30)
For the initial distributions, \( \rho_{uv}^{(0)} = \delta_{uv} \), which are diagonal for each state. It is convenient to use

\[
\gamma_{uv} = \frac{1}{(T_1)_{uv}} \quad (9.31)
\]

\[
\gamma_{uv} = \frac{1}{(T_2)_{uv}} \quad \text{for } u \neq v
\]

Taking the \( uv \) component of equation of motion (Equation 9.27) and using

\[
\langle u | H_\alpha \rho - \rho H_\alpha | v \rangle = (E_u - E_v) \rho_{uv}
\]

we obtain the density matrix equation in the presence of an optical excitation

\[
\frac{\partial}{\partial t} \rho_{uv} = -i \frac{\hbar}{\hbar} (E_u - E_v) \rho_{uv} + i \hbar \sum_u \sum_j \left( \mathcal{H}_{uv}^j \rho_{uv} - \rho_{uv} \mathcal{H}_{uv}^j \right) E_j(t) - \gamma_{uv} \left( \rho_{uv} - \rho_{uv}^{(0)} \right) \quad (9.33)
\]

In general, we may define

\[
w_{uv} = \frac{E_u - E_v}{\hbar} \quad (9.34)
\]

and consider the interaction term \( H' = -\mu \cdot \mathbf{E}(t) \) as a small perturbation. The perturbation series gives

\[
\rho = \rho^{(0)} + \rho^{(1)}(E) + \rho^{(2)}(E^2) + \cdots \quad (9.35)
\]

One obtains

\[
\frac{\partial}{\partial t} \rho_{uv}^{(n+1)} = (-i w_{uv} - \gamma_{uv}) \rho_{uv}^{(n+1)} + i \frac{\hbar}{\hbar} \sum_u \sum_j \left( \mathcal{H}_{uv}^j \rho_{uv}^{(n)} - \rho_{uv}^{(n)} \mathcal{H}_{uv}^j \right) \tilde{E}_j(t) \quad (9.36)
\]

For \( n \geq 0 \), consider an optical field given by

\[
\tilde{E}(t) = \sum_{a=1}^{N} \tilde{E}_a(t) e^{-iw_{uv} t}
\]

The polarization per unit volume is calculated from the trace of the matrix product of the dipole moment matrix \( \mu \) and the density matrix

\[
\tilde{P}(t) = \frac{1}{V} Tr[\rho(t)\mu] = \frac{1}{V} \sum_{uv} \rho_{uv}(t) \mu_{uv} = \frac{1}{V} \left( \rho_{aa} \mu_{aa} + \rho_{bb} \mu_{bb} + \rho_{ab} \mu_{ab} + \rho_{ba} \mu_{ba} \right) \quad (9.38)
\]
The $i$th component of the polarization density, to the first order in the optical electric field, is given by

$$\tilde{P}^{(i)}(t) = \frac{1}{V} \left( \mu_w \rho_{ab}^{(i)}(w) + \mu_{ab} \rho_{wa}^{(i)}(w) \right) e^{i \omega t} + \frac{1}{V} \left( \mu_w \rho_{ab}^{(i)}(-w) + \mu_{ab} \rho_{wa}^{(i)}(-w) \right) e^{-i \omega t} \quad (9.39)$$

The definition of the electric susceptibility $\chi_{ij}$ is obtained using

$$\tilde{P}^{(m)}(t) = e_0 \chi_{ij}^{(m)}(w) E(w) e^{i \omega t} + e_0 \chi_{ij}^{(m)}(-w) E(-w) e^{-i \omega t} \quad (9.40)$$

By calculating the density operator $\rho^{(n)}$ for the $n$th order for the two- or three-level system and substituting into Equation 9.39 and comparing with Equation 9.40, we obtain the optical susceptibility $\chi^{(n)}(w)$.

In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in a manner that can often be described by the relationship

$$\tilde{P}^{(1)}(t) = e_0 \chi^{(1)}(w) E(t) \quad (9.41)$$

where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and $e_0$ is the permittivity of free space. In nonlinear optics, the optical response can often be described by generalizing Equation 9.41 by expressing the polarization $P(t)$ as a power series in the field strength $E(t)$ as

$$\tilde{P}(t) = e_0 \chi^{(1)}(w) E(t) + \chi^{(2)}(w) \tilde{E}^2(t) + \chi^{(3)}(w) \tilde{E}^3(t) + \cdots \quad (9.42)$$

The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second- and third-order nonlinear optical susceptibilities, respectively.

In the three-level system considered (Figure 9.11) here, only $2 \rightarrow 1$ and $3 \rightarrow 2$ transitions are dipole allowed [29]. From the earlier relations, the IB transition, $\mu_{21}$, can be derived. Then, SONS for IB transition is written as

$$\chi^{(2)}(w) = \frac{1}{\hbar e_0} \left[ \frac{\Omega \mu_{21} (\rho_{21}^{(0)} - \rho_{21}^{(0)}) (\mu_{22} - \mu_{11})}{[(w_{21} - w_s)^2 - \Gamma_{21}]^2} \right] \quad (9.43)$$

![FIGURE 9.11 Schematic diagram of the potential profiles and relevant parameters in a semiconductor quantum dot system. (H1 = the heavy-hole ground state, C1 = the conduction band ground state, and C2 = the first excited state of conduction band.)](image-url)
Similarly, for ISB transitions, ISB SONS was derived. It can be written as

$$\chi^{(2)}(w_p) = \frac{1}{\hbar \varepsilon_0} \left\{ \frac{\Omega_s \mu_{32} (\rho^{(0)} - \rho^{(0)} \phi_{33} - \mu_{32})}{(w_{32} - w_p)^2} \right\}$$

(9.44)

where $\omega_s$ and $\omega_p$ are their frequency separations of the signal and the pump, respectively, $\Omega_s = \mu_{21} E_s / \hbar$, $w_{21} = (E_2 - E_1) / \hbar$ and $\Omega_p = \mu_{32} E_p / \hbar$, $w_{32} = (E_3 - E_2) / \hbar$. The ISB dipole moment ($\mu_{32}$) between the GS (C1 or level 2) and the first ES (C2 or level 3) of the conduction band is calculated according to [25]

$$\mu_{32} = \langle \phi_{3j}(r) | \hat{e} | \phi_{2j}(r) \rangle$$

(9.45)

where

- $e$ is the unit charge
- $|r|$ is the distance

On the other hand, the IB dipole moment ($\mu_{21}$) is expressed as follows [25]:

$$\mu_{21} = e \left( \frac{1}{m_0 w_{21}} - \zeta \langle u | \hat{\rho} | u \rangle \langle \phi_{2j}(r) | \phi_{2j}(r) \rangle \right)$$

(9.46)

where

- $\zeta$ is an enhancement factor due to excitonic effects
- $m_0$ is the free electron mass

9.11 RESULTS ON SONS

The real and imaginary parts of the SONS for IB transition at 10–100 kV/cm electric field strengths are shown in Figure 9.12. From Figure 9.12a through c, it is shown that both real and imaginary parts of susceptibility were reduced and the peak wavelength was shifted toward the longer wavelength by increasing the electric field strength. The susceptibility was reduced by two times and the peak wavelength was increased by 36 nm when the electric field increases to 50 kV/cm and by 1.5 times and 89 nm when the electric field increases to 100 kV/cm. This is consistent with the experimental evidence that the applied electric field quenches the photoluminescence in QDs [16]. It is a result of the reduced overlap between electron and hole wave functions, where they are separated by the electric field due to their opposite charges. Our results of SONS in Figure 9.12 are on the order of $10^{-2}$ m/V, which is in the range of He and Xie results [48].

For the case of conduction ISB transitions, SONS is shown in Figure 9.13, both real and imaginary parts of SONS were increased by more than two orders of magnitude, and their peak wavelengths were increased more than 7000 nm when the field changes from 10 to 100 kV/cm. Note that the peak wavelength was reduced when the field is 50 kV/cm than that at 10 and 100 kV/cm. This relates to the position of subband energy when the field was increased to 50 kV/cm as shown in Figures 9.8 and 9.10.

SONS, for valence ISB transitions, is shown in Figure 9.14. The peak values are of the same order of that of conduction ISB transitions, while their wavelengths are increased by more than one order of magnitude. Their obtained wavelengths lie between 33 and 157 µm, which are important in terahertz applications. The subband energy difference at 10 kV/cm is 0.8, 0.14, and 0.037 eV for the first IB transition, conduction ISB transition, and first valence ISB, respectively. These differences can explain the ranges of wavelengths of these structures shown in Figures 9.12 through 9.14.
FIGURE 9.12  The imaginary (the blue line) and the real (the red line) second-order nonlinear susceptibility for interband transition under applied electric field with strengths of (a) 10 kV/cm, (b) 50 kV/cm, and (c) 100 kV/cm.
FIGURE 9.13  The imaginary (the blue line) and the real (the red line) second-order nonlinear susceptibility for conduction intersubband transition under applied electric field with strengths of (a) 10 kV/cm, (b) 50 kV/cm, and (c) 100 kV/cm.
FIGURE 9.14  The imaginary (the blue line) and the real (the red line) second-order nonlinear susceptibility for valence intersubband transition under applied electric field with strengths of (a) 10 kV/cm, (b) 50 kV/cm, and (c) 100 kV/cm.
Our result of SONS for both conduction and valence ISB transitions in Figures 9.13 and 9.14 is higher by one order of magnitude than that of IB transitions shown in Figure 9.12. The main factor that controls SONS in QDs, here, is the momentum matrix element. For conduction ISB transitions, the factor $\mu_{23}(\mu_{33} - \mu_{22})$ in Equation 9.44 is higher by one order of magnitude than the factor $\mu_{12}(\mu_{22} - \mu_{11})$ in Equation 9.43 for IB transitions. This can explain why SONS of ISB transitions is higher than that of IB structure. Figure 9.15 shows the ratio $|(M_{22} - M_{11})/M_{21}|$ for the IB structure where a nonmonotonic change is shown.

9.12 SHG, SFG, DFG, AND OR

The second-order nonlinear processes SHG, SFG, DFG, and OR are the simplest examples of nonlinear molecular spectroscopes and will serve as our example of diagrams that describe nonlinear spectroscopy. Second-order spectroscopes vanish for isotropic samples and are therefore surface selective. There are various nonlinear optical processes. Some of them involve the generation of a new frequency that is different from that of the pump source, while some others do not. The former includes SHG, SFG, and DFG. They are also the topics that will be involved in this chapter. The processes of SHG, SFG, and DFG are all due to the second-order optical nonlinearity [49].

An electromagnetic field incident on a medium induces bound electrons to oscillate about their equilibrium position. In the linear regime, the resulting dielectric polarization is proportional to the applied electric field [8]. The polarization is described by Equation 9.42, where

$$E(t) = E_1 e^{-i\omega t} + E_2 e^{-i2\omega t} + c.c. \tag{9.47}$$

It can be shown that the nonlinear polarization is given by

$$P^2(t) = \varepsilon_0 \chi^{(2)} e \left[ E_1^2 e^{-2i\omega t} + E_2^2 e^{-2i2\omega t} + 2E_1E_2 e^{-i(\omega_1 + \omega_2) t} + 2E_1 E_2^* e^{-i(\omega_1 - \omega_2) t} + c.c. \right] + 2\varepsilon_0 \chi^{(2)} \left[ E_1 E_1^* + E_2 E_2^* \right] \tag{9.48}$$
Second-Order Nonlinear Susceptibility in Quantum Dot Structures

It is convenient to express this result using the notation

\[ P^{(2)}(t) = \sum_n P(w_n) e^{-i\omega_n t} \]  

(9.49)

where the summation extends over positive and negative \( \omega_n \) frequencies. The complex amplitudes of various frequency components of the nonlinear polarization are hence given by [8]

\[ P(2w_1) = \varepsilon_0 \chi^{(2)}_1 E_1^2 \quad \text{(SHG)} \]
\[ P(2w_2) = \varepsilon_0 \chi^{(2)}_2 E_2^2 \quad \text{(SHG)} \]
\[ P(w_1 + w_2) = 2\varepsilon_0 \chi^{(2)} E_1 E_2 \quad \text{(SFG)} \]
\[ P(w_1 - w_2) = 2\varepsilon_0 \chi^{(2)} E_1^* E_2^* \quad \text{(DFG)} \]
\[ P(0) = 2\varepsilon_0 \chi^{(2)} (E_1 E_1^* + E_2 E_2^*) \quad \text{(OR)} \]

(9.50)

Note that, in accordance with our complex notation, there is also a response at the negative of each of the nonzero frequencies just given by

\[ P(-2w_1) = \varepsilon_0 \chi^{(2)} E_1^{*-2} \quad \text{(SHG)} \]
\[ P(-2w_2) = \varepsilon_0 \chi^{(2)} E_2^{*-2} \quad \text{(SHG)} \]
\[ P(-w_1 - w_2) = 2\varepsilon_0 \chi^{(2)} E_1^* E_2^* \quad \text{(SFG)} \]
\[ P(-w_1 + w_2) = 2\varepsilon_0 \chi^{(2)} E_1 E_2^* \quad \text{(DFG)} \]

(9.51)

However, since each of these quantities is simply the complex conjugate of one of the quantities given in Equation 9.50, it is not necessary to take explicit account of both the positive and negative frequency components.

For SFG, according to Equation 9.51, the complex amplitude of the nonlinear polarization describing this process is given by the expression [8]

\[ P(w_1 + w_2) = 2\varepsilon_0 \chi^{(2)} E_1 E_2 \]

(9.52)

In many ways, the process of SFG is analogous to that of SHG, except that in SFG where the two input waves are at different frequencies.

For DFG, the process of DFG is described by a nonlinear polarization of the form [8]

\[ P(w_1 - w_2) = 2\varepsilon_0 \chi^{(2)} E_1^* E_2^* \]

(9.53)

Here, the frequency of the generated wave is the difference of those of the applied fields, and DFG and SFG appear to be of very similar processes. We see that the conservation of energy requires that for every photon that is created at the difference frequency \( \omega_3 = \omega_1 - \omega_2 \), a photon at the higher input frequency \( (\omega_1) \) must be destroyed, and a photon at the lower input frequency \( (\omega_2) \) must be
created. Thus, the lower frequency input field is amplified by the process of DFG. For this reason, the process of DFG is also known as optical parametric amplification. According to the photon energy–level description of DFG, the atom, first, absorbs a photon of frequency \( \omega_1 \) and jumps to the highest virtual level. This level decays by a two-photon emission process that is stimulated by the presence of the \( \omega_2 \) field, which is already present. Two-photon emission can occur even if the \( \omega_2 \) field is not applied. The generated fields in such a case are very much weaker, since they are created by spontaneous two-photon emission from a virtual level [8].

The definition of the electric susceptibility \( \chi_{ij} \) is obtained using

\[
\tilde{P}^{(n)}(2w_s - 2w_r) = \varepsilon_0 \chi^{(n)}(2w_s) \tilde{E}(2w_s) e^{-i(2w_s)t} \\
+ \varepsilon_0 \chi^{(n)}(-2w_r) \tilde{E}(-2w_r) e^{i(2w_r)t} \tag{9.54}
\]

It is not necessary to take explicit account of both the positive and negative frequency components [8].

Using the three-level system shown in Figure 9.11. In this configuration, only \( 2 \rightarrow 1 \) and \( 3 \rightarrow 2 \) dipole transitions are allowed, where \( \omega_s \) and \( \omega_p \) are their frequency separations of the signal and the pump, respectively, and the optical susceptibility \( \chi^{(2)}(2w_s) \) can be written as

\[
\chi^{(2)}(2w_s) = \frac{N \mu_1 \mu_2 \mu_{12}}{\hbar^2 \varepsilon_0} \left( \frac{\rho^{(0)}_1 - \rho^{(0)}_2}{(w_s - 2w_r) - i\gamma_{21}} \right) \tag{9.55}
\]

Similarly, the SONS for ISB transitions can be written as

\[
\chi^{(2)}(2w_p) = \frac{N \mu_3 \mu_{32}}{\hbar^2 \varepsilon_0} \left( \frac{\rho^{(0)}_3 - \rho^{(0)}_{32}}{(w_s - 2w_p) - i\gamma_{23}} \right) \tag{9.56}
\]

Similarly, calculated SFG, DFG, and OR for IB and ISB transitions are derived by the same method.

### 9.12.1 Sum-Frequency Generation

Its relation for our system can be written as

\[
\chi^{(2)}(w_s + w_p) = \frac{N \mu_1 \mu_3 \mu_{13}}{2\hbar^2 \varepsilon_0} \left( \frac{\Omega \mu_{32} (\rho^{(0)}_1 - \rho^{(0)}_2)}{(w_s - w_r - i\gamma_{21})[w_s - w_r - w_p - i\gamma_{23}]} \right) \\
- \frac{\Omega \mu_{31} (\rho^{(0)}_3 - \rho^{(0)}_{32})}{(w_s - w_r - i\gamma_{21})[w_s - w_r - w_p - i\gamma_{23}]} \tag{9.57}
\]

where \( \Omega_s = \mu_{21} E_s / \hbar \), \( w_{21} = (E_2 - E_1) / \hbar \) and \( \Omega_p = \mu_{32} E_p / \hbar \), \( w_{32} = (E_3 - E_2) / \hbar \).

### 9.12.2 Difference-Frequency Generation

Its relation for our system can be written as

\[
\chi^{(2)}(w_s - w_p) = \frac{N \mu_1 \mu_3 \mu_{13}}{2\hbar^2 \varepsilon_0} \left( \frac{\Omega \mu_{32}^*(\rho^{(0)}_1 - \rho^{(0)}_2)(\rho^{(0)}_3 - \rho^{(0)}_{32})(\mu_{12} - \mu_{23})}{(w_s - w_r - i\gamma_{21})[w_s + w_p + i\gamma_{23}]} \right) \tag{9.58}
\]

where \( \Omega_p^* = \mu_{12} E_p^* / \hbar \).
9.12.3 OPTICAL RECTIFICATION

For IB transitions (see Figure 9.11)

\[
\chi^{(2)}(0) = \frac{N\mu_{21}\mu_{23}}{2\hbar^2\epsilon_0} \left[ \frac{\Omega_p\Omega_p^* (p_{21}^{(0)} - p_{22}^{(0)}) (p_{21}^{(0)} - p_{11}^{(0)}) (\mu_{22} - \mu_{11}) (\mu_{23} - \mu_{12})}{[w_{21} - \gamma_{21}]^2 [w_{21} + \gamma_{12}]^2} \right] \quad (9.59)
\]

For ISB transitions

\[
\chi^{(2)}(0) = \frac{N\mu_{12}\mu_{23}}{2\hbar^2\epsilon_0} \left[ \frac{\Omega_p\Omega_p^* (p_{22}^{(0)} - p_{23}^{(0)}) (p_{33}^{(0)} - p_{22}^{(0)}) (\mu_{22} - \mu_{23}) (\mu_{22} - \mu_{33})}{[w_{32} - \gamma_{32}]^2 [w_{23} + \gamma_{23}]^2} \right] \quad (9.60)
\]

9.13 INHOMOGENEITY IN QDS

The aforementioned works consider either parabolic confinement or infinite potential. The parabolic confinement gives an equidistant energy subband that is far from experiment. Also, the use of an infinite barrier limits the accuracy comparison with experimental data. Although this type of calculations to get an overview of the physical problem is important, it is impractical to consider a finite barrier for real calculations.

Consider that QD inhomogeneity is important from the practical point of view. The inhomogeneity was included in the study of SONS in QDs in the work of Brunhes et al. [23,24], but they took a QD distribution normalized to the dot height and not as energy distribution. The QD height is not the only factor that is causing inhomogeneous distribution. Many other factors, such as size, dot distribution, and imperfections in the QD shape, contribute to the QD inhomogeneity. Thus, one must cover the spectrum of the dots through the emission spectrum of each one. The energy is the adequate factor to represent. This is what the authors have done here. We need to deal with SONS in QDs and derive that their relations depend on the structure consideration. This is preferred than the present forms applied for any structure atom, QW, QD, or any other types of electronic transition system studied. This is done also here.

The inhomogeneous SONS in QDs is, then, given by

\[
\chi^{(2)} = \int \chi^{(2)}(w_i + w_p, w_p, w_e) D(w)dw
\]

Including QD inhomogeneity makes our formula different from all other researches that deal with SONS calculations in QDs. It is done, here, via the convolution over the inhomogeneous density of states, which is given by [22]

\[
D(w) = \frac{s^i}{V_{\text{eff}}^{\text{dot}}} \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left( -\frac{1}{2\sigma^2} \right) \quad (9.62)
\]

where

- \( s^i \) is the degeneracy number at the QD state \((s^i = 2)\) in the quantum disk model used here
- \( \sigma \) is the spectral variance of QDs
- \( V_{\text{eff}}^{\text{dot}} (= h/N_D) \) is the effective volume of QDs, \( h \) is the dot height, and \( N_D \) is the areal density of QDs
The transition energy at the QD maximum distribution of the $i$th optical transition is $E_{\text{max}}^i$. Note that although the inhomogeneity is included in the study of SONS in QDs in the work of Brunhes et al. [16], they take a QD distribution normalized to the dot height not as energy distribution as in Equation 9.62. Many other factors such as size, dot distribution, and imperfections in the QD shape. Thus, one must cover the spectrum of the dots through the emission spectrum of each one as was done earlier.

### 9.14 RESULTS AND DISCUSSION OF SHG, SFG, DFG, AND OR IN QDS

Figure 9.16 shows SONS for the first structure versus SHG wavelength at a 10 kV/cm applied field (Figure 9.16a), where 0.4 m/V SONS peak is obtained at 5095.5 nm peak wavelength. Increasing the field to 100 kV/cm reduces SONS peak to 0.12 m/V, and its peak wavelength is red shifted by approximately 200 nm as in Figure 9.16b.

![Figure 9.16](image-url)

**FIGURE 9.16** Second-order nonlinear susceptibility real (red lines) and imaginary (blue lines) parts by second-harmonic generation (SHG) versus SHG wavelength for homogeneous (solid lines) and inhomogeneous (dotted lines) of the first quantum dot structure at (a) 10 kV/cm and (b) 100 kV/cm electric field strengths.
Including the QD inhomogeneity in the calculations is important to cover synthesis imperfections. The SONS calculated with inhomogeneous density of states is shown as dashed curves in Figure 9.16a and b. It reduces the peak value of SONS to approximately its half value, this result is shown for both real and imaginary parts of SONS, and this is with our recent result in [24] for the third-order nonlinear susceptibility. Thus, it is important to include inhomogeneity in SONS calculations in QDs.

The ISB case (second structure) is shown in Figure 9.17. When the applied field is 10 kV/m, the spectrum is peaked at 1.18 mm as shown in Figure 9.17a, that is, it is extended by 1.175 mm as compared with Figure 9.16a, while at a 100 kV/m applied field, it is peaked at 0.28 mm as shown in Figure 9.17b, and at this latter case, SONS is reduced by more than three times (in both real and imaginary parts).

**FIGURE 9.17** Second-order nonlinear susceptibility real (red lines) and imaginary (blue lines) parts by second-harmonic generation (SHG) versus SHG wavelength for homogeneous (solid lines) and inhomogeneous (dotted lines) of the second quantum dot structure at (a) 10 kV/cm and (b) 100 kV/cm electric field strengths.
Semiconductor Nanocrystals and Metal Nanoparticles

SFG in the first structure is shown in Figure 9.18a, where SONS is peaked at 10 µm wavelength under the 10 kV/cm applied field and its value (imaginary SONS) is increased to 1.1 m/V. Figure 9.18b shows SONS when the applied field is increased to 100 kV/cm, where SONS peak becomes 0.35 m/V at 8 µm wavelength peak.

SFG for the second structure (valence ISB case) under 10 kV/cm applied electric field is shown in Figure 9.19a, where SONS peaks at 1.363 mm and its value is reduced by three times compared with IB case. Increasing the field to 100 kV/cm peaks SONS at 0.293 mm, as shown in Figure 9.19b, and its value was reduced by two orders compared with Figure 9.19a.

DFG in the first structure is shown in Figure 9.20a, where SONS is peaked at 7.4 µm under 10 kV/cm applied field and its value is reduced by seven orders compared with SONS of SHG and SFG of the first structure (Figures 9.16a and 9.18a). Figure 9.20b shows the case when the field is...
increased to 100 kV/cm, where SONS is peaked at 5.3 µm and its value is reduced by one order of magnitude compared with Figure 9.20a.

Figure 9.21a shows DFG for the second structure at 10 kV/m applied electric field, where a high SONS is obtained, and it is peaked at 0.468 mm wavelength. Increasing the field to 100 kV/cm, Figure 9.21b, SONS is peaked at 0.1 mm and its value is reduced by two orders compared with Figure 9.21a.

Figure 9.22a shows OR for the first structure under the applied electric field 10 kV/m, where it is peaked at 1275 nm and its value is 7.8 × 10⁻⁵ m/V. Increasing the field to 100 kV/cm reduces SONS peak by more than two times and the peak wavelength is red shifted to 1323 nm.

For OR in the second structure, Figure 9.23a, SONS is reduced by two times compared with Figure 9.22a, while the peak wavelength is 0.285 mm. Reducing the field to 100 kV/cm as in
Figure 9.23b reduces SONS by four times, while the peak wavelength is 64 µm. For both structures, SONS was reduced with increasing field in all SHG, SFG, DFG, and OR, which refers to a higher asymmetry at a low applied field.

This reduction in SONS is due to the Stark shift of both conduction and valence subband energies under the application of the electric field. For the first (IB) structure, the difference between the first two conduction subbands is 186.3 meV for 100 kV/cm, while this difference is reduced to 142 meV for 10 kV/cm applied field. Additionally, the momentum matrix element $\mu_{12}$ is reduced when the field was reduced from 10 to 100 kV/cm. These factors cause the reduction of SONS when the field increases to 100 kV/cm. A nonmonotonic behavior of SHG in QDs with field is also noticed by Shao et al. [21]. Dugas et al. [44] show the reduction of OR in QDs with an increasing electric field and their results are in the range of $10^{-6}$ m/V, which is on the order of our results of IB case.
Second-Order Nonlinear Susceptibility in Quantum Dot Structures

Results of Baskoutas et al. range between $10^{-8}$ and $10^{-3}$ m/V depending on the type of confinement of QDs [18]. Our results here for peak OR range between $6.5 \times 10^{-11}$ m/V, for the second structure under 100 kV/cm (Figure 9.23b), and $7.5 \times 10^{-5}$ m/V, for the first structure under 10 kV/cm (Figure 9.22a). This shows the difference between the confinements of the two structures. The momentum matrix elements of the IB structure are higher than that of the ISB structure.

The difference between the first two valence subbands at 10 kV/cm applied field was 4.2 meV, while this difference increases to 36.7 meV when the field increases to 100 kV/cm, that is, the subbands of the second structure shift by approximately one order of magnitude, while the first (subband) structure increases by 1.3 times with an increasing field. This is with the wavelength shift

FIGURE 9.21 Second-order nonlinear susceptibility real (red lines) and imaginary (blue lines) parts by difference-frequency generation (DFG) versus DFG wavelength for inhomogeneous broadening of the second quantum dot structure at (a) 10 kV/cm and (b) 100 kV/cm electric field strengths.
When the field shifts from 10 to 100 kV/cm, the peak wavelength is shifted by 1–2 µm (or less) for the IB structure, while it is shifted by one order of magnitude for the ISB structure.

One of the main results that must be discussed in the study is the very long wavelengths obtained in the second structures, millimeter wavelengths. Energy subbands of the structures can also explain it. While the peak wavelength ranges between 1.2 and 10 µm for the first structure, it ranges between 0.064 and 1.363 mm for the second structure; the reason for this also lies in the values of energy difference between energy states of the two structures. This difference is only few milli–electron volts for the ISB (second) structure, while it is few electron volts for IB (first) structure. Thus, ISB structures can be used in the application of millimeter wavelength.

**FIGURE 9.22** Second-order nonlinear susceptibility real (red lines) and imaginary (blue lines) parts by optical rectification (OR) versus OR wavelength for inhomogeneous broadening of the first quantum dot structure at (a) 10 kV/cm and (b) 100 kV/cm electric field strengths.
FIGURE 9.23  Second-order nonlinear susceptibility real (red lines) and imaginary (blue lines) parts by optical rectification (OR) versus OR wavelength for inhomogeneous broadening of the second quantum dot structure at (a) 10 kV/cm and (b) 100 kV/cm electric field strengths.

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[AQ1] Please check if edit to the sentence starting “In nanostructures, normally…” is correct.

[AQ2] Please check if edit to the sentence starting “Although this type…” is correct.

[AQ3] $\varepsilon_0$ has been changed to $\varepsilon_0$ throughout the chapter. Please check if correct.

[AQ4] Please check if edit to the sentence starting “The second part…” is correct.

[AQ5] Please check the sentence starting “Here, a laser…” for clarity.

[AQ6] Please check if edit to the sentence starting “In addition to …” is correct.

[AQ7] Please check if inserted citation for Table 9.2 is correct.

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