27 Nonlinear Optics with Clusters

27.1 General Introduction: Fundamentals of Nonlinear Optics and Different Nonlinear Optical Effects

In recent years, nonlinear optical (NLO) materials have attracted substantial research interests due to their potential applications in information processing and telecommunications [1–4]. NLO processes are particularly useful in photonic devices where photons are used to transmit and process information. Modification in the optical properties of a material by the strong oscillating electric fields of a laser beam is in general discussed in the study of NLO. NLO processes have been observed in a wide variety of materials starting from molecules and clusters to bulk materials [5–14]. In molecular systems, the optical nonlinearity depends on the geometrical arrangement of molecules, whereas in case of bulk systems, the electronic characteristics of the system determine the optical nonlinearity. Various experimental as well as theoretical results have reported that NLO properties of small atomic clusters depend on the geometry and the electronic structure property of these materials [15,16].

In general, the electric dipole moment $\mu_a$ of a molecular system is expressed as

$$\mu_a = \mu_a(E^a(\vec{r}, t) = E^a(\vec{r}, t) = E^a(\vec{r}, t), ..., = 0)$$

\[= \sum_b \alpha_{ab} E^b(\vec{r}, t) + \frac{1}{2!} \sum_{bc} \beta_{abc} E^b(\vec{r}, t) E^c(\vec{r}, t) + \frac{1}{3!} \sum_{bcd} \gamma_{abcd} E^b(\vec{r}, t) E^c(\vec{r}, t) E^d(\vec{r}, t) + \cdots, \tag{27.1}\]

In the above equation, $E^a(\vec{r}, t)$, $E^b(\vec{r}, t)$, ..., are the external electric fields consisting of a monochromatic and a static part, and $a$, $b$, ... are equal to the Cartesian directions $x$, $y$, or $z$. The first term in Equation 27.1 denotes the dipole moment of the system. $\alpha_{ab}$, $\beta_{abc}$, and $\gamma_{abcd}$ represent the elements of the linear polarizability tensor, the first-order hyperpolarizability tensor, and the second-order hyperpolarizability tensor, respectively. The time dependence of the dipole moment leads to various frequency-dependent polarizabilities and hyperpolarizability tensors. The first-order hyperpolarizability tensor is described in terms of static first-order hyperpolarizability $[\beta(0; 0, 0, 0)]$, second-harmonic generation (SHG) $[\beta(\pm 2\omega; \omega, 0)]$, electro-optical Pockels effect (EOPE) $[\beta(\pm \omega; 0, 0)]$, optical rectification (OR) $[\beta(0; \omega, -\omega, 0)]$, sum-frequency generation (SGF), and difference-frequency generation (DFG). Similarly, in the case of the second-order hyperpolarizability tensor, apart from the static part $[\gamma(0; 0, 0, 0)]$, there exists frequency-dependent components, namely, the third-harmonic generation (THG) $[\gamma(3\omega; 0, 0, 0)]$, the electro-optical Kerr effect (EOKE) $[\gamma(\omega; 0, 0, 0)]$, the dc-induced second-harmonic generation (dc-SHG or electric field-induced second-harmonic generation (EFISH)) $[\gamma(2\omega; 0, 0, 0)]$, and the intensity-dependent refractive index (IDRI) $[\gamma(0, 0, 0)]$ or the degenerate four-wave mixing (DFWM). Among the different NLO properties, the first-order hyperpolarizability is important because it is the simple third-order molecular property and responsible for phenomena such as the SHG and the EOPE. On the other hand, the second-order hyperpolarizability tensor is related to physical properties like the EOKE. It is also significant in the perspective of quantum optical effects like self-focusing and self-defocusing effects in a material.

In the presence of an electric field of field strength

$$E(t) = E_0 e^{-i\omega t} + E_2 e^{-i\omega t} + c.c., \tag{27.2}$$

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the second-order nonlinear polarization induced in a crystal is expressed as

\[ P^{(2)}(t) = \chi^{(2)}(E(t))^2, \]

\[ P^{(2)}(t) = \chi^{(2)}[E_1(t) e^{i\omega_0 t} + E_2(t) e^{-i\omega_0 t} + 2 E_1 E_2(t) e^{i(\omega_0 + \omega_f)t} + 2 E_1 E_2(t) e^{i(\omega_0 - \omega_f)t} + c.c.] + 2 \chi^{(2)}[E_1 E_1^* + E_2 E_2^*], \]

The first and second terms in Equation 27.4 represent the SHG, and the third-order contribution to the nonlinear polarization is given by

\[ P^{(3)}(t) = \chi^{(3)}E(t)^3, \]

In the case of the monochromatic applied electric field \( E(t) = \xi \cos \omega t \), the nonlinear polarization is expressed as

\[ P^{(3)}(t) = \frac{1}{4} \chi^{(3)} \xi^3 \cos 3\omega t + \frac{3}{4} \chi^{(3)} \xi^3 \cos \omega t. \]

The first term of Equation 27.6 illustrates the third-harmonic generation (THG), which describes the response of the system at the frequency of \( 3\omega \). The second term in Equation 27.6 leads to a nonlinear contribution to the refractive index of the electromagnetic wave of frequency \( \omega \). This is recognized as the intensity-dependent refractive index (IDRI). In the presence of such nonlinearity, the refractive index becomes

\[ n = n_0 + n_1 I, \]

where \( n_0 \) is the linear refractive index and

\[ n_1 = \frac{12\pi^2}{n_0 c} \chi^{(3)}. \]

\( n_1 \) is an optical constant that characterizes the strength of the optical nonlinearity. \( I \) is the intensity of the incident wave expressed as \( I = (n_0 c / 8\pi \xi^2) \). The intensity-dependent refractive index (IDRI) is related to optical phenomenon, such as the self-focusing of the electromagnetic wave. Self-focusing occurs in a material in which \( n_1 \) is positive and the electromagnetic waves, with a nonuniform transverse intensity distribution, curve towards each other after passing through such material.

27.2 Quantum Formulation of Nonlinear Optics

A large number of quantum chemical techniques have been employed for the evaluation of the NLO properties of materials. Jensen et al. have developed a dipole interaction model. This model successfully describes the response properties of large aggregates of molecular clusters [17]. The density-matrix renormalization group (DMRG)-based formalism was proposed by Pati and coworkers and successfully applied in the description of the frequency-dependent NLO properties of \( \pi \)-conjugated systems [18]. Standard techniques like the time-density functional theory, the time-dependent Hartee Fock technique, as well as the finite-field methods [19] based on DFT are also very successful in describing the NLO responses of several classes of materials. The quantum chemical approach, like the density functional theory, had its limitations in the case of long-range dispersion interaction and has been improved by the introduction of the dispersion-corrected DFT DFD-D [20, 21] technique. Higher-order wavefunction-based methods like the coupled cluster approach and the MP2 technique are also efficient but they are excessively expensive. In addition to these, the response properties are also evaluated through semi-empirical methods like ZINDO/MRDCI (multi reference doubles-configuration interaction) formalism with a correction vector. [22]. Another well-celebrated quantum chemical approach is the use of the two-state model proposed by Oudar and Chemla [23]. This model relates the nonlinear optical coefficients to the excited-state energy, the oscillator strength and the dipole moment of the molecule under consideration. The theoretical results of Zyss [24] and Andrews et al. [25] successfully established the two-state model of Oudar and Chemla. Datta and Pati [26] employed the two-state model to discuss the role of dipolar interaction and H-bonding in tuning the response properties in molecular aggregates. This model is simple and particularly useful in the case of charge-transfer systems [27]. In this two-state model, the expression of \( \beta \) is given by

\[ \beta_{two-level} = \frac{3e^2}{2 \hbar} \frac{\omega_0 f \Delta \mu_{01}}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \]

where

- \( f \) is the oscillator strength
- \( \omega \) is the applied frequency
- \( \omega_{01} \) is the frequency of the optical transition between the ground state and the first dipole-allowed state
- \( \Delta \mu_{01} \) is the difference in moments between the ground state and the first dipole-allowed state

In the absence of an applied frequency, the above equation results in a first-order static hyperpolarizability tensor

\[ \langle \beta(0; 0, 0) \rangle = 3\pi f \frac{\omega_{01} \Delta \mu_{01}}{\omega_{01}^2}. \]

In two-state formalism, the parameters like \( f, \omega_{01} \) and \( \Delta \mu_{01} \) are estimated through standard excited approaches like the
configuration interaction scheme (CIS) or the time-dependent density-functional theory (TDDFT).

Apart from all those techniques described in the above paragraph, another widely accepted quantum chemical technique of response calculation is the analytic approach. In this context, it will be useful to point out some of the basic differences between the finite-difference technique and the analytic approach. In the finite-difference technique, the energy is calculated at different values of the electric field; there after, the finite differentiation is performed to obtain the derivative of energies. The finite-difference method is suitable for any program capable of energy calculation in a perturbed system. However, the main limitation of this method is the prolonged computational time and it is not good enough when higher order derivatives of the energy are involved. On the contrary, in the analytical approach, physical properties are obtained by analytically evaluating the derivatives of the energy and are often preferred in response calculations. The main advantage of this technique is that it gives access to frequency-dependent properties and the data obtained are more accurate. This technique has been successfully applied by van Gisbergen et al. [28] in case of a set of small molecules. Sen et al. employed the same technique in case of CdSe clusters and Al4M4 clusters [11,13].

In the density-functional theoretical formulation of the analytic approach, the starting equation is a variation on the time-dependent Kohn–Sham (TDKS) equation. In order to obtain the starting equation of the analytic approach in the time-dependent Kohn–Sham (TDKS) equation. In order to obtain the starting equation for the NLO calculation in the analytic approach, the physical properties are obtained by evaluating the derivatives of the energy and are often preferred in response calculations. The main advantage of this technique is that it gives access to frequency-dependent properties and the data obtained are more accurate. This technique has been successfully applied by van Gisbergen et al. [28] in case of a set of small molecules. Sen et al. employed the same technique in case of CdSe clusters and Al4M4 clusters [11,13].

In Equation 27.11, \( v(\vec{r}, t) \) is the time-dependent Kohn–Sham potential and \( \epsilon_\mu(\vec{r}, t) \) is the Lagrangian multiplier. Different choices of Lagrangian multipliers are allowed. With \( \epsilon_\mu(\vec{r}, t) = 0 \) we attain the canonical form of the Kohn–Sham equation. In the case of orbitals varying rapidly with time, \( \epsilon_\mu(\vec{r}, t) \) is suitably chosen to avoid an unphysical divergence in the Kohn–Sham equation. The time-dependent density \( \rho(\vec{r}, t) \) is obtained from the relation

\[
\rho(\vec{r}, t) = \sum_i \psi_i(\vec{r}, t)^\dagger \psi_i(\vec{r}, t),
\]

(27.12)

When \( \psi(\vec{r}, t) \) is expanded in a fixed time-dependent basis set of atomic orbitals \( \{\chi_\mu(\vec{r})\} \), the resulting expression becomes

\[
\psi(\vec{r}, t) = \sum_\mu \chi_\mu(\vec{r}) C_\mu(t),
\]

(27.13)

In Equation 27.13, the coefficient \( C_\mu(t) \) manifests the time dependence of \( \psi(\vec{r}, t) \). Finally, Equations 27.11 through 27.13 produces the time-dependent Kohn–Sham equation in the matrix form given by

\[
F \psi - i \frac{\partial}{\partial t} \psi = S C \psi,
\]

(27.14)

where \( S \) is the overlap matrix of the atomic orbitals with

\[
S_{\mu \nu} = \int d\vec{r} \chi_\mu(\vec{r})^\dagger \chi_\nu(\vec{r}),
\]

(27.15)

The density matrix \( (D) \) is expressed in terms of the coefficient matrix \( C \) and the occupation number matrix \( n \) is and is expressed as

\[
D = C n C^\dagger.
\]

(27.16)

The Kohn–Sham equation expressed in Equation 27.14 is the starting point of the perturbative expansion. Equation 27.14 is similar to the starting equation for the NLO calculation in the time-dependent Hartree–Fock technique (TDHF). In Equation 27.14, the term \( F \) represents the Kohn–Sham matrix or the Fock matrix. This is expressed as

\[
F = \hbar + DX 2J + \nu_{xc}.
\]

(27.17)

In the above equation, \( \hbar \) is the one-electron integral matrix comprising kinetic energy, the Coulomb field of the nuclei, and the applied external electric field. \( J \) is the four-index Coulomb supermatrices.

When all matrices are expanded in different orders of external perturbation and \( \epsilon \) is chosen as the time-dependent zero-order matrix, the canonical Kohn–Sham equation for the ground-state DFT is obtained and given by the following expression:

\[
F_0^{(0)} C^{(0)} = S^{(0)} C^{(0)} \epsilon^{(0)}.
\]

(27.18)
The Lagrangian multiplier matrix \([e^{(0)}]\) can be chosen at each order of perturbation. Now, if an external electric field of \(E(t)\) is applied, the mathematical form of \(E(t)\) being

\[
E^s(t) = E^s(t)[1 + e^{iωt} + e^{-iωt}] ,
\]

then in the dipolar approximation, the external perturbation term \((H)\) to the Kohn–Sham Hamiltonian becomes

\[
H = μ \cdot E(t) ,
\]

(27.20)

where \(μ\) is the dipole–moment operator of the electrons.

The time dependence of the dipole moment produces various frequency-dependent hyperpolarizability tensors. Frequency-dependent polarizability and hyperpolarizability tensors are obtained from the trace of the dipole moment matrix \([H]\) and the \(n\)th-order density matrix \([D^{(n)}]\) (where \(n = 1\) for the linear polarization \(α\), \(n = 2\) for the first-order hyperpolarizability tensor \(β\), \(n = 3\) for the second-order hyperpolarizability \(γ\) and so on). If the inducing electric field of frequency \(ω_a\), \(ω_b\), \(ω_c\) ... acts in the direction \(a\), \(b\), \(c\) ... the tensors can be represented as

\[
α_{ab}(-ω_a; ω_b) = -Tr \left[ H^a D^b (ω_b) \right] ,
\]

(27.21)

\[
β_{abc}(-ω_a; ω_b, ω_c) = -Tr \left[ H^a D^{bc} (ω_b, ω_c) \right] ,
\]

(27.22)

\[
γ_{abcd}(-ω_a; ω_b, ω_c, ω_d) = -Tr \left[ H^a D^{bcd} (ω_b, ω_c, ω_d) \right] ,
\]

(27.23)

where \(ω_a = ω_a + ω_b + ...\) These expressions are a set of generalized equations in terms of frequencies. The polarizability and the hyperpolarizability tensors defined above are determined through the iterative solution of the time-dependent Kohn–Sham (TDKS) equations given in Equation 27.14.

In ordinary TDDFT, the zeroth-order Kohn–Sham matrix is used, which is given by

\[
F_s^{(0)} = h^{(0)} + D^{(0)}X(2J) + ν^{(0)} ,
\]

(27.24)

where \(h^{(0)}\) contains the external potential terms that are of zero order in the external field, kinetic energy and the nuclear Coulomb field. The Coulomb super matrix \(J\) is independent of the external electric field and results in a Coulomb term of the form \(D^{ab}X(2J)\) in the \(n\)th-order Kohn–Sham matrix \(F_s^{(n)}(ω_a, ω_b, ... , ω_n)\). The external perturbation appears only in the first-order Kohn–Sham matrices. Higher-order Kohn–Sham matrices consist of a Coulomb and an exchange-correlation part. Therefore, the general formula for the higher-order Kohn–Sham matrices becomes

\[
F_s^{(n)}(ω_a, ω_b, ... , ω_n) = D^{ab}X(2J) + ν^{(n)}(ω_a, ω_b, ... , ω_n) ,
\]

(27.25)

The Taylor expansions of \(F_s\), \(C\), \(ε\), and \(D\) are inserted in the time-dependent Kohn–Sham equation (Equation 27.14), the normalization condition, and the density matrix (Equation 27.16). This results in a first-order time-dependent Kohn–Sham equation as

\[
F_s(ω)C^{(0)} + F_s^{(0)}C(ω) + ωSDC(ω) = S^{(0)}C(ω)e^{(0)} + S^{(0)}C^{(0)}ε(ω) .
\]

(27.26)

Higher-order coupled equations are obtained by equating the left and the right hand sides of the TDKS equation, the normalization condition and the density matrix. The NLO properties are estimated through the iterative solution of the time-dependent Kohn–Sham equations up to a certain order \(n\). Primarily, the static Kohn–Sham equations are solved that result in matrices \(F_s^{(n)}\), \(C^{(n)}\), \(S^{(n)}\), \(D^{(n)}\), and the converged SCF density \(ρ^{(0)}\). These matrices are needed for the solution of the first-order Kohn–Sham equation, which produces the first-order density matrix. The first-order density matrix yields the frequency-dependent first-order hyperpolarizability \(β\(ω, ω, ω\)) through Equation 27.21. The solution of the first-order equation provides matrices required for an iterative solution of the second-order equation. In either case, the technique adopted is called the \((2n + 1)\) theorem. The second-order equation is solved to get the second-order density matrix elements from which the frequency-dependent first-order hyperpolarizability tensor is obtained through Equation 27.23. If the external fields of the frequency zero and a common frequency \(ω\) are considered, a number of very important NLO properties become accessible. These are SHG \(β(−2ω, ω, ω)\), EOPE \(β(−ω, ω, 0)\), THG \(γ(−3ω, ω, ω, ω)\), EOKE \(γ(−ω, ω, 0, 0)\), dc-SHG \(γ(−2ω, ω, ω, 0)\), and IDRI \(γ(−ω, −ω, −ω, 0)\) become accessible.

In practice, the average polarization tensor is defined in terms of Cartesian components such as

\[
\langle α \rangle = \frac{α_{xx} + α_{yy} + α_{zz}}{3} ,
\]

(27.27)

where, \(α_{xx}\), \(α_{yy}\), and \(α_{zz}\) are the diagonal elements of the polarization-tensor matrix. The first-order hyperpolarizability tensor is defined as the third derivative of the energy with respect to the electric field components, and hence, involves one additional field differentiation compared to polarizabilities. The average first-order hyperpolarizability is defined as

\[
\langle β \rangle = \left( \sum_i β_{i}β_{i}^{*} \right)^{1/2} ; \quad β = \frac{1}{3} \sum_j (β_{ij} + β_{ji} + β_{ji}) .
\]

(27.28)
where the sums are over the coordinates \( x, y, z \) \((i, j = x, y, z)\), and \( \beta^{*} \) refers to the conjugate of the vector \( \beta \). The second-order hyperpolarizability tensor involves one additional field differentiation compared to the first-order analog. The average second-order hyperpolarizability is defined as

\[
\langle \gamma \rangle = \frac{1}{15} \sum_{ij} (2\gamma_{ij\pi} + \gamma_{ij\pi}) \quad (i, j = x, y, z). \tag{27.29}
\]

In some of the theoretical approaches second-order hyperpolarizability tensors are determined from a combination of analytical and finite-difference techniques [28]. All components of the \( \gamma \) tensor of interest \((\text{dc-SHG}/\text{EOKE}/\text{static second-order hyperpolarizability})\) are obtained from the analytical time-dependent calculation of the SHG/EOKE/static first-order hyperpolarizability in the presence of small electric fields. E.g., the relation used in the evaluation of EOKE is

\[
\gamma_{\text{abcd}}(-\omega; 0, 0, 0) = \lim_{\omega \to 0} \frac{\beta_{\text{abc}}(-\omega; 0, 0)}{E^d}, \tag{27.30}
\]

Frequency-dependent response properties can also be calculated from the time-averaged quasienergy [29]. In this formalism, the response properties are obtained as the derivative of the quasi energy and the same is estimated by using the variational criterion for the quasienergy and the time-averaged time-dependent Hellmann–Feynman theorem. Molecular properties are obtained by using the variational Lagrangian technique in accordance with the \( 2n + 1 \) and the \( 2n + 2 \) rules. Within this approach, the different frequency-dependent response properties are obtained from the simple extension of the variational perturbation theory to the Fourier component variational perturbation theory.

### 27.3 Nonlinear Optics with Materials

Much of the present research work in the field of nonlinear optics is motivated by certain nonlinear optical phenomena in suitable materials [14]. Some of these potentially useful phenomena include the ability to alter the frequency or color of light, to amplify one source of light with another, and to alter its transmission features through a medium. The nonlinear optical materials require unusual stability with respect to ambient conditions and high-intensity light sources. These materials can broadly be categorized into two major classes. The first is the class of inorganic materials, which includes semiconducting and metallic clusters, inorganic crystals, bulk materials, etc. The second belongs to the organic or, in general, molecular materials that include mainly organic crystals and polymers. For these systems, the optical nonlinearities are usually derived from their structures. In the present chapter, we will focus only on the first type, i.e., semiconducting and metallic clusters and their NLO behavior.

### 27.4 Why Are Clusters So Important?

Nonlinear optical processes in cluster materials provide the necessary information about the exact understanding of the quantum confinements and the surface effects in these systems [11]. In general, the properties at the nanoscale are usually non-monotonic and oscillating in nature due to the quantum size effects, and as such, cluster materials can exhibit properties, which are quite different from those of the bulk [5,11,30]. More specifically, the energy band structure and the phonon distribution of cluster materials may differ from that of the bulk systems. Numerous theoretical as well as experimental investigations have been performed that show that the cluster-assembled materials have novel mechanical, electrical, and optical properties [5–16]. As mentioned earlier in this chapter, these NLO materials find huge applications in high-speed electro-optic devices for information processing and telecommunications [1–4]. In Section 27.5, we present a review on nonlinear optics with various cluster materials.

### 27.5 Review of Nonlinear Optics with Clusters

In this section, semiconducting clusters will be discussed first followed by metallic clusters. An example of a class of materials with a manifestation of unusual physicochemical and optical properties is cadmium selenide clusters \([\text{CdSe})_n]\. These \((\text{CdSe})_n\) clusters are found to be the precursors of a wide range of low-dimensional materials such as quantum dots [7,10], tetrapods [31], and nanowires [32] that exhibit a variety of optical and electronic properties. The electronic properties of cadmium selenide clusters \((\text{CdSe})_n\), and quantum dots are semiconducting in nature and these materials find tremendous application in the design and the development of novel nonlinear optical \((\text{NLO})\) materials. There have been a lot of experimental investigations [15,33] on the exploration of the NLO properties in \(\text{CdSe}\) clusters and nanoparticles. The Hyper-Rayleigh scattering technique provides the experimental basis for NLO properties in \(\text{CdSe}\) clusters and nanoparticles. Aktsipetrov et al. [33] have shown the size dependence of SHG from the surface of a composite material consisting of \(\text{CdSe}\) nanoparticles embedded in a glass matrix. The first-order hyperpolarizability in \(\text{CdSe}\) and \(\text{CdS}\) nanoparticles is reported to be very high [34].

Apart from the experimental works, theoretical ab initio investigations [8,11,12] have also been performed in order to calculate the NLO coefficients in \(\text{CdSe}\) clusters. Troparevsky and Chelikowsky [35], in their work, reported on the structural and the electronic properties \((\text{the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)})\) of small \((\text{CdS})_n\) and \((\text{CdSe})_n\) clusters, where \(n\) ranges from 2 up to 8 using the pseudopotential method in real space. Karamanis et al. [36] have used DFT for the computation of static polarizability and anisotropy in the static polarizability of small \(\text{CdSe}\) clusters up to tetramer units (see Figure 27.1).
Their investigations suggest that the optical properties of the bulk system can also be predicted from a plot of dipole polarizability per atom.

Later on, the same group of Karamanis extended their work on CdSe clusters, highlighting the importance of basis sets and electron correlation in these systems [12]. However, the calculations of the frequency-dependent optical polarizability, as well as that of hyperpolarizability tensors using theoretical methods remained an unresolved issue for CdSe clusters.

Recently, Sen and Chakrabarti [11], for the first time, investigated the frequency-dependent nonlinear optical properties (first- and second-order hyperpolarizability tensors) of (CdSe)$_n$ clusters up to the tetramer using the time-dependent density functional theory (TDDFT). Within the TDDFT, both the local-density approximation (LDA) and the generalized-gradient approximation (GGA) technique have been used. The more accurate LB94 (van Leeuwen and Baerends 94) [37] functional has been used under the GGA scheme. Response calculations have been implemented in the Amsterdam density functional package (ADF 2004.01) [38]. The analytical approach has been used for the evaluation of all the NLO coefficients. The calculated polarizability and hyperpolarizabilities depend on the choice of the basis set and the exchange-correlation potential. While the results obtained within the DFT are overestimated under the normal LDA and GGA functional, the coupled Hartree–Fock procedure exhibits exactly the opposite trend [39,40]. The static values of the average first-order hyperpolarizability (〈β(0; 0, 0)〉) and the average second-order hyperpolarizability (〈γ(0; 0, 0, 0)〉) of CdSe, Cd$_2$Se$_2$, Cd$_3$Se$_3$, and Cd$_4$Se$_4$ are depicted in Table 27.1.

The frequency dependence of the SHG [β(−2ω; ω, 0)], the EOPE [β(−ω; ω, 0)], the EFISH [γ(−2ω; ω, 0, 0)], and the

**TABLE 27.1** Average Static First and Second Order Static Hyperpolarizability in CdSe, Cd$_2$Se$_2$, Cd$_3$Se$_3$, and Cd$_4$Se$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Static First-Order Hyperpolarizability, 〈β(0; 0, 0)〉 (a.u.)</th>
<th>Average Static Second-Order Hyperpolarizability, 〈γ(0; 0, 0, 0)〉 (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>−540.07 (LDA)</td>
<td>−556,680 (LDA)</td>
</tr>
<tr>
<td>Cd$_2$Se$_2$</td>
<td>Absent</td>
<td>7,306.5 (LDA)</td>
</tr>
<tr>
<td>Cd$_3$Se$_3$</td>
<td>−0.12258 (LDA)</td>
<td>4,398.6 (LB94)</td>
</tr>
<tr>
<td>Cd$_4$Se$_4$</td>
<td>Absent</td>
<td>12,200 (LDA)</td>
</tr>
<tr>
<td></td>
<td>89,565 (LDA)</td>
<td>8,929.3 (LB94)</td>
</tr>
<tr>
<td></td>
<td>50,124 (LB94)</td>
<td>89,565 (LDA)</td>
</tr>
</tbody>
</table>


EOKE [γ(−ω; ω, 0, 0)] was paid premier attention in the investigation of Sen and Chakrabarti [11]. For a complete evaluation of the frequency dependence of NLO properties in different CdSe clusters, a wide range of frequencies (0 to 0.45 a.u.) was considered.

Figure 27.2 manifests the frequency behavior of 〈β(−2ω; ω, 0)〉 and 〈β(−ω; ω, 0)〉 in the case of CdSe and Cd$_2$Se$_2$ respectively. 〈β(−2ω; ω, 0)〉, being a frequency-dependent property, is of paramount interest and has been investigated extensively in numerous previous investigations [15,41,42]. High degrees of fluctuations in 〈β(−2ω; ω, 0)〉 are observed in all the cases. Experimentally, 〈β(−2ω; ω, 0)〉 in CdSe nanocrystals and quantum dots has been observed by the HRS technique and its size dependence was also verified [15]. It is evident from Figure 27.2 that 〈β(−2ω; ω, 0)〉 is negative over a wide range of frequencies. This makes CdSe and Cd$_2$Se$_2$ more significant in the perspective of quantum optics. The frequency variation in 〈β(−2ω; ω, 0)〉 divulges one more significant information, i.e., the abrupt increase in 〈β(−2ω; ω, 0)〉 at specific frequencies. At specific frequencies the magnitude of 〈β(−2ω; ω, 0)〉 becomes very high. It is a common notion that larger values of 〈β(−2ω; ω, 0)〉 are obtained at a near resonance of the input energy [5]. The presence of the near resonance indicates that linear absorption can occur at such frequencies.

Similar to the components of the first-order hyperpolarizability tensors, the components of the second-order hyperpolarizability tensors (〈γ(−2ω; ω, 0)〉) and (〈γ(−ω; ω, 0, 0)〉) were reported to be highly sensitive to frequency variation. Figure 27.3 demonstrates the frequency dependence of different γ tensors. It was concluded from both LDA and LB94 results that both 〈γ(−2ω; ω, 0)〉 and 〈γ(−ω; ω, 0)〉 are negative over a wide range of frequencies. The change in the sign of 〈γ(−2ω; ω, 0)〉 and 〈γ(−ω; ω, 0)〉 due to the change in frequency is a significant observation. This led to a frequency selection in assigning the optical activity of the particular cluster.

In a separate study, Chakrabarti and coworkers [43] investigated the evolution of electric polarizability and the anisotropy of the polarizability at static as well as dynamic (Nd:YAG laser) frequencies with an increase in the cluster size for small, as well
Nonlinear Optics with Clusters

FIGURE 27.2 Variation of \( \langle \beta (−2\omega; \omega, \omega) \rangle \) (SHG) and \( \langle \beta (−\omega; \omega, 0) \rangle \) (EOPE) with a frequency at (a) LDA scheme for the CdSe cluster, (b) LDA, and (c) GGA (LB94) scheme for the \( \text{Cd}_3\text{Se}_3 \) cluster. (From Sen, S. and Chakrabarti, S., Phys. Rev. B, 74, 205435, 2006. With permission.)

FIGURE 27.3 Variation of \( \langle \gamma (−2\omega; \omega, \omega, 0) \rangle \) and \( \langle \gamma (−\omega; \omega, 0, 0) \rangle \) with a frequency at LDA. (a) Scheme for the CdSe cluster, (b) LDA and (continued)
FIGURE 27.3 (continued) (c) GGA (LB94) scheme for the Cd$_2$Se$_2$ cluster, (d) LDA and (e) GGA (LB94) scheme for the Cd$_3$Se$_3$ cluster, (f) LDA and (g) GGA (LB94) scheme for the Cd$_4$Se$_4$ cluster. (From Sen, S. and Chakrabarti, S., Phys. Rev. B, 74, 205435, 2006. With permission.)
as medium-sized (CdSe)$_n$ ($n = 1–16$) clusters within the density functional theory (DFT). The main motivation of that investigation was

1. None of the theoretical studies reported had gone beyond a cluster size of eight for the polarizability calculations for the CdSe clusters.

2. Except the study by Sen and Chakrabarti [11], no one was aware of any investigations where the dynamic hyperpolarizability for any system size was reported for the CdSe clusters.

Knowing the strong dependence of polarizability on the cluster diameter (the cluster size), they performed polarizability calculations beyond the cluster size of eight and calculated both static and dynamic polarizabilities.

Table 27.2 describes computed polarizability values at static and Nd:YAG laser frequencies. An even-odd oscillating behavior is observed in the anisotropy values between the dimer and the heptamer CdSe clusters.

Just like the CdSe clusters, GaAs is one such semiconducting cluster, which has gained a lot of importance over the past few years [5]. These cluster materials display long absorption tails in the low energy region [44] owing to the existence of free surfaces in it. Moreover, the static polarizabilities of these systems exceed the bulk value and follow a decreasing tendency with the increase in the cluster size [45]. The variable nature in the polarizabilities also indicates its “metallic-like” behavior. In the experimental investigation [46], it has been observed that the polarizabilities for small and medium-sized Ga$_{m}$As$_n$ clusters reside above and below the bulk limit. Albeit, there have been a lot of experimental and theoretical investigations [47–49] based on the NLO properties of GaAs bulk materials which suggest that GaAs clusters should possess very large static second- and third-order susceptibilities, only a few of them deal with the theoretical evaluation of the hyperpolarizabilities of these cluster materials [50,51]. A recent work by Lan et al. [5] provides a systematic insight into the NLO properties of medium-sized and small Ga$_{m}$As$_n$ clusters, where $m + n$ runs up to 10. They employed the TDDFT method in combination with the sum-over-states (SOS) formalism to calculate the first- and second-order hyperpolarizability tensors. The results indicate the presence of large second- and third-order nonlinear susceptibilities in GaAs cluster materials similar to that of the bulk. These results also suggest that resonance absorption can be avoided in the frequency-dependent NLO experiments. Furthermore, the frequency dependence of second- and third-harmonic generation reveals that these clusters are good candidates for future NLO materials.

Besides these two clusters, investigations of the NLO properties have also been carried out on various other III-V atomic nanoclusters. Pineda and Karna [52] estimated the linear and the nonlinear polarizabilities of isolated GaN nanoclusters employing the ab initio time-dependent Hartree–Fock (TDHF) method. Their results suggest a strong dependence of the NLO properties on the size and the shape of the clusters. The linear and the nonlinear optical properties of (CdS)$_n$ clusters were analyzed and the merits of the DFT level calculations have been compared with different ab initio results, as well as the basis set dependence of the optical properties of these clusters have been evaluated by Maroulis and Pouchan [53].

Figure 27.4 depicts the variation in the mean polarizability and the mean second-order hyperpolarizability values in small (CdS)$_n$ clusters. The values suggest a reduction in the mean

<table>
<thead>
<tr>
<th>Samples</th>
<th>$n$</th>
<th>$2n$</th>
<th>Polarizability per Atom ($\langle \alpha \rangle/2n$) (a.u.)</th>
<th>Anisotropy in Polarizability ($\Delta \alpha$) (a.u.)</th>
<th>At 0.0 a.u. Frequency</th>
<th>Polarizability per Atom ($\langle \alpha \rangle/2n$) (a.u.)</th>
<th>Anisotropy in Polarizability ($\Delta \alpha$) (a.u.)</th>
<th>At Nd:YAG Laser (0.04283 a.u.) Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>1</td>
<td>2</td>
<td>34.0349</td>
<td>36.5416</td>
<td>31.3777</td>
<td>49.7528</td>
<td>32.5664</td>
<td>59.0703</td>
</tr>
<tr>
<td>Cd$<em>{2}$Se$</em>{2}$</td>
<td>2</td>
<td>4</td>
<td>30.9670</td>
<td>60.5853</td>
<td>30.5716</td>
<td>102.1434</td>
<td>30.8635</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cd$<em>{3}$Se$</em>{3}$</td>
<td>3</td>
<td>6</td>
<td>29.8098</td>
<td>99.7527</td>
<td>29.5301</td>
<td>0.0000</td>
<td>29.8635</td>
<td>0.0169</td>
</tr>
<tr>
<td>Cd$<em>{4}$Se$</em>{4}$</td>
<td>4</td>
<td>8</td>
<td>29.5301</td>
<td>0.0000</td>
<td>29.5301</td>
<td>0.0000</td>
<td>29.5301</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cd$<em>{5}$Se$</em>{5}$</td>
<td>5</td>
<td>10</td>
<td>32.4484</td>
<td>159.8706</td>
<td>32.4484</td>
<td>159.8706</td>
<td>32.4484</td>
<td>159.8706</td>
</tr>
<tr>
<td>Cd$<em>{6}$Se$</em>{6}$</td>
<td>6</td>
<td>12</td>
<td>29.1341</td>
<td>134.4511</td>
<td>29.1341</td>
<td>134.4511</td>
<td>29.1341</td>
<td>134.4511</td>
</tr>
<tr>
<td>Cd$<em>{7}$Se$</em>{7}$</td>
<td>7</td>
<td>14</td>
<td>29.0036</td>
<td>99.7527</td>
<td>29.0036</td>
<td>99.7527</td>
<td>29.0036</td>
<td>99.7527</td>
</tr>
<tr>
<td>Cd$<em>{8}$Se$</em>{8}$</td>
<td>8</td>
<td>16</td>
<td>29.5565</td>
<td>159.8706</td>
<td>29.5565</td>
<td>159.8706</td>
<td>29.5565</td>
<td>159.8706</td>
</tr>
<tr>
<td>Cd$<em>{9}$Se$</em>{9}$</td>
<td>9</td>
<td>18</td>
<td>29.0036</td>
<td>134.4511</td>
<td>29.0036</td>
<td>134.4511</td>
<td>29.0036</td>
<td>134.4511</td>
</tr>
<tr>
<td>Cd$<em>{10}$Se$</em>{10}$</td>
<td>10</td>
<td>20</td>
<td>29.8171</td>
<td>124.1952</td>
<td>29.8171</td>
<td>124.1952</td>
<td>29.8171</td>
<td>124.1952</td>
</tr>
<tr>
<td>Cd$<em>{11}$Se$</em>{11}$</td>
<td>11</td>
<td>22</td>
<td>29.8559</td>
<td>124.1952</td>
<td>29.8559</td>
<td>124.1952</td>
<td>29.8559</td>
<td>124.1952</td>
</tr>
<tr>
<td>Cd$<em>{12}$Se$</em>{12}$</td>
<td>12</td>
<td>24</td>
<td>29.8171</td>
<td>124.1952</td>
<td>29.8171</td>
<td>124.1952</td>
<td>29.8171</td>
<td>124.1952</td>
</tr>
<tr>
<td>Cd$<em>{13}$Se$</em>{13}$</td>
<td>13</td>
<td>26</td>
<td>30.9808</td>
<td>271.1190</td>
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<td>271.1190</td>
<td>30.9808</td>
<td>271.1190</td>
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<td>Cd$<em>{14}$Se$</em>{14}$</td>
<td>14</td>
<td>28</td>
<td>30.5716</td>
<td>192.7016</td>
<td>30.5716</td>
<td>192.7016</td>
<td>30.5716</td>
<td>192.7016</td>
</tr>
<tr>
<td>Cd$<em>{15}$Se$</em>{15}$</td>
<td>15</td>
<td>30</td>
<td>30.1422</td>
<td>158.9999</td>
<td>30.1422</td>
<td>158.9999</td>
<td>30.1422</td>
<td>158.9999</td>
</tr>
</tbody>
</table>

dipole polarizability, as well as in the second-order hyperpolarizability values with an increase in the cluster size. Moreover, the results obtained from B3LYP and other conventional *ab initio* methods are well in accordance with each other and also with the earlier theoretical results [35]. However, in the case of the monomer geometry, the difference in the hyperpolarizability values between these methods is quite large. Champagne et al. estimated [54] average second-order hyperpolarizabilities of Si<sub>n</sub> (<i>n</i> = 3–38) clusters using MP2, MP3, MP4, CCSD, and CCSD(T) levels of approximations and demonstrated the variation of polarizability and hyperpolarizability against the cluster size.

Apart from these semiconducting materials, cluster science has also made rapid progress in determining the electric properties of various metal clusters [55] including that of mixed metal. At first, a review of the some of the works based on the metal clusters containing only one type of atom is discussed, which is followed by some detailed analysis on mixed metal clusters. There are investigations on lithium [18,56,57], sodium [58], copper [59,60], nickel [61], niobium [62], and zinc [63] clusters. Maroulis and Xenides [57] reported highly accurate *ab initio* calculations on the polarizability and the hyperpolarizabilities of lithium tetramer, Li<sub>4</sub>, with specially designed basis sets for Li. The molecule, Li<sub>4</sub>, has got a very high anisotropic dipole polarizability and quite large second-order hyperpolarizability values. The main feature of this work is the extensive analysis of the basis set and the correlation effects in calculating the electric properties. The results indicate a discrepancy in dipole polarizabilities between theory and experiment, which might be resolved by measuring the anisotropy values experimentally. The same group also presented a thorough analysis of the performance of several density functional theoretical (DFT) calculations of the (hyper) polarizability of Li<sub>4</sub>. Their investigations elucidated that of the various DFT methods employed; only the mPW1PW91 and the O3LYP methods produce reliable results. Papadopoulos et al. [63] studied the (hyper) polarizabilities of small and medium-sized zinc clusters employing a hierarchy of basis sets and computational methods. The relativistic effect on the electric polarizabilities has also been investigated by employing the Douglas–Kroll approximation. It has been observed that the relativity contribution is significant in these cluster materials; however, the correlation effect plays a major part in influencing the electro-optic properties.

The NLO properties of Ag nanoparticles embedded in a Si<sub>3</sub>N<sub>4</sub> matrix was investigated by Traverse et al. [64]. They performed a two-color sum-frequency generation (2c-SFG) spectroscopy experiment, which exhibited a surface plasmon resonance at a 421 nm wavelength in the visible region and absorption in the infrared region. The third-order optical nonlinearity of dielectrics in the presence of nanoparticles has been experimentally investigated by Flytzanis [65]. Chen and coworkers performed [66] high-level *ab-initio* calculations [HF, MP2, the fourth-order perturbation theory using single, double, quadrupole substitutions, CCSD, and QCISD] on (HCN)<sub>n</sub>…Li and Li…(HCN)<sub>n</sub> clusters with electrode characteristics. A high value of static first hyperpolarizability is reported in both samples. The static second-order hyperpolarizability of a series of tri-nuclear metal cluster MS4(M’PPh<sub>3</sub>)(M’PPh<sub>3</sub>) (M = Mo, W; M’ = Cu, Ag, Au) have been estimated by [67] Chen and coworkers. They employed a finite-field approach using the hybrid density functional theory (B3LYP) and reported a very high value of second-order hyperpolarizability. The NLO properties of Au<sub>n</sub> clusters

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**FIGURE 27.4** Mean (a) dipole polarizability and (b) second-order hyperpolarizability in (CdS)<sub>n</sub> clusters. (From Maroulis, G. and Pouchan, C., *J. Phys. Chem. B*, 107, 10683, 2003. With permission.)
TABLE 27.3  Average Hirshfeld Charge on the Al₄ Ring, Ground State Dipole Moment, Magnitude of Average Static First- and Second-Order Hyperpolarizability in AlₓM₄ (M = Li, Na, and K)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Hirshfeld Charge on the Al₄ Ring</th>
<th>Ground-State Dipole Moment (Debye)</th>
<th>Average Static First-Order Hyperpolarizability, (\langle \beta(0; 0, 0) \rangle) (a.u.)</th>
<th>Average Static Second-Order Hyperpolarizability, (\langle \gamma(0; 0, 0, 0) \rangle) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₄Li₄ (2D)</td>
<td>−0.247</td>
<td>0.049</td>
<td>145.922</td>
<td>1.299 × 10⁶</td>
</tr>
<tr>
<td>Al₄Li₄ (3D)</td>
<td>−0.202</td>
<td>0.018</td>
<td>33.079</td>
<td>2.406 × 10⁶</td>
</tr>
<tr>
<td>Al₄Na₄ (2D)</td>
<td>−0.258</td>
<td>0.003</td>
<td>21.537</td>
<td>1.275 × 10⁶</td>
</tr>
<tr>
<td>Al₄Na₄ (3D)</td>
<td>−0.229</td>
<td>0.054</td>
<td>187.843</td>
<td>1.961 × 10⁶</td>
</tr>
<tr>
<td>Al₄K₄ (2D)</td>
<td>−0.303</td>
<td>0.080</td>
<td>316.781</td>
<td>3.380 × 10⁶</td>
</tr>
<tr>
<td>Al₄K₄ (3D)</td>
<td>−0.297</td>
<td>6.513</td>
<td>8863.074</td>
<td>1.149 × 10⁷</td>
</tr>
</tbody>
</table>

27.6 Conclusions

Therefore, it is well established from both the theoretical as well as the experimental standpoint that cluster materials can be considered as promising candidates for future NLO devices due to their high nonlinear optical coefficient. However, the exploration of the fundamentals of the unique physicochemical behavior of these clusters is a challenge to modern physical and chemical research. A theoretical determination of a higher-order nonlinear optical coefficient is still a matter of extensive computation and there is need for further developments to provide a proper physical background for some of the higher-order optical coefficients. There is enough scope for future research work in the field of cluster science and the design of new cluster materials with interesting physical behavior.

References
