Two-photon Absorption Processes in Semiconductor Quantum Dots

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The two-photon absorption process is a nonlinear phenomenon that shows very low optical efficiency in bulk semiconductors. For this reason the detection of these processes becomes very difficult from the experimental point of view. Nevertheless, when dealing with semiconductor QD's with few nanometer radii, these transitions are enhanced and the detection is possible. In this contribution we present analytical calculations for the absorption coefficient in *CdSe* spherical QD's subjected to these second order processes, as a function of the characteristic dot parameters. The intensities of the absorption peaks, as well as the statistical treatment involving QD's ensembles, are also reported.

Keywords: Nonlinear absorption; Two-photon absorption; Quantum dots

I. INTRODUCTION

As a result of the spatial confinement of charged carriers in small volumes, semiconductor quantum dots (QD's), although having the size of relatively large clusters, exhibit some atomic-like characteristics, in particular, the complete quantization of the energy levels. Such attributes of the QD's makes, indeed, quite a difference when compared with the physical behavior of isolated atoms or bulk materials. Consequently, some unfledged applications in optics and electronics technology, as well as new nonlinear optical responses, have been disclosed in recent researches [1] on these low dimensional systems. As a natural consequence, QD systems based on III-V materials as well as II-VI semiconductor nanocrystallites embedded in glass have been systematically investigated during the last years [2,3]. The importance of these nonlinear optical processes are related to the fabrication of devices exploring second harmonic generation, sum and difference frequency generation, parametric oscillation, optical rectification and linear electrooptic effect.

Following this tendency, we have developed a theoretical study of two-photon absorption processes in semiconductor QD's applied, in particular, to spherical *CdSe* zinc-blende-type nanocrystals. It is a well known fact that the simultaneous absorption of two photons in bulk semiconductors is difficult to be detected because the associated peak intensities are very small if compared with the one-photon absorption peaks. The two-photon-related absorption coefficient is inversely proportional to the volume and to the photon mean-free-path of the irradiated sample. Therefore, we may expect that intense laser beams, illuminating QD's with dimensions up to few nanometer, show high two-photon optical efficiency.

Let us consider an isolated *CdSe* spherical QD described in the framework of the parabolic effective-mass approach. Exact solutions for electron and hole quantum states, satisfying Dirichlet's boundary conditions in the presence of an infinite potential barrier, are well known [4]. In general, the sample could be illuminated using photons with two different frequencies and/or polarization, supplied by independent monochromatic laser beams. For the sake of simplicity, here we will consider only photons with equal frequencies and parallel linear polarizations along an axis perpendicular to the wave-vector. Under these restrictions, which can be explored in future generalization, we have obtained exact formulae for the transition matrix elements involving two-photon absorption processes. Thus, we report an explicit expression for the nonlinear absorption coefficient which is graphically illustrated in this work.

In order to take into account the broadening of the energy levels, due to the temperature effects or defects, we introduce in our calculations a Lorentzian line-shape function replacing the standard energy conservation represented by a Dirac delta-function. Furthermore, since real QD samples present size and shape distributions, at the end of this communication we performed a study of the absorption coefficient for an ensemble of spherical QD's characterized by a Gaussian distribution over radii. In this general situation, no compact analytical formula for the description of two-photon transitions is available and only numerical calculation allows an insight on this question, except if the Lorentzian line-shape function is treated by the standard Dirac delta-function. Both cases will be illustrated in this work. In the next section we present the theoretical model as well as the numerical results.

II. THEORETICAL MODEL AND NUMERICAL RESULTS

We shall start by considering the simultaneous absorption of two photons, of different frequencies ($\omega_i, i = 1,2$) and polarization ($\eta_i, i = 1,2$), in a semiconductor. The diagrams involved in these processes are shown in Fig. 1.

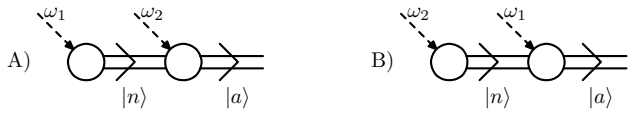

FIG. 1: Feynman diagrams for absorption processes involving two photons of frequencies ω_1 and ω_2.

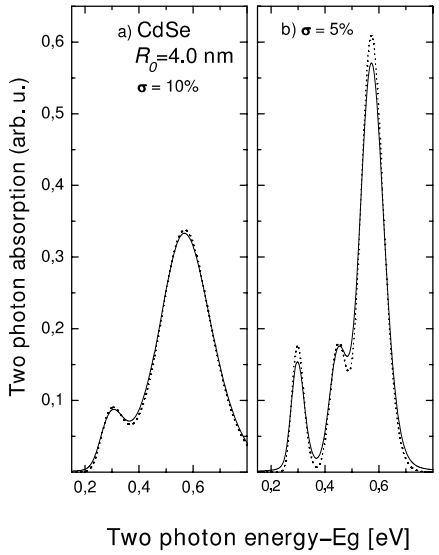

FIG. 2: First three peaks intensities for two-photon absorption processes in a spherical *CdSe* QD of radius $R = 3$ nm, as a function of the difference between the two-photon ($2\hbar\omega$) and gap (Eg) energies of the material.

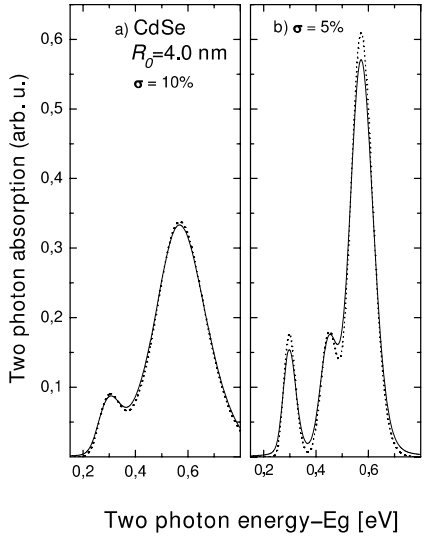

FIG. 3: Calculated two-photon absorption for an ensemble of spherical *CdSe* dots with an average radius $R_0 = 4$ nm. We used a Gaussian distribution, with half-width $\sigma = 0.4$ nm (panel a)) and $\sigma = 0.2$ nm (panel b)), for the spreading over R_0. The dashed lines are analytical solutions using delta-functions and the solid lines use Lorentzian functions with $\Gamma = 5$ meV.

The corresponding transition matrix elements are given as $M_T = M_A + M_B$, where

$$M_{A(B)} = \sum_{|a\rangle} \frac{\langle n\,|\,\widehat{H}^{(k)}_{E-R}\,|\,a\rangle\langle a\,|\overline{A}_i\widehat{\eta}_i\cdot\widehat{\mathbf{p}}\,|\,\hbar\omega_i\rangle}{\hbar\omega_i - E_a}. \qquad (2.1)$$

The index A or B labels the associated diagram involved in each process or, more specifically, A corresponds to $i = 1$, $k = 2$ and B to $i = 2$, $k = 1$ processes, respectively.

After the absorption of the first photon, identified by ω_i, $\mathbf{k}_i$, and η_i, one electron is created at the "intermediate state" $|a\rangle$ ($E_a = E_e + E_h + E_g$). In the next step, the interaction with the second photon ($\omega_k, \mathbf{k}_k, \eta_k$) induces a transition to the final electron state $|n\rangle$. Here, E_e and E_h are the energies of the electron and hole, respectively. The first one is measured with respect to the bottom of the conduction band, and the second one is referred to the top of the valence band. Finally, E_g is the energy band gap. Finally, $\overline{A}_i = (e \times m_0^{-1}\sqrt{V})\sqrt{2\pi\hbar/\omega_i \times \varepsilon_i^2}$ is associated to the average density of energy in the radiation field, V is the volume of the sample, e is the electron charge, m_0 its rest mass and $\varepsilon_i = \varepsilon(\omega_i)$ the refractive index of the material for the incident frequency ω_i. The Hamiltonian, in the left side of Eq. (2.1) is composed of, $\widehat{H}^{(k)}_{E-R} = \widehat{H}^{(k)}_{e-R} - \widehat{H}^{(k)}_{\nu-R}$. Each component has a similar expression as the right side, except that m_0^{-1} in $\overline{A}_i$ is replaced by the effective-mass tensors $\widetilde{M}^{-1}$ for electron ($e-R$) or for holes ($h-R$). The absorption coefficient is written as $K = \langle\varepsilon\rangle W/c$, where c is the speed of light in vacuum, $\langle\varepsilon\rangle$ is an "average refractive index" for the frequencies, and

$$W = \frac{2\pi}{\hbar}\sum_{|n\rangle}|M_A + M_B|^2\delta(\hbar\omega_1 + \hbar\omega_2 - E_n), \qquad (2.2)$$

is the number of optical transitions per unit of volume and per unit of time. For spherical QD with radius R and under Dirichlet's conditions for infinite barriers, the parabolic solutions can be written as[4] $|a_\nu\rangle = N_{l_\nu,n_\nu} j_{l_\nu}\left(\frac{\mu^{(l_\nu)}_{n_\nu} r}{R}\right) Y_{l_\nu,m_\nu}\,|\,u_\nu\rangle$, $(\nu = e,h)$ with eigen-values $E_{a_\nu} = \frac{\hbar^2\left(\mu^{(l_\nu)}_{n_\nu}\right)^2}{2m_\nu R^2}$. Here $N_{l_\nu,n_\nu} = \frac{\sqrt{2/R^3}}{j_{l_\nu+1}\left(\mu^{(l_\nu)}_{n_\nu}\right)}$ is the normalization, $\mu^{(l)}_n$ is the n'th root of the spherical Bessel function of order l ($j_l(x)$), Y_{l_ν,m_ν} is the spherical Harmonic and $|u_\nu\rangle$ is the periodic Bloch states at the zone-center. For two photons of frequencies ($\omega_1 = \omega_2 = \omega$) and linear polarizations perpendicular to the common wave-vector $\mathbf{k}$, we obtain

$$W = \frac{2\pi}{\hbar}\sum_{\substack{l,m\\ n_e,n_h}}\left\{|M_+|^2\delta\left(2\hbar\omega - E_g - \frac{\hbar^2(\mu^{(l+1)}_{n_e})^2}{2m_e^*R^2} - \frac{\hbar^2(\mu^{(l)}_{n_h})^2}{2m_h^*R^2}\right)\right.$$

$$\left. + |M_-|^2\delta\left(2\hbar\omega - E_g - \frac{\hbar^2(\mu^{(l-1)}_{n_e})^2}{2m_e^*R^2} - \frac{\hbar^2(\mu^{(l)}_{n_h})^2}{2m_h^*R^2}\right)\right\}. \qquad (2.3)$$

The sum should run over all quantum numbers of electron and hole states. Note that the sum is restricted to states with $l \geq 1$ in the second term. The matrix elements $M_\pm$ determining the oscillator strength, can be expressed as

$$M_{\pm} = \frac{2\alpha^2 \mathbf{e}_z \cdot \pi_{cv}}{R} C^{\pm}_{n_e m_h} \frac{\left[(l+\frac{1}{2}\pm\frac{1}{2})^2 - m^2\right]}{(2l+1)(2l+1\pm 2)} \left[\frac{m_0/m_e^*}{\hbar\omega - E_g - \frac{\hbar^2\left(\mu^{(l)}_{n_h}\right)^2}{2m^* R^2}} + \frac{m_0/m_h^*}{\hbar\omega - E_g - \frac{\hbar^2\left(\mu^{(l\pm1)}_{n_e}\right)^2}{2m^* R^2}} \right], \tag{2.4}$$

and

$$C^{\pm}_{ne,nh} = \frac{\mu^{(l)}_{nh}\mu^{(l\pm1)}_{ne}}{\left(\mu^{(l)}_{nh}\right)^2 - \left(\mu^{(l\pm1)}_{ne}\right)^2}, \tag{2.5}$$

m_e^* and m_h^* are the electron and hole effective masses, respectively, m^* is the effective reduced mass ($m^* = m_e^* m_h^*/(m_e^* + m_h^*)$), and $\pi_{cv} = \langle u_c \,|\, \widehat{\mathbf{p}} \,|\, u_v \rangle$, at $\mathbf{k} = 0$ is the element determining the optical selection rules for interband transitions.

The first three peaks of two-photon absorption in spherical *CdSe* QD with radius $R = 3$ nm, as a function of the difference between the two-photon energy ($2\hbar\omega$) and E_g, are illustrated in Fig. 2. The *CdSe* parameter used in our calculation are $m_e^* = 0.12$, $m_h^* = 0.45$, $E_g = 1.865$ eV. Note the strong dependence of the intensity on the transition energy.

To study the nonlinear absorption in an ensemble of spherical dots, we introduced a distribution function over radii, in Eq. (2.3), for the dot-size variable R. Using spherical coordinates, the Gaussian distribution assumes the form $\exp\left[-(R-R_0)^2/\sigma^2\right]$, where R_0 is the average value and σ its half-width spreading. Because of the presence of Dirac delta-functions in Eq. (2.3), the analytical integration is easy. Nevertheless, to be more realistic, we could also replace the delta-function by a Lorentzian line-shape function and the integrals can only be calculated numerically.

The Fig. 3 shows the absorption coefficient for an ensemble of spherical *CdSe* QD's, using both the approximations described above. The parameters used are $R_0 = 4$ nm with delta-function spreading $\sigma = 10\%$ (a) and $\sigma = 5\%$ (b) around R_0, respectively. For the Lorentzian function case, we consider a Gaussian distribution half-width $\Gamma = 5$ meV. As can be noted, the spectra almost overlap each other, revealing the fact that the analytical approach using the delta-function with appropriated spreading can be quite reasonable to the description of nonlinear optical absorption effects in QD's ensembles, at least for dots with the characteristic parameters shown here. Also, in low quality samples (large Γ), weak nonlinear transitions may be washed-out. Further calculations concerning more general situations with different photon frequencies and polarizations are now in progress and will be published elsewhere.

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