INSTITUTE OF PHYSICS PUBLISHING SEMICONDUCTOR SCIENCE AND TECHNOLOGY
Semicond. Sci. Technol. **19** (2004) S312–S315 PII: S0268-1242(04)72092-1

Polaron effect on Raman scattering in semiconductor quantum dots

M I Vasilevskiy[1], R P Miranda[1], E V Anda[2] and S S Makler[3]

[1] Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal
[2] Departamento de Física, Pontifícia Universidade Católica, Rio de Janeiro, RJ, Brazil
[3] Instituto de Física, Universidade Federal Fluminense, Niterói, RJ, Brazil

Received 28 July 2003
Published 10 March 2004
Online at stacks.iop.org/SST/19/S312 (DOI: 10.1088/0268-1242/19/4/104)

Abstract
Strong coupling of a confined exciton to optical phonons in semiconductor quantum dots (QDs) leading to the formation of a polaron is considered for a model system including two lowest exciton states and several optical phonon modes. Both intra- and inter-level terms are taken into account. The Hamiltonian has been exactly diagonalized including a finite number of phonons allowed for each mode, large enough to guarantee that the result can be considered exact in the physically important region of energies. Based on this polaron spectrum, the Raman scattering probability is obtained, which is compared with the one calculated using the standard perturbation theory approach. It is shown that, when either diagonal or non-diagonal coupling is sufficiently strong, the Raman spectrum line shape and especially its resonant behaviour differ considerably from the perturbation theory predictions. The dependence of the scattering intensity on the excitation wavelength contains features similar to those expected in the optical absorption spectra of QDs.

1. Introduction

In the last few years there has been increased interest in studying the properties of quantum dot (QD) systems using optical absorption and photoluminescence (PL) spectroscopy, Raman scattering, FIR absorption and other experimental techniques [1]. These studies emphasized the important role that phonons play in the processes which determine the corresponding QD properties. As known, because of the electron confinement in the dot, a strong electron–phonon interaction, and accordingly, multi-phonon processes taking place in all these optical phenomena can be expected. Even though the Fröhlich-type coupling of optical phonons to an exciton confined in a QD is reduced owing to the partial compensation of the phonon interactions with the electron and the hole, it still can be quite strong [2]. Phonon-mediated inter-level coupling can be even stronger because there should be little compensation effect for it. Owing to the intensity of this interaction, the very idea of an electron emitting or absorbing a phonon, based on the perturbation theory concept, is probably wrong in a QD [3, 4]. The situation is more likely described by polaronic quasi-particle excitations, which require a non-adiabatic and non-perturbative treatment of the many-body interactions taking place in these systems.

Raman scattering is known to be a powerful tool for studying not only the phonons but also the underlying electronic structure of the scattering medium. It has been applied to systems containing self-assembled and spherical QDs in many works (e.g. [5–8]) with the objective of probing phonon confinement [5], strain [6] or disorder effects [7]. Resonant behaviour of the scattering was also studied [8], although without much interpretation of the experimental results. Meanwhile, it could help to assess the confined exciton states participating in the resonant scattering, which would be particularly useful for self-assembled QDs where optical absorption measurements are not directly possible. These states themselves are affected by the electron–phonon interaction (in fact, the incident light creates not an exciton but a polaron). The importance of taking into account this non-adiabaticity while considering effects such as PL or Raman scattering was pointed out by Fomin *et al* [9]. The aim of the present paper is to demonstrate what kind of effect one can expect in the Raman scattering when the electron–phonon interaction in QDs is considered exactly, without making the

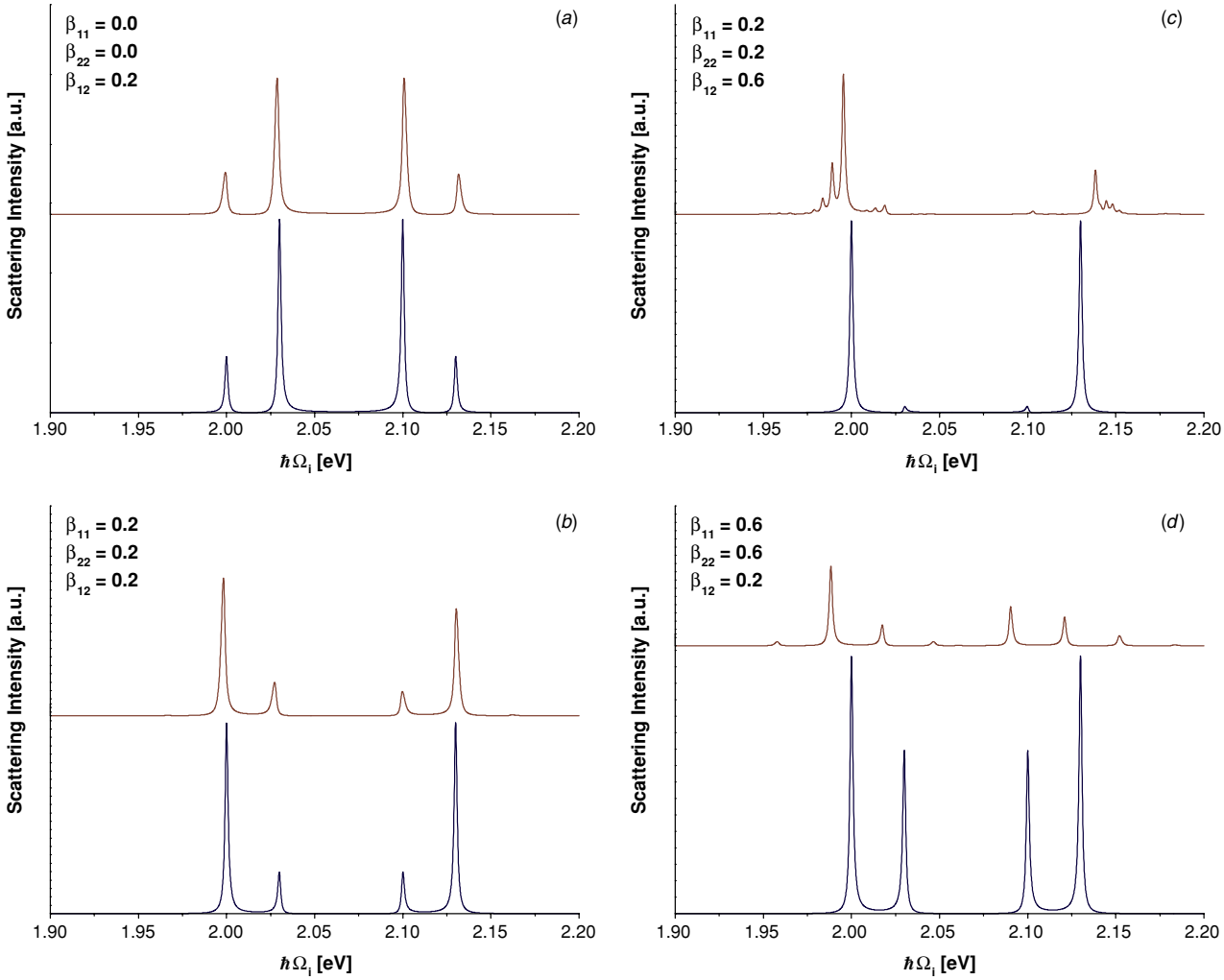

Figure 1. Resonance behaviour of the Raman scattering probability calculated using equation (2) (upper curve in each plot) for a QD with two optically active exciton levels ($E_1 = 2.0$ eV and $E_2 = 2.1$ eV, $p_{01} = p_{02}$) considering a single optical phonon mode $\hbar\omega_0 = 30$ meV. For comparison, spectra obtained using equation (3) (and the same parameters) are also presented (lower curve in each plot). Graphs (a)–(d) correspond to different sets of the exciton–phonon interaction constants as given on the figure.

adiabatic approximation and virtually including all the multi-phonon processes.

2. Model and formalism

Our model system consists of two electronic levels representing the ground and first excited states of, for instance, a hole in a chemically grown spherical CdSe QD or electrons in self-assembled InAs QDs possessing two split levels due to anisotropy in the growth plane. Both levels are coupled to N phonon modes characterized by different harmonic oscillator frequencies within the optical phonon band of the corresponding bulk material. The system is described by the Hamiltonian,

$$H = \sum_{i=1}^{2} \varepsilon_i c_i^+ c_i + \sum_{\nu=1}^{N} \hbar\omega_\nu b_\nu^+ b_\nu + \sum_{i,j=1}^{2} \sum_{\nu=1}^{N} \alpha_{ij}^\nu c_i^+ c_j \left(b_\nu^+ + b_\nu\right), \tag{1}$$

where c_i^+, c_i are the fermion creation and annihilation operators for electrons (or holes) and b_ν^+, b_ν are the operators for phonons and α_{ij}^ν are the respective electron–phonon interaction constants [2]. In order to diagonalize this Hamiltonian, we consider a basis of uncoupled states, $|n_1 n_2\{m_\nu\}\rangle$, where $n_r = 0, 1$ is the number of fermions on level r and $m_\nu = 0, 1, 2, \ldots$ is the number of phonons of mode ν. In principle, the Hamiltonian matrix is infinite but one can truncate the Hilbert space by allowing a certain maximum number of phonons for each mode and obtain a very accurate solution as shown in [2]. Since we are interested in the case when there is a single fermion in the dot, it is necessary to consider only the states $|10\{m_\nu\}\rangle$ and $|01\{m_\nu\}\rangle$. Then the Hamiltonian matrix has the dimension $2m_1 m_2 \cdots m_N$. For a small number of modes and a reasonable number of phonons for each mode, it can be easily diagonalized numerically yielding the polaron states of the QD. Given the eigenvalues (E_k) and eigenvectors of the Hamiltonian (1) (denoted by $|k\rangle$), we can calculate different observable quantities for the QD, such as the electronic spectral function and the optical absorption and emission spectra (by using the Kubo formula [10]).

In this paper, we limit ourselves to calculating the one-phonon Raman scattering probability. The eigenstates of the

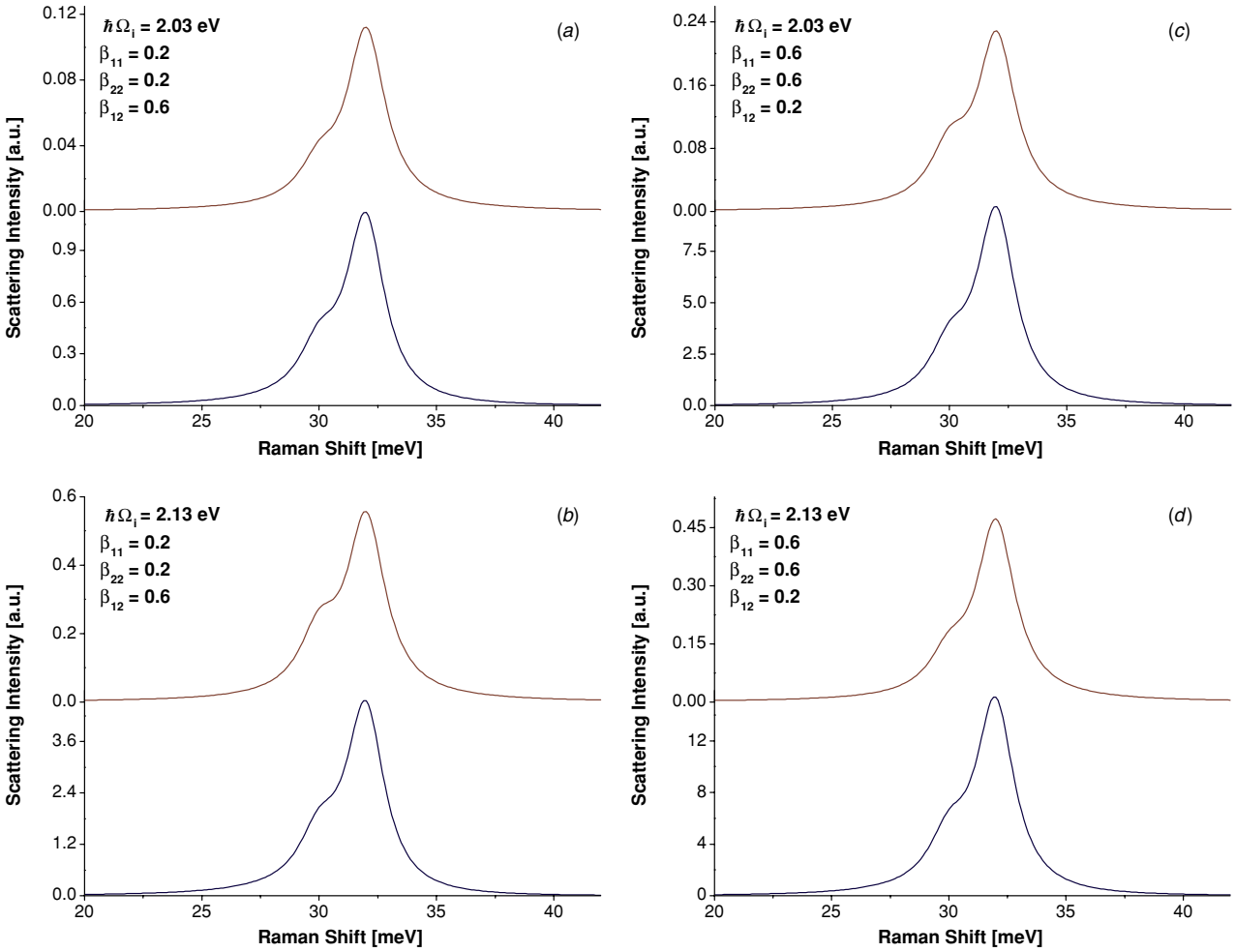

Figure 2. Resonant Raman scattering spectra calculated using equation (2) (upper curve in each plot) for a QD with the same exciton parameters as for figure 1 but including *two* optical phonon modes with the energies $\hbar\omega_1 = 32$ meV and $\hbar\omega_2 = 30$ meV. Each phonon mode was described by a Lorentzian with a (homogeneous) width of 1 meV. Lower curves in all plots were calculated using equation (3). Graphs (a)–(d) correspond to two different excitation energies ((a), (c) and (b), (d)) and two sets of the exciton–phonon interaction constants which are given in the figure for the phonon mode 1. For the phonon mode 2 all the interaction constants are 50% smaller.

Hamiltonian (1) are now interpreted as the excited states of the exciton–polaron. The ground state (exciton vacuum) contains only phonons. Using the second-order perturbation theory for the light–polaron interaction, the (Stokes process) scattering probability is

$$w(\Omega_I,\omega) = \frac{(2\pi)^3}{V^2\Omega_I\Omega_S}\left(\frac{\mathrm{e}}{m_e\eta}\right)^4 \frac{1}{Z}\sum_{\{m_\nu\}}\exp\left(-\beta\sum_\nu m_\nu\hbar\omega_\nu\right) \times \sum_{\nu'}\left|\sum_k \frac{\sum_{l,l'} p_{0l}p^*_{0l'}\left(C^k_l(\{m_\nu\})\right)^* C^k_{l'}(\{m_{\nu'}\}')}{E_k - \sum_\nu m_\nu\hbar\omega_\nu - \hbar\Omega_I}\right|^2 \times \delta(\omega_{\nu'}-\omega) \qquad (2)$$

where Ω_I and Ω_S are the frequencies of the incident and scattered light, respectively, $\omega = \Omega_I - \Omega_S$ is the Raman shift, V the scattering volume, η the refractive index, m_e the free electron mass, $Z = \sum_{\{m_\nu\}}\exp\left(-\beta\sum_\nu m_\nu\hbar\omega_\nu\right)$, $\beta = 1/(k_BT)$, $C^k_i(\{m_\nu\})$ are the eigenvectors expressed in terms of the basis vectors $|10\{m_\nu\}\rangle$ ($l = 1$) and $|01\{m_\nu\}\rangle$ ($l = 2$), p_{0l} is the momentum matrix element between the exciton vacuum and state l and $\{m_{\nu'}\}' = \{m_1, m_2, \ldots, m_{\nu'}+1, \ldots, m_N\}$.

For comparison, we also present below the scattering probability calculated using the standard perturbation-theory expression (see e.g. [11]),

$$w(\Omega_I,\omega) = \frac{(2\pi)^3}{V^2\Omega_I\Omega_S}\left(\frac{\mathrm{e}}{m_e\eta}\right)^4 \sum_\nu [n(\omega_\nu)+1] \times \left|\sum_{l,l'}\frac{p_{0l}p^*_{0l'}\alpha^\nu_{ll'}}{(E_{l'}-\hbar\Omega_I)(E_l-\hbar\Omega_S)}\right|^2 \delta(\omega_\nu-\omega) \qquad (3)$$

where $n(\omega_\nu)$ is the Bose factor.

3. Results and discussion

We applied the formalism outlined in the previous section to the calculation of the resonance behaviour (dependence on Ω_I) and line shape (dependence on ω) of the Raman scattering probability for a model QD with two lowest optically active exciton levels separated by the energy $\Delta = E_2 - E_1$ of the order of several tens of meV. The exciton–phonon interaction constants have been calculated in [2] for a spherical QD taking into account the electrostatic mechanism and the effects of hole

bands mixing and phonon confinement. For the QD size in the range of 2–3 nm, the non-diagonal interaction constant (hereafter we refer to dimensionless values, $\beta_{ij}^{v} = \alpha_{ij}^{v}/(\hbar\omega_v)$) was found to be of the order of the bulk Fröhlich constant (e.g., 0.4 for CdSe). The calculated diagonal coupling constants are smaller, as mentioned in the introduction, however, the deformation potential mechanism can contribute significantly to the diagonal interaction, especially for III–V materials. In the present calculations, the coupling constants were varied in the range of 0–0.6 in order to see where the polaron effect becomes important for the Raman scattering. Some of the results calculated for room temperature are presented in figures 1 and 2.

The dependence of the scattering probability on Ω_I for small values of β_{ij} (figures 1(a), (b)) has two pairs of peaks known as incoming and outgoing resonances [11] for each bare exciton level. For the case of only intra-level interactions ($\beta_{12} = 0$, not shown here) all the resonances have similar intensities (in fact, they are exactly equal according to equation (3) and only slightly different according to equation (2)). 'Switching on' the inter-level coupling changes the situation, the intensities of different resonances become rather different depending on all β_{ij} (note, however, the symmetry of the spectra with respect to the mid-point between E_1 and $E_2 + \hbar\omega_0$). With the increase in the interaction strengths (figures 1(c), (d)), the spectra calculated using the two approaches begin to differ substantially. When the inter-level coupling dominates (figure 1(c)), the spectrum calculated using equation (2) shows characteristic features similar to those obtained in the electron spectral function and known as Rabi splitting [2, 12]. They correspond to the exciton oscillating between its two states and (many times) emitting and absorbing a phonon. Note that this structure is observed when two levels are far from resonance with the phonon ($\Delta \gg \hbar\omega_0$). In the case of strong intra-level coupling (figure 1(d)) the spectrum resembles the Huang–Rhys progression in absorption spectra calculated for the one-level 'independent boson model' [10] (by the way, this model is commonly used for the interpretation of the QD spectra, e.g. [13]). Of course, none of these features appear in the spectra calculated using equation (3).

The Raman line shape is determined by relative intensities of a small number of phonon modes confined in the QD [5, 7]. The strongest one usually corresponds to the spectral maximum while the others form an asymmetrically broadened band extending to the lower ω. We included two modes with different β_{ij}^{v} in the calculations of the line shape. Comparing the spectra of figure 2 calculated in the framework of the polaron concept to those obtained using the perturbation theory expression, we note that the line shape, generally, is not changed much. However, the weaker mode can be resonantly enhanced (figure 2(b)) or suppressed (figure 2(c)) under certain excitation conditions, resulting in a noticeable effect on the line shape.

In conclusion, we proposed a non-perturbative and non-adiabatic approach for the calculation of the polaron effect on the Raman scattering in QDs. It becomes important for the Raman scattering at the same conditions as for the absorption and emission. The dependence of the scattering intensity on the incident photon energy shows characteristic polaron-related features and therefore can be used, along with the PLE spectroscopy, for studying the details of the exciton spectra in QDs.

Acknowledgments

This work was supported by the project FCT-POCTI/FIS/10128/98 (Portugal) and ICCTI-CNPq Cooperation Program (Portugal–Brazil).

References

[1] Grundmann M (ed) 2002 *Nano-Opoelectronics. Concepts, Physics and Devices* (Berlin: Springer)
[2] Vasilevskiy M I, Anda E V and Makler S S 2002 *Proc. 26th Int. Conf. on the Physics of Semiconductors (Institute of Physics Conference Series 171)* (Bristol: IOP Publishing) p 229
[3] Hameau S *et al* 1999 *Phys. Rev. Lett.* **83** 4152–5
[4] Stauber T, Zimmermann R and Castella H 2000 *Phys. Rev.* B **62** 7336–43
[5] Chamberlain M P, Trallero-Giner C and Cardona M 1995 *Phys. Rev.* B **51** 1680–91
[6] Tenne D A *et al Phys. Rev.* B **61** 13785–8
[7] Vasilevskiy M I, Rolo A G, Gomes M J M, Vikhrova O V and Ricolleau C 2001 *J. Phys.: Condensed Matter* **13** 3491–509
[8] Shiang J J, Craig I M and Alivisatos A P 1993 *Z. Phys.* D **26** 358–60
[9] Fomin V M *et al* 1998 *Phys. Rev.* B **57** 2415–25
[10] Mahan G D 2000 *Many-Particle Physics* (New York: Kluwer)
[11] Yu P Y and Cardona M 1996 *Fundamentals of Semiconductors* (Berlin: Springer)
[12] Li X Q, Nakayama H and Arakawa Y 1999 *Phys. Rev.* B **59** 5069–73
[13] Jungnickel V and Henneberger F 1996 *J. Lumin.* **70** 238–46