Theory of quasi-elastic secondary emission from a quantum dot in the regime of vibrational resonance

Ivan D. Rukhlenko,1,∗ Anatoly V. Fedorov,2 Anvar S. Baymuratov,2 and Malin Premaratne1

1Advanced Computing and Simulation Laboratory (AxL), Department of Electrical and Computer Systems Engineering, Monash University, Clayton, VIC 3800, Australia
2Center of Information Optical Technologies, Saint Petersburg State University of Information Technologies, Mechanics and Optics, St. Petersburg 197101, Russia

∗ivan.rukhlenko@monash.edu

Abstract: We develop a low-temperature theory of quasi-elastic secondary emission from a semiconductor quantum dot, the electronic subsystem of which is resonant with the confined longitudinal-optical (LO) phonon modes. Our theory employs a generalized model for renormalization of the quantum dot’s energy spectrum, which is induced by the polar electron-phonon interaction. The model takes into account the degeneration of electronic states and allows for several LO-phonon modes to be involved in the vibrational resonance. We give solutions to three fundamental problems of energy-spectrum renormalization—arising if one, two, or three LO-phonon modes resonantly couple a pair of electronic states—and discuss the most general problem of this kind that admits an analytical solution. With these results, we solve the generalized master equation for the reduced density matrix, in order to derive an expression for the differential cross section of secondary emission from a single quantum dot. The obtained expression is then analyzed to establish the basics of optical spectroscopy for measuring fundamental parameters of the quantum dot’s polaron-like states.

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OCIS codes: (160.4236) Nanomaterials; (300.6470) Spectroscopy, semiconductors; (250.5590) Quantum -well, -wire, and -dot devices; (290.5870) Scattering, Rayleigh; (300.6280) Spectroscopy, fluorescence and luminescence; (300.3700) Linewidth.

References and links

#146499 - $15.00 USD  Received 26 Apr 2011; revised 24 Jun 2011; accepted 11 Jul 2011; published 28 Jul 2011  
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1. Introduction

The coupling between electrons and phonons is one of the most influential interactions occurring inside semiconductor quantum dots, which results in the scattering of electrons, holes, and excitons [1, 2]. In the photoluminescence experiments performed on quantum dots, this coupling is often manifested in enhanced dephasing rates of spectroscopic transitions [3–6] and reduced lifetimes of electronic excitations [7–11]. Electron-phonon interaction may also cause a significant modification of the quantum dot’s energy spectrum, known to be especially prominent in the regime of vibrational resonance [12, 13]. This regime is realized where the energy of a phonon coincides with the energy spacing between a pair of states of the quantum dot’s electronic subsystem. Renormalization of the electron-phonon energy spectrum in this situation leads to the formation of hybrid energy states characterizing a new class of polaron-like excitations, which are similar to the polarons in a bulk semiconductor.

Although quantum dots are generally affected by a multitude of phonon-related elementary excitations—residing both inside them and in various distant parts of the host heterostructures [14–17]—the renormalizations of the quantum dot’s energy spectra, that have been experimentally observed so far, predominantly resulted from polar interaction with longitudinal-optical (LO) phonons [13, 18–23]. Despite a relatively high strength of polar interaction compared to other types of electron-phonon coupling [1, 2], the energy splitting of polaron-like states induced by the vibrational resonance is typically of the order of few millielectronvolts. Such a fine structure of the quantum dot’s energy spectra can be experimentally resolved only at cryogenic temperatures, when both dephasing rates of optical transitions and spectral widths of energy levels are relatively small. Another challenge that hampers observation of singularities in the quantum dots’ optical spectra in the regime of vibrational resonance stems from the relatively broad size distribution of quantum dots, which is present even in the most finely fabricated samples. Quantum dots of different sizes emit light of different wavelengths leading to the inhomogeneous broadening of spectroscopic transitions. This obstacle can be avoided by applying size-selective optical methods, such as persistent spectral hole burning in an inhomogeneously broadened light absorption profile [20, 24], one- and two-photon excited pho-
toluminescence [13, 22], or a single-quantum-dot spectroscopy [25, 26]. Using these methods for studying the effect of vibrational resonance requires an adequate theoretical treatment of the underlying optical phenomena, taking into account specific features characteristic to the quantum dot’s polaron-like spectrum.

Several physical theories of polaron-like excitations in semiconductor quantum dots were developed by different research groups [13, 22, 23, 27–30], and subsequently employed for the interpretation of experimental data. For example, the first theory proposed in Ref. [13] helped to explain the shape of the excitonic luminescence spectra obtained under the resonant size-selective excitation of CuCl-nanocrystals. The model of Ref. [23] was applied for the analysis of data on intraband transitions obtained with far-infrared magnetospectroscopy for self-assembled quantum dots made of InAs [18, 19, 21, 23]. Another model, reported in Ref. [22], proved useful in interpreting the effect of renormalization for the lowest excitonic states in CuCl-quantum dots embedded into NaCl-matrix, which were studied with the spectroscopy of secondary emission under two-photon resonance excitation. Unlike theoretical treatment of the vibrational resonance itself, the mathematical description of its manifestation in optical spectra is developed rather poorly, and the information these spectra are capable of providing is not perfectly understood. To the best of our knowledge, the only technique that has been placed on solid theoretical ground up to date is the persistent spectral hole burning in an inhomogeneously broadened light absorption profile [27]. Thus, a fundamental theory of quantum dot optical response allowing for the renormalization of the electron-LO-phonon energy spectrum is still in demand.

In this work, we present a comprehensive theoretical study of quasi-elastic secondary emission from a single quantum dot that exhibits a vibrational resonance. The paper is organized as follows. In Section 2, we outline the model for renormalization of the quantum dot’s energy spectrum due to the resonant polar interaction with LO phonons. This model generalizes our previous results [22, 27], by extending them to degenerate electronic levels and an arbitrary number of LO-phonon modes involved in the vibrational resonance. Section 3 is devoted to the solution of the generalized master equation for the reduced density matrix, and calculation of the differential cross section of the quasi-elastic secondary emission at low temperatures. In this section, we also analyze the effect of spectral filtration of secondary emission due to the finite bandwidth of the photon detector, and present a general expression for the intensity of secondary emission in the case of vibrational resonance between 3-fold and 9-fold degenerate electronic states. In Section 4, we illustrate the potential of optical spectroscopy based on probing polaron-like states, by the example of a spherical quantum dot in the regime of strong confinement. Specifically, we consider two different scenarios in which vibrational resonance occurs between either a pair of lowest degenerate or a pair of lowest nondegenerate electronic states. In Section 5, we summarize our results and conclude the paper.

2. Theory of vibrational resonance in a semiconductor quantum dot

We start our theoretical treatment of vibrational resonance arising in a quantum dot due to the polar electron-phonon interaction, by introducing the Hamiltonian formalism for the physical system being of interest.

2.1. Hamiltonian formalism

The physical system to be analyzed is composed of a semiconductor quantum dot, classical excitation light, and vacuum (quantum electromagnetic) radiation field. It is convenient to take the total Hamiltonian of this system to be of the form

$$H(t) = H_0 + H_{\text{int}}(t),$$ (1)
where

\[ H_0 = \sum_p E_p a_p^\dagger a_p + \sum_q \hbar \Omega_q b_q^\dagger b_q + \sum_k \hbar \omega_k c_k^\dagger c_k \]  

(2)
gives the contribution from noninteracting electron-hole pairs, LO phonons, and photons, while

\[ H_{\text{int}}(t) = H_{e,ph} + H_{e,L}(t) + H_{e,\lambda} \]  

(3)
describes the interaction of electron-hole pairs \((e)\) with phonons \((ph)\), excitation light \((L)\), and radiation field \((\lambda)\). The notations on the right-hand side of Eq. (2) are as follows: \(a_p^\dagger\) \((a_p)\), \(b_q^\dagger\) \((b_q)\), and \(c_k^\dagger\) \((c_k)\) are the creation (annihilation) operators of electron-hole pairs, LO phonons, and photons, respectively; \(E_p = E_g + E_{pe} + E_{ph}\) is the energy of electron-hole pair state \(|p\rangle \equiv |p_e; p_h\rangle\), which depends on the quantum numbers of electron \((p_e)\) and hole \((p_h)\), and the band gap, \(E_g\) of the bulk semiconductor; \(\hbar \Omega_q\) and \(\hbar \omega_k\) are the energies of LO-phonon mode \(q\) and photon mode \(\lambda\).

For simplicity, we restrict our analysis to the quantum dot in the regime of strong confinement, and describe its electronic subsystem using the two-band approximation [1,2]. Although polar electron-phonon interaction in quantum dots is relatively strong, it does not excite electrons from the valence \((v)\) band to the conduction \((c)\) band, but induces only intraband transitions between the different states of electron-hole pairs. This fact allows electron-phonon Hamiltonian to be represented as

\[ H_{e,ph} = \sum_q \sum_{p_1, p_2 \neq 0} \left( V_{p_2, p_1}^{(q)} a_{p_2}^\dagger a_{p_1} b_q + \text{H.c.} \right), \]  

(4)

where the second summation does not extend over the quantum numbers \(p_1 = p_2 = 0\), representing vacuum of electron-hole pairs, and the matrix element of polar electron-phonon interaction is given by the expression

\[ V_{p_2, p_1}^{(q)} = -e \left( \varphi_{p_2, p_1}^{(q)} \delta_{p_2, p_1} - \varphi_{p_1, p_2}^{(q)} \delta_{p_2, p_1} \right), \]  

(5)
in which \(-e\) is the charge of the electron; \(\varphi_{p_2, p_1}^{(q)}\) and \(\varphi_{p_1, p_2}^{(q)}\) are the matrix elements of the electric potential induced by the LO-phonon mode \(q\); \(\delta_{p_2, p_1}\) and \(\delta_{p_2, p_1}\) are the products of Kronecker deltas for the quantum numbers of electron and hole. In writing Eq. (5) in the form shown, we assumed that the spatial confinement provided by a quantum dot for electrons, holes, and phonons is approximated suitably enough by an infinitely deep potential well.

An explicit form of the matrix elements in Eq. (5) depends on the specific shape of the quantum dot [1,2]. For a spherical quantum dot of radius \(R\), which will be used to illustrate our results in Section 4, can be expressed compactly as [31]

\[ \varphi_{p_2, p_1}^{(q)} = \varphi_{p_2, p_1}^{(q)} = \sqrt{\frac{4(2l_q + 1)(2l_{p_1} + 1)\hbar \Omega_p}{(2l_{p_2} + 1)e^* R}} \varphi_{n_2 l_2 p_2}^{(q)} n_2 l_2 p_2 n_1 l_1 p_1 C_{l_2 0}^{l_1 0} C_{l_2 m_2}^{l_1 m_1} ; \]  

(6)

where \(e^* = (1/\varepsilon_0 - 1/\varepsilon_\infty)^{-1}\), \(\varepsilon_0\) and \(\varepsilon_\infty\) are the low- and high-frequency dielectric permittivities of the bulk semiconductor,

\[ \varphi_{n_2 l_2 p_2}^{(q)} = \int_0^1 dx j_{l_2}(\xi_n) j_{l_1}(\xi_{n_2}) \]  

(7)

and \(j_l(z)\) is the spherical Bessel function of the first kind, with \(\xi_m\) being its \(m\)th zero [i.e., \(j_l(\xi_m) = 0\)]. Clebsch-Gordan coefficients \(C_{l_2 m_2}^{l_1 m_1}\) appearing in this expression set the selection rules for electron-electron and hole-hole transitions. The quantities \(n_d\), \(l_d\), and \(m_d\)
\( (a=q, p_1, p_2) \) denote the principal quantum number, angular momentum, and its projection for LO phonon \((a=q)\), electron \((a=p_2, p_1, p_2)\), or hole \((a=p_{h1}, p_{h2})\).

The second and third terms in Eq. (3) account for the two mechanisms of interband transitions: (i) generation of electron-hole pairs through absorption of excitation light by the quantum dot’s electronic subsystem; and (ii) recombination of electron-hole pairs with emission of photons due to their interaction with the vacuum radiation field. The Hamiltonians describing these mechanisms can be represented in the forms [31, 32]

\[
\begin{align*}
H_{e,L}(t) & = \sum_{\lambda \neq 0} \left( V_{p_0,0}^{(L)}(t) a_{p}^+ + \text{H.c.} \right), \\
H_{e,\lambda} & = \sum_{\lambda \neq 0} \left( i\hbar g_{\lambda} V_{p_0,0}^{(\lambda)} a_{p}^+ c_{\lambda} + \text{H.c.} \right),
\end{align*}
\]

where \( V_{p_0,0}^{(L)}(t) = V_{p_0}^{(L)}(t) \exp(-i\omega_L t) \), \( \phi(t) \) is the complex envelope of classical optical field, \( g_{\lambda} = \sqrt{2\pi\omega_L/(\epsilon_\infty n V)} \), \( V \) is the normalization volume, and

\[
V_{p_0,0}^{(\eta)} = -e \langle u_c | \mathbf{r} \cdot \hat{\eta} | u_{\eta} \rangle \delta_{p_c,p_h} \tag{7}
\]

is the matrix element of the electric dipole moment operator \(-e\mathbf{r}\), calculated on Bloch functions \( u_c \) and \( u_{\eta} \) at the Brillouin zone center, for excitation light \((\eta=L)\) or emitted photon \((\eta=\lambda)\) of frequency \( \omega_\eta \) and polarization vector \( \hat{\eta} \). Kronecker’s delta following the matrix element shows that the dipole-allowed generation and recombination of electron-hole pairs occur only if the quantum numbers of electron and hole are the same. In what follows, we shall consider only quantum dots made of semiconductors with either \( T_d \) and \( O_h \) symmetry. In this case, matrix element in Eq. (7) is expressed through the Kane’s parameter, \( P \) of bulk material as [33, 34]

\[
\langle u_c | \mathbf{r} \cdot \hat{\eta} | u_{\eta} \rangle \equiv \sqrt{2} Z_{cv} = \sqrt{2} P / E_g.
\]

2.2. Formation of polaron-like states

In the case of no interaction occurring between electrons and phonons inside a quantum dot, a number of the total system “electrons plus phonons” energy states may be degenerate. This happens in the situation of vibrational resonance, where energy of a particular LO-phonon mode is close to the energy spacing between a pair of electron-hole states, i.e., when \( E_{p_2} - E_{p_1} \approx \hbar \Omega_q \). The degeneracy is removed by the polar electron-phonon interaction, which results in the splitting of degenerate levels into two or more polaron-like states with different energies [35].

The energies and wave functions of the polaron-like states can be found by diagonalizing Hamiltonian in Eq. (1) with respect to the electron-phonon interaction. We begin this procedure by employing the unitary transformation

\[
U = \exp \left[ -\sum_{p,q} \left( \Phi^{(q)}_{p,p} b_q - \text{H.c.} \right) a_{p}^+ a_{p} \right]
\]

with \( \Phi^{(q)}_{p,p} = \frac{V^{(q)}_{p,p}}{\hbar \Omega_q} \) to eliminate the diagonal part of electron-hole coupling. Keeping only the linear part of the electron-phonon interaction in the transformed Hamiltonian, yields [27]:

\[
\tilde{H}(t) = U^+ H(t) U = \tilde{H}_0 + \tilde{H}_{e,ph} + \tilde{H}_{e,L}(t) + \tilde{H}_{e,\lambda}, \tag{8}
\]
where

$$
\hat{H}_0 = \sum_p \hat{E}_p \hat{a}_p^+ \hat{a}_p + \sum_q \hbar \Omega_q \hat{b}_q^+ \hat{b}_q + \sum_{\lambda} \hbar \omega_{\lambda} \hat{c}_{\lambda}^+ \hat{c}_{\lambda}, \quad \hat{E}_p = E_p - \sum_q \hbar \Omega_q |\Phi^{(q)}_{p,p}\rangle^2,
$$
\hspace{1cm} (9a)

$$
\hat{H}_{e,ph} = \sum_q \sum_{p_1 \neq p_2 \neq 0} \left( V^{(q)}_{p_2,p_1} \hat{a}_p^+ \hat{a}_{p_2} \hat{b}_q^+ \hat{b}_q + \text{H.c.} \right),
$$
\hspace{1cm} (9b)

$$
\hat{H}_{e,\lambda} = \sum_{\lambda} \sum_{p \neq 0} \left( \hbar g_{\lambda p} \left[ 1 + \sum_q \left( \Phi^{(q)}_{p,p} \hat{b}_q - \text{H.c.} \right) \right] \hat{a}_p^+ \hat{c}_{\lambda} + \text{H.c.} \right),
$$
\hspace{1cm} (9c)

$$
\hat{H}_{e,\lambda} = \sum_{\lambda} \sum_{p \neq 0} \left( \hbar g_{\lambda p} \left[ 1 + \sum_q \left( \Phi^{(q)}_{p,p} \hat{b}_q - \text{H.c.} \right) \right] \hat{a}_p^+ \hat{c}_{\lambda} + \text{H.c.} \right).
$$
\hspace{1cm} (9d)

It is seen from Eq. (9a) that the vibrational resonance occurs in the event that the energy of one or several LO phonons approximately coincide with the energy spacing of electron-hole states shifted due to the electron-phonon interaction, i.e., $E_{p_2} - E_{p_1} \approx \hbar \Omega_q$. To complete the diagonalization procedure of the Hamiltonian $\hat{H}(t)$, we exclude from Eq. (9b) electron-phonon interaction coupling the states being in vibrational resonance. This can be done with an appropriately constructed unitary operator $S$, via the transformation

$$
\hat{H}(t) = S^+ \hat{H}(t) S.
$$
\hspace{1cm} (10)

The eigenstates $|\psi\rangle$ of the resulting Hamiltonian $\hat{H}(t)$ are related to the eigenstates $|\Psi\rangle$ of the Hamiltonian $\hat{H}(t)$ through the same operator $S$ via $|\Psi\rangle = S^+ |\psi\rangle$. The matrix representing operator $S$ is found by solving a standard eigenvalue problem, $\hat{H}|\Psi\rangle = \lambda|\Psi\rangle$; in the general case that the resonant condition is simultaneously satisfied for $k$ LO phonon modes, it requires solving the $(k + 1)$-degree algebraic equation.

2.3. Vibrational resonance involving one, two, and three phonon modes

Let us now consider those eigenvalue problems associated with Hamiltonian $\hat{H}$ that admit analytical solutions. The simplest problems of this type arise where two nondegenerate states $|E_{p_2}\rangle$ and $|E_{p_1}\rangle$ are coupled via one $(q_1)$, two $(q_1, q_2)$, or three $(q_1, q_2, q_3)$ LO-phonon modes. Using Eqs. (9a) and (9b) and assuming that the temperature of the system is low enough for the phonon modes to be unoccupied, we first draw the matrices that represent the electron-phonon part of the Hamiltonian (9) in these three cases,

$$
\hat{H}^{(1)}_{e,ph} = \begin{pmatrix}
\hat{E}_{p_2} & V^{(q_1)}_{p_2,p_1} \\
V^{(q_1)*}_{p_2,p_1} & E_{p_1} + \hbar \Omega_{q_1}
\end{pmatrix},
$$
\hspace{1cm} (11a)

$$
\hat{H}^{(2)}_{e,ph} = \begin{pmatrix}
\hat{E}_{p_2} & V^{(q_1)}_{p_2,p_1} & V^{(q_2)}_{p_2,p_1} \\
V^{(q_1)*}_{p_2,p_1} & E_{p_1} + \hbar \Omega_{q_1} & 0 \\
V^{(q_2)*}_{p_2,p_1} & 0 & E_{p_1} + \hbar \Omega_{q_2}
\end{pmatrix},
$$
\hspace{1cm} (11b)

$$
\hat{H}^{(3)}_{e,ph} = \begin{pmatrix}
\hat{E}_{p_2} & V^{(q_1)}_{p_2,p_1} & V^{(q_2)}_{p_2,p_1} & V^{(q_3)}_{p_2,p_1} \\
V^{(q_1)*}_{p_2,p_1} & E_{p_1} + \hbar \Omega_{q_1} & 0 & 0 \\
V^{(q_2)*}_{p_2,p_1} & 0 & E_{p_1} + \hbar \Omega_{q_2} & 0 \\
V^{(q_3)*}_{p_2,p_1} & 0 & 0 & E_{p_1} + \hbar \Omega_{q_3}
\end{pmatrix}.
$$
\hspace{1cm} (11c)

The diagonal elements of matrix $\hat{H}^{(1)}_{e,ph}$ give the energies of states $|E_{p_2};0_{q_1}\rangle = |E_{p_2}\rangle |0_{q_1}\rangle$ and $|E_{p_1};1_{q_1}\rangle = |E_{p_1}\rangle |1_{q_1}\rangle$, where kets $|0_{q_1}\rangle$ and $|1_{q_1}\rangle$ stand for the vacuum of the phonon modes.
Here, phonon interaction, these states change their energies and wave functions according to the re-
matrices in Eqs. (11b) and (11c) can also be found. Generally, these expressions are rather 

The Hamiltonian in Eq. (11a) is reduced to the diagonal form

\[ \tilde{H}_{\text{e.ph}} = \begin{pmatrix} \delta_+^{(1)} & 0 \\ 0 & \delta_-^{(1)} \end{pmatrix} \]

by the matrix

\[ S_1 = \begin{pmatrix} c_1^{(1)} & c_2^{(1)} \\ 0 & -c_4^{(1)*} c_1^{(1)} \end{pmatrix} \]

We see that the electron-phonon interaction completely removes the degeneracy of states \(|\tilde{E}_{p_2}; 0_{q_1}\rangle\) and \(|\tilde{E}_{p_1}; 1_{q_1}\rangle\). The formation of new energy-shifted levels of the polaron-like states \(|\tilde{\delta}^+_1\rangle\) and \(|\tilde{\delta}^-_1\rangle\) is illustrated in Figs. 1(a)–1(c).

Closed expressions for energies and wave functions of the polaron-like states corresponding to matrices in Eqs. (11b) and (11c) can also be found. Generally, these expressions are rather
cumbersome, because their derivation amounts to solving cubic and quartic equations [36]. We, therefore, restrict ourselves to a specific situation of dispersionless phonon modes, in which simplified solutions to both eigenvalue problems can be obtained.

Assuming that the energies of phonons in the modes \( q_1 \) and \( q_2 \) are equal to the energy, \( \hbar \Omega_{LO} \) of the bulk LO phonon at the Brillouin zone center, we find the polaron-like states of the Hamiltonian \( \hat{H}_{e,ph}^{(2)} \) to be

\[
\begin{align}
\varepsilon_{\pm}^{(2)} &= \frac{1}{2}(\tilde{E}_{p_2} + \tilde{E}_{p_1} + \hbar \Omega_{LO} \pm \delta_2), \quad \varepsilon_3^{(2)} = \tilde{E}_{p_1} + \hbar \Omega_{LO}, \\
|\varepsilon_{+}^{(2)}\rangle &= c_1^{(2)}|\tilde{E}_{p_2};0\rangle + c_6^{(2)*}|\tilde{E}_{p_1};1\rangle, \quad |\varepsilon_{-}^{(2)}\rangle = c_3^{(2)}|\tilde{E}_{p_1};1\rangle + c_6^{(2)*}|\tilde{E}_{p_1};1\rangle, \\
|\varepsilon_3^{(2)}\rangle &= -c_5^{(2)}|\tilde{E}_{p_1};1\rangle + c_3^{(2)}|\tilde{E}_{p_1};1\rangle, \\
|\varepsilon_-^{(2)}\rangle &= c_2^{(2)}|\tilde{E}_{p_2};0\rangle - c_4^{(2)*}|\tilde{E}_{p_1};1\rangle - c_5^{(2)*}|\tilde{E}_{p_1};1\rangle, \\
\end{align}
\]

(14a) - (14d)

where \( c_1^{(2)} \) and \( c_2^{(2)} \) are given by Eq. (13) after the replacement \( \Omega_{q_2} \rightarrow \Omega_{LO} \), \( c_3^{(2)} = 2V_{p_2,p_1}/\Delta_2 \), \( c_4^{(2)} = V_{p_2,p_1}/V_2 \), \( c_5^{(2)} = V_{p_2,p_1}/V_2 \), \( c_6^{(2)} = 2V_{p_2,p_1}/\Delta_2 \), and \( \mathbf{q} = (q_1,q_2) \). The matrix that puts \( \hat{H}_{e,ph}^{(2)} \) in the diagonal form \( \hat{H}_{e,ph}^{(2)} = \text{diag}(\varepsilon_{+}^{(2)}, \varepsilon_3^{(2)}, \varepsilon_-^{(2)}) \) is

\[
S_2 = \begin{pmatrix}
0 & c_2^{(2)} & c_4^{(2)*} \\
-c_3^{(2)*} & -c_5^{(2)*} & -c_4^{(2)*} \\
c_3^{(2)*} & c_5^{(2)*} & c_4^{(2)*}
\end{pmatrix}
\]

(14a)

Figure 1(d) shows how the energy level that was initially triply degenerate splits into three nondegenerate levels given in Eq. (14a).

Finally, by setting the energies of all phonon modes in Eq. (11c) alike, \( \hbar \Omega_{q_1} = \hbar \Omega_{q_2} = \hbar \Omega_{q_3} = \Omega_{LO} \), we may represent the polaron-like states as

\[
\begin{align}
\varepsilon_{\pm}^{(3)} &= \frac{1}{2}(\tilde{E}_{p_2} + \tilde{E}_{p_1} + \hbar \Omega_{LO} \pm \delta_3), \quad \varepsilon_3^{(3)} = \tilde{E}_{p_1} + \hbar \Omega_{LO}, \\
|\varepsilon_{+}^{(3)}\rangle &= c_1^{(3)}|\tilde{E}_{p_2};0\rangle + c_9^{(3)*}|\tilde{E}_{p_1};1\rangle, \quad |\varepsilon_{-}^{(3)}\rangle = c_3^{(3)}|\tilde{E}_{p_1};1\rangle + c_9^{(3)*}|\tilde{E}_{p_1};1\rangle, \\
|\varepsilon_3^{(3)}\rangle &= -c_5^{(3)}|\tilde{E}_{p_1};1\rangle + c_3^{(3)}|\tilde{E}_{p_1};1\rangle, \\
|\varepsilon_-^{(3)}\rangle &= c_2^{(3)}|\tilde{E}_{p_2};0\rangle - c_10^{(3)*}|\tilde{E}_{p_1};1\rangle - c_11^{(3)*}|\tilde{E}_{p_1};1\rangle - c_3^{(3)*}|\tilde{E}_{p_1};1\rangle, \\
\end{align}
\]

(15a) - (15e)

where \( c_1^{(2)} \) and \( c_2^{(2)} \) are given by Eq. (13), \( c_3^{(2)} = 2V_{p_2,p_1}/\Delta_3 \), \( c_4^{(2)} = 2V_{p_2,p_1}/\Delta_3 \), \( c_5^{(2)} = V_{p_2,p_1}/V_2 \), \( c_6^{(2)} = V_{p_2,p_1}/V_2 \), \( c_7^{(2)} = V_{p_2,p_1}/V_3 \), \( c_8^{(2)} = V_{p_2,p_1}/V_3 \), \( c_9^{(2)} = 2V_{p_2,p_1}/\Delta_3 \), \( c_{10}^{(2)} = V_{p_2,p_1}/V_3 \), \( c_{11}^{(2)} = V_{p_2,p_1}/V_3 \), and \( \mathbf{q} = (q_1,q_2,q_3) \). The diagonalization \( \hat{H}_{e,ph}^{(3)} \rightarrow \hat{H}_{e,ph}^{(3)} = \text{diag}(\varepsilon_{+}^{(3)}, \varepsilon_3^{(3)}, \varepsilon_-^{(3)}) \) is realized by the matrix

\[
S_3 = \begin{pmatrix}
0 & c_2^{(3)} & c_4^{(3)*} \\
-c_3^{(3)*} & -c_5^{(3)*} & -c_4^{(3)*} \\
c_3^{(3)*} & c_5^{(3)*} & c_4^{(3)*}
\end{pmatrix}
\]

(15a)

It is seen that electron-phonon interaction is unable to completely remove the degeneracy of the four states in the present case. This is a consequence of the initial triple degeneracy of the LO-phonon mode.
By looking at Eqs. (12a), (14a), and (15a), it may be noted that they admit a straightforward generalization to the situation in which an arbitrary number of degenerate phonon modes $(q_1, q_2, \ldots, q_k)$ are resonant with the quantum dot’s electronic subsystem. The resulting energies of the polaron-like states are of the form

$$
\varepsilon^{(k)}_{\pm} = \frac{1}{2} (\tilde{E}_{p_2} + \tilde{E}_{p_1} + \hbar \Omega_{LO} \pm \delta_k), \quad \varepsilon^{(k)}_{3} = \varepsilon^{(k)}_{4} = \ldots = \varepsilon^{(k)}_{k+1} = \tilde{E}_{p_1} + \hbar \Omega_{LO}.
$$

Thus, whenever the $k$ degenerate LO-phonon modes couple a pair of quantum-dot electronic states, it results in the formation of two nondegenerate and one $(k-1)$-degenerate polaron-like states.

### 2.4. Polaron-photon interaction

We saw in the previous two subsections that vibrational resonance modifies the interaction of electrons and holes residing in a quantum dot, with excitation light and emitted photons. This fact is described mathematically by the transformations of the Hamiltonians $\tilde{H}_{e,L}$ and $\tilde{H}_{e,\lambda}$ given in Eqs. (8) through (10). In order to evaluate the efficiency of low-temperature secondary emission in the presence of vibrational resonance with one, two, or three LO-phonon modes, the following matrix elements of the transformed Hamiltonians $\tilde{H}_{e,\eta}$ ($\eta = L, \lambda$) are required:

\begin{equation}
\tilde{H}_{e,1}^{(1)} = \begin{pmatrix}
0 & 0 & c_1^{(1)} V_{p_2,0}^{(\eta)} & 0 \\
0 & 0 & 0 & c_2^{(1)} V_{p_2,0}^{(\eta)} \\
c_1^{(1)} V_{p_2,0}^{(\eta)*} & c_2^{(1)} V_{p_2,0}^{(\eta)*} & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\end{equation}

\begin{equation}
\tilde{H}_{e,1}^{(3)} = \begin{pmatrix}
0 & 0 & 0 & c_1^{(2)} V_{p_2,0}^{(\eta)} \\
0 & 0 & 0 & 0 \\
c_1^{(2)} V_{p_2,0}^{(\eta)*} & c_2^{(2)} V_{p_2,0}^{(\eta)*} & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\end{equation}

\begin{equation}
\tilde{H}_{e,1}^{(3)} = \begin{pmatrix}
0 & 0 & 0 & 0 & c_1^{(3)} V_{p_2,0}^{(\eta)} \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
c_1^{(3)} V_{p_2,0}^{(\eta)*} & c_2^{(3)} V_{p_2,0}^{(\eta)*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0
\end{pmatrix}.
\end{equation}

Here the rows from top to bottom, and columns from left to right, correspond to the states $| \varepsilon^{(k)}_{\pm} \rangle_{\eta_L}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_L}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_L}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_L}$ for $\eta = L$, and $| \varepsilon^{(k)}_{\pm} \rangle_{\eta_{\lambda}}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_{\lambda}}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_{\lambda}}, | \varepsilon^{(k)}_{\pm} \rangle_{\eta_{\lambda}}$ for $\eta = \lambda$. $|0^{(k)}\rangle$ denotes the vacuum of polaron-like excitations, while $|0_{\lambda}\rangle$ and $|1_{\lambda}\rangle$ stand for zero and one photons in the mode $\lambda$. Equations (17) are obtained with the same $S$-matrices that were used to diagonalize Hamiltonians $\tilde{H}_{e,ph}^{(1)}, \tilde{H}_{e,ph}^{(2)}$, and $\tilde{H}_{e,ph}^{(3)}$. They show that in dipole approximation, direct generation or recombination of electron-hole pairs can occur only for states $| \varepsilon^{(k)}_{\pm} \rangle$ and $| \varepsilon^{(k)}_{\pm} \rangle$, provided the quantum numbers of electron and hole coincide ($p_{e_2} = p_{h_2}$).

By analogy, the matrices representing transformed electron-photon Hamiltonians for an ar-
Arbitrary number of phonon modes can be obtained,

\[
\hat{H}_{e,\eta}^{(k)} = \begin{pmatrix}
0 & 0 & \cdots & 0 & c_1^{(k)} V^{(\eta)}_{p_2,0} \\
0 & 0 & \cdots & 0 & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & \cdots & 0 & 0 \\
c_1^{(k)} V^{(\eta)*}_{p_2,0} & 0 & \cdots & 0 & c_2^{(k)} V^{(\eta)*}_{p_2,0} \\
\end{pmatrix},
\]

(18)

Notice that these matrices are Hermitian.

2.5. Analytically solvable eigenvalue problems

Since the quantum dot usually has a large number of electronic states and confined LO-phonon modes, multiple vibrational resonances may occur between them. Suppose that \( N \) vibrational resonances simultaneously occur for the different electron-hole states of a single quantum dot, such that the first pair of states is resonant to \( k_1 \) phonon modes, the second pair is resonant to \( k_2 \) modes, and so on. By combining interaction matrices \( \hat{H}_{e,\eta}^{(k)} \) describing the individual resonances, we can build an electron-phonon Hamiltonian of the entire system,

\[
\hat{\mathcal{H}}_{e,\eta} = \begin{pmatrix}
\hat{H}_{e,\eta}^{(k_1)} & 0 & \cdots & 0 \\
0 & \hat{H}_{e,\eta}^{(k_2)} & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \hat{H}_{e,\eta}^{(k_N)} \\
\end{pmatrix}.
\]

This quasi-diagonal block Hamiltonian allows for various types of degeneration of the electron-hole pairs’ states and LO-phonon modes. Its diagonalization is realized with an \( S \)-matrix of a similar block structure,

\[
S = \begin{pmatrix}
S_{k_1} & 0 & \cdots & 0 \\
0 & S_{k_2} & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & S_{k_N} \\
\end{pmatrix}.
\]

Diagonalization of the Hamiltonian \( \hat{\mathcal{H}}_{e,\eta} \) with matrix \( S \) can be performed analytically in the special case of any \( N \) vibrational resonances involving no more than three phonon modes, i.e., if \( \max(k_1, k_2, \ldots, k_N) \leq 3 \). It becomes particularly simple if, in addition, all modes are of the same frequency. In this case, renormalization of electron-hole spectra is described by Eqs. (12)–(16). The matrix \( \hat{\mathcal{H}}_{e,\eta}^{(k)} \) of the polaron-photon interaction is self-adjoint and similar in form to Eq. (18); its last row can be written as

\[
\begin{pmatrix}
c_1^{(k_1)} V^{(\eta)*}_{p_2,0} & 0 & \cdots & 0 \\
c_2^{(k_2)} V^{(\eta)*}_{p_2,0} & 0 & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots \\
c_1^{(k_N)} V^{(\eta)*}_{p_2,0} & 0 & \cdots & 0 \\
\end{pmatrix}.
\]
3. Quantum dot secondary emission

Let us next mathematically describe the process of secondary emission from a single quantum dot exhibiting vibrational resonance with confined LO-phonon modes. We assume weak optical excitation of the system—to ensure that the interband transitions are not saturated—and restrict ourselves, as before, to the case of low temperatures \( T \ll \hbar \omega_q \), in order to avoid turning the phonon subsystem out of its state of thermodynamic equilibrium. In this situation, it is convenient to describe the phenomenon of secondary emission within the density matrix formalism. The dynamics of spectroscopic transitions in the considered quantum system is then governed by the generalized master equation for the reduced density matrix, \( \rho(t) \) [37–40]

\[
\frac{\partial \rho_{\mu\nu}(t)}{\partial t} = \frac{1}{\hbar} \left[ \hat{H}(t), \rho(t) \right]_{\mu\nu} - \gamma_{\mu\nu} \rho_{\mu\nu}(t) + \delta_{\mu\nu} \sum_{\nu' \neq \nu} \zeta_{\nu\nu'} \rho_{\nu\nu'}(t),
\]

(19)

where \( \hat{H}(t) \) is the transformed Hamiltonian given in Eq. (10), \( \gamma_{\mu\nu} = \gamma_{\nu\mu} = (\gamma_{\mu\mu} + \gamma_{\nu\nu})/2 + \tilde{\gamma}_{\mu\nu} \)

for \( \mu \neq \nu \) is the coherence relaxation rate, \( \gamma_{\mu\mu} = \tau_{\mu}^{-1} \) is the population relaxation rate (inverse lifetime) of state \( \mu \), and \( \tilde{\gamma}_{\mu\nu} = \tilde{\gamma}_{\nu\mu} \) is the pure dephasing rate. The last term on the right-hand side of the master equation accounts for the transitions \( |\nu'\rangle \to |\nu\rangle \) due to the thermal interaction with a bath through the relaxation parameters \( \zeta_{\nu\nu'} \). We allow for this interaction in our subsequent discussion of quasi-elastic secondary emission, but neglect it in Section 4.

3.1. Secondary emission in the case of resonance with nondegenerate electronic states

In order to calculate the intensity of secondary emission for the case in which vibrational resonance of the \( k \) phonon modes occurs between the nondegenerate states of the electron-hole pairs, we take the four eigenstates of the Hamiltonian \( \hat{H}_0 \)

\[
|1\rangle = |0^{(k)}\rangle|q_0\rangle|0_k\rangle, \quad |2\rangle = |\phi_+^{(k)}\rangle|q_0\rangle|0_k\rangle, \quad |3\rangle = |\phi_-^{(k)}\rangle|q_0\rangle|0_k\rangle, \quad |4\rangle = |0^{(k)}\rangle|q_0\rangle|1_k\rangle.
\]

These eigenstates form the minimal sufficient basis for our system, since the rest of the polaron-like states given in Eq. (16) are not involved in the direct dipole-allowed optical transitions. The absence of the degeneration with reference to the spherical quantum dot adopted in our model, implies that the angular momenta of the electrons and holes must be zero, \( l_e = l_h = l_c = l_{\beta} = 0 \).

Through use of Eq. (18), it is easy to show that the emission of photons of frequency \( \omega_\lambda \) due to the annihilation of the polaron-like excitations is characterized by the rate [37,38]

\[
W = \frac{1}{\hbar} \left[ \hat{H}(t), \rho(t) \right]_{44} = -g_\lambda \left( c_1^{(k)}(t) c_2^{(k)}(t) + c_2^{(k)}(t) c_1^{(k)}(t) \right) \rho_{24}(t) + c.c.,
\]

where \( c_1^{(k)} \) and \( c_2^{(k)} \) are given in Eq. (13), while the density matrix elements \( \rho_{24}(t) \) and \( \rho_{34}(t) \) are to be found from the master equation.

We now solve Eq. (19) for the case of stationary excitation, \( \phi(t) = E_L \), using the method of perturbation theory and assuming the inverse lifetime of the ground state \( |1\rangle \) to be zero. The solution we obtain leads to the following expression for the differential cross section of secondary emission per unit solid angle, \( d\Omega \) and unit frequency interval, \( d\omega_\lambda \):

\[
\frac{d^2\sigma}{d\Omega d\omega_\lambda} = \frac{V_0^2}{4(\pi c)^3} \left( \frac{\hbar^3}{4\pi c^3} \right) W = \delta_{p_{24};p_{22}} C(\omega_\lambda) \left( \frac{3}{4} \sum_{n=2}^{\infty} \frac{\gamma_{0n}}{\gamma_{nn}} \left( \frac{c_{n-1}^{(k)}}{\Delta_{nn}^2 + \gamma_{nn}^2} \right)^2 + \frac{\gamma_{0n}}{\gamma_{nn}^2} \frac{c_{n}^{(k)}}{\Delta_{nn}^2 + \gamma_{nn}^2} \right) + \frac{2\gamma_{12}\gamma_{23}}{\gamma_{12}\gamma_{23}} \left( \frac{c_{1}^{(k)}}{\Delta_{12}^2 + \gamma_{12}^2} \right)^2 + \frac{2\gamma_3}{\gamma_1} \left( \frac{c_{3}^{(k)}}{\Delta_{3}^2 + \gamma_{3}^2} \right)^2 \left( \frac{\gamma_{0}}{\omega_\lambda - \omega_k} \right)^2 + \frac{3}{4} \sum_{n=2}^{\infty} \left( \frac{c_{n-1}^{(k)}}{\Delta_{nn}^2 + \gamma_{nn}^2} \right)^2 \left( \frac{\gamma_{0}}{\omega_\lambda - \omega_k} \right)^2 + \frac{3}{4} \sum_{n=2}^{\infty} \left( \frac{c_{n-1}^{(k)}}{\Delta_{nn}^2 + \gamma_{nn}^2} \right)^2 \left( \frac{\gamma_{0}}{\omega_\lambda - \omega_k} \right)^2 \left( \frac{\gamma_{0}}{\omega_\lambda - \omega_k} \right)^2 \right).
\]

(20)

\#146499 - $15.00 USD
Received 26 Apr 2011; revised 24 Jun 2011; accepted 11 Jul 2011; published 28 Jul 2011
(C) 2011 OSA
1 August 2011 / Vol. 19, No. 16 / OPTICS EXPRESS 15470
where \( I_L = \sqrt{\varepsilon_0cE_L^2/(2\pi)} \) is the intensity of the excitation light, \( C(\omega_x) = 4Z_c^4\omega_x^4/(\pi c^4\hbar^2) \), \( c \) is the speed of light in a vacuum, and \( \gamma_0 \) is the inverse photon lifetime. The quantities \( \Delta \gamma_n = \omega_n^{(k)} - \omega_n \) denote detunings from the frequencies, \( \omega_n^{(k)} = \Sigma_n^{(k)}/\hbar \) of the polaron-like energy states \( \Sigma_n^{(k)} = \delta_+^{(k)} \) and \( \Sigma_n^{(k)} = \delta_-^{(k)} \).

The first, second, and third terms in the parenthesis of Eq. (20) describe the process of luminescence, whereas the fourth term corresponds to the resonant quasi-elastic scattering. For the given frequency detunings \( \Delta \gamma_n \), the relative importance of these terms is set by: (i) pure dephasing rates \( \gamma_12 \) and \( \gamma_33 \); (ii) lifetimes, \( \gamma_2^{-1} \) and \( \gamma_3^{-1} \), of the electron-hole pairs in states [2] and [3]; (iii) coherence relaxation rates, \( \gamma_2 = \gamma_2/2 + \gamma_12 \) and \( \gamma_3 = \gamma_3/2 + \gamma_33 \), for optical transitions with generation and recombination of the electron-hole pairs; (iv) relaxation rate \( \zeta_2 \); and (v) photon lifetime. The values of these parameters depend on many factors, which makes their precise determination a challenging experimental task that has not still been accomplished [41]. For example, \( \gamma_12 \) and \( \gamma_33 \) substantially increase if the transitions between states \( |\delta_+^{(k)}\rangle \) and \( |\delta_-^{(k)}\rangle \) are intensified through the emission of acoustic phonons with a continuous energy spectrum [42, 43]. The quantity \( \zeta_2 \) is determined by the relaxation processes with the emission of local excitations of the quantum dot, and elementary excitations of the environment [16, 17, 44, 45]. These processes are sensitive to the design and fabrication quality of the sample, as well as excitation conditions. Although in most practical situations the population relaxation rates satisfy the inequality \( \gamma_0 \ll \gamma_2, \gamma_3 \), their absolute values also vary in a broad range. It is reasonable, therefore, to treat parameters appearing in Eq. (20) as adjustable phenomenological constants, which should be determined (separately for each individual case) from the experimental data.

### 3.2. Spectral filtration of secondary emission

The spectrum expressed according to Eq. (20) cannot be directly compared with experimental data, since the treatment of the previous subsection implicitly assumed that the photon detection system possesses infinite frequency resolution. We can obtain expression for the secondary emission spectrum registered by a real photon detector, by convoluting Eq. (20) with a filter function \( g_F(\omega_F - \omega_x) \) centered at frequency \( \omega_F \). Following Ref. [46], we take the filtering properties of the detector to be identical to those of a Fabry–Perot interferometer characterized by the function

\[
g_F(\omega_F - \omega_x) = \frac{\Gamma_F/2}{\pi (\omega_F - \omega_x)^2 + (\Gamma_F/2)^2},
\]

with \( \Gamma_F \) being the detector's bandpass. Using this expression for \( g_F \) and taking into account that \( \Gamma_F \gg \gamma_0 \) in the majority of practical instances, we obtain after the convolution

\[
\left\langle \frac{d^2\sigma}{d\Omega d\omega_x} \right\rangle = \delta_{\nu_2,\nu_2} C(\omega_F) \frac{2\gamma_12}{\gamma_2} \left( \frac{c_1^{(k)}(c_2^{(k)})^2}{\Delta_2^2 + \gamma_2^2/\Delta_F^2 + (\gamma_3 + \Gamma_F/2)^2} \right)
\]

\[
+ \frac{2\zeta_22\gamma_33}{\gamma_2\gamma_33} \left( \frac{c_1^{(k)}(c_2^{(k)})^2}{\Delta_2^2 + \gamma_2^2/\Delta_F^2 + (\gamma_3 + \Gamma_F/2)^2} \right)
\]

\[
+ \sum_{n=2}^{3} \frac{(c_{n-1}^{(k)})^2}{\Delta_{Ln}^2 - i\gamma_n} \left( \frac{\Gamma_F}{(\omega_n - \omega_F)^2 + (\Gamma_F/2)^2} \right),
\]

where \( \Delta_{Fn} = \omega_n^{(k)} - \omega_F \).

For experimental measurement of the coherence relaxation rates \( \gamma_12 \) and \( \gamma_33 \), the bandpass is
usually chosen to satisfy the inequalities

$$\Gamma_F \ll \gamma_2, \gamma_3,$$

in which case Eq. (21) acquires the form

$$\langle \frac{d^2\sigma}{d\Omega d\omega_N} \rangle = \delta_{\omega_1-\omega_2} \sum_{n=2}^{3} \frac{2\gamma_1}{\gamma_{1n}} \left( \frac{c_{n-1}^{(k)}}{\Delta_{Ln}^2 + \gamma_{Ln}^2 + \gamma_{Ln}^2} \right)^4 \frac{2\gamma_2}{\gamma_{12}^2 + \gamma_{12}^2 + \gamma_{12}^2} \frac{2\gamma_3}{\gamma_{13}^2 + \gamma_{13}^2} \frac{2\gamma_3}{\gamma_{13}^2 + \gamma_{13}^2} + \frac{3}{2} \left( \frac{c_{n-1}^{(k)}}{\Delta_{Ln}^2 - i\gamma_{Ln}} \right)^2 \left( \frac{\Gamma_F}{(\omega_L - \omega_F)^2 + (\Gamma_F/2)^2} \right).$$

This expression is a function of the excitation frequency $\omega_L$ and detection frequency $\omega_F$. The possibility to vary one of them while keeping the other constant results in two types of spectroscopic experiments. If $\omega_L$ is fixed and $\omega_F$ is varied, then an ordinary spectrum of secondary emission is obtained. On the other hand, in the situation where $\omega_F$ is fixed and $\omega_L$ is altered, an excitation spectrum of secondary emission is recorded.

Comparison of luminescence and scattering contributions to the total signal of secondary emission given in Eqs. (20), (21), and (23) reveals several important differences between their spectra. First, if the frequency of excitation is out of resonance with either of the electronic transitions, then the position of the scattering maximum coincides with $\omega_L$, whereas the luminescence intensity peaks at frequencies $\omega_F = \omega_n^{(k)} = \omega_n^{(k)} / \hbar$. Second, should conditions in Eq. (22) be satisfied, the scattering linewidth is narrower than the linewidths of the luminescence. Third, scattering strongly masks luminescence, as the peak intensity of the scattering signal is by far greater than the peak luminescence intensity. The domination of scattering over luminescence in the spectra of secondary emission is due to the factors $2\gamma_2 / \gamma_{12} \ll 1$ and $2\gamma_3 / \gamma_{13} \ll 1$ entering the luminescence terms, and because of $\Gamma_F \ll \gamma_2, \gamma_3$.

For the same reasons, scattering prevails in the excitation spectra of the secondary emission. The excitation spectrum of scattering consists of two peaks at $\omega_L = \omega_n^{(k)}$, whose widths are determined by the coherence relaxation rates. This fact allows parameters $\gamma_2$ and $\gamma_3$ to be calculated through fitting the experimentally measured excitation spectra with Eq. (23).

3.3. Secondary emission in the case of resonance with degenerate electronic states

The above approach allows the secondary emission to be treated analytically in the event that the degenerate states (with nonzero angular momenta) of the electron-hole pairs are involved in the vibrational resonance. In principle, this can be done for the situation discussed in Subsection 2.5; however, such a general treatment results in rather cumbersome mathematical formulas not suitable for this paper. The simplest problem that can be solved exactly is the case of vibrational resonance between the 9-fold degenerate state $|p_2\rangle = |n_e 1_em_c; n_h 1_h m_h\rangle$ and either of the 3-fold degenerate states $|p_1\rangle = |n_e 1_em_c; n_0 0_h\rangle$ or $|n_e 0_e 0_c; n_h 1_h m_h\rangle$ (which correspond to resonance in the valence or conduction band, respectively). Clearly, the 9-fold degeneracy of the upper state is the lowest possible degeneracy for optically excitable states with equal quantum numbers of electrons and holes [see Eq. (7)]. Eigenvectors for the state $|p_2\rangle$ are obtained as a direct product of the three degenerate eigenstates for electrons and the three degenerate eigenstates for holes,

$$\left\{ |n_e 1_em_c; n_h 1_h m_h\rangle \right\} = \left\{ |n_e 1_em_c; -1_e\rangle \right\} \otimes \left\{ |n_h 1_h, -1_h\rangle \right\} \oplus \left\{ |n_e 1_em_c; 0_e\rangle \right\} \otimes \left\{ |n_h 1_h, 0_h\rangle \right\} \oplus \left\{ |n_e 1_em_c; 1_e\rangle \right\} \otimes \left\{ |n_h 1_h, 1_h\rangle \right\}.$$
For the two lower states, the eigenvectors are

\[ |n_h, 0_e, 0_h, 0_e \rangle \otimes \begin{cases} \{ n_e, l_e, 1_e \} \\ \{ n_e, l_e, 0_e \} \\ \{ n_e, l_e, 1_e \} \end{cases} \]

and

\[ |n_e, 0_e, 0_e \rangle \otimes \begin{cases} \{ n_h, l_h, 1_h \} \\ \{ n_h, l_h, 0_h \} \\ \{ n_h, l_h, 1_h \} \end{cases} \]

Employing the results of Section 2 for the above pair of degenerate states, we solve Eq. (19) with a new minimal basis for the Hamiltonian \( H_0 \) based on the renormalized electron-phonon spectrum. The obtained density matrix elements are then introduced into the expression similar to Eq. (20) to find that the differential cross section of the secondary emission is given by

\[
\frac{d^2 \sigma}{d\Omega d\omega_k} = \delta_{p_2 p_3} C(\omega_F) \left( \sum_{n=2}^{7} \frac{\tilde{\gamma}_n}{\gamma_n} \frac{d_n^2}{\delta_n} \frac{2(\gamma_n + \Gamma_F/2)}{(\gamma_n + \Gamma_F/2)^2} \right)
+ \sum_{r=3}^{7} \frac{2 \tilde{\gamma}_r}{\gamma_r} \frac{d_r^2}{\delta_r} \frac{2(\gamma_r + \Gamma_F/2)}{(\gamma_r + \Gamma_F/2)^2}
+ \sum_{n=2}^{7} \frac{d_n^2}{\Delta_n - i\gamma_n} \left( \frac{\Gamma_F}{(\omega_L - \omega_F)^2 + (\Gamma_F/2)^2} \right).
\] (24)

In deriving this expression, we took into account six optically allowed polaron-like states of energies

\[
\Sigma_2^{(k)} = \frac{1}{2} \left( E_{p_2} + \tilde{E}_{p_1} + h\Omega_{LO} - \delta_k \right), \quad \Sigma_5^{(k)} = \frac{1}{2} \left( E_{p_2} + \tilde{E}_{p_1} + h\Omega_{LO} - \delta_k \right),
\]

\[
\Sigma_3^{(k')} = \frac{1}{2} \left( E_{p_2} + \tilde{E}'_{p_1} + h\Omega_{LO} - \delta_{k'} \right), \quad \Sigma_6^{(k')} = \frac{1}{2} \left( E_{p_2} + \tilde{E}'_{p_1} + h\Omega_{LO} - \delta_{k'} \right),
\]

\[
\Sigma_4^{(k'')} = \frac{1}{2} \left( E_{p_2} + \tilde{E}''_{p_1} + h\Omega_{LO} - \delta_{k''} \right), \quad \Sigma_7^{(k'')} = \frac{1}{2} \left( E_{p_2} + \tilde{E}''_{p_1} + h\Omega_{LO} - \delta_{k''} \right),
\]

where \( E_{p_1}, \tilde{E}_{p_1}, \tilde{E}'_{p_1}, \text{ and } \tilde{E}''_{p_1} \) are the energies of the electron-hole pairs shifted due to the interaction with \( k, k' \), and \( k'' \) LO-phonon modes according to Eqs. (5) and (9a);

\[
\delta_k = \sqrt{\chi^2 + 4V_k^2}, \quad \delta_{k'} = \sqrt{\chi'^2 + 4V_{k'}^2}, \quad \delta_{k''} = \sqrt{\chi''^2 + 4V_{k''}^2},
\]

\[
\chi = E_{p_2} - E_{p_1} - h\Omega_{LO}, \quad \chi' = E_{p_2} - E'_{p_1} - h\Omega_{LO}, \quad \chi'' = E_{p_2} - E''_{p_1} - h\Omega_{LO},
\]

and the parameters \( V_k \) are given by Eq. (13b). It was also taken into account that the diagonal part of the electron-phonon interaction does not change the energy of the state \( |p_2 \rangle \), which resulted in \( E''_{p_2} = \tilde{E}'_{p_2} = \tilde{E}_{p_2} = E_{p_2} \). The quantities \( d_n \) in Eq. (24) are the constants describing renormalization of the electron-phonon spectrum, given by

\[
d_2 = (\chi + \delta_k)/\Delta_k, \quad d_3 = (\chi' + \delta_{k'}/\Delta_{k'}, \quad d_4 = (\chi'' + \delta_{k''}/\Delta_{k''},
\]

\[
d_5 = 2V_k/\Delta_k, \quad d_6 = 2V_{k'}/\Delta_{k'}, \quad d_7 = 2V_{k''}/\Delta_{k''},
\]

where

\[
\Delta_k = \sqrt{(\chi + \delta_k)^2 + 4V_k^2}, \quad \Delta_{k'} = \sqrt{(\chi' + \delta_{k'})^2 + 4V_{k'}^2}, \quad \Delta_{k''} = \sqrt{(\chi'' + \delta_{k''})^2 + 4V_{k''}^2}.
\]
4. Examples and discussion

We now illustrate the results of the previous two sections by the example of the InAs-quantum dot, located in either vacuum or some dielectric. The material parameters are chosen to be $\varepsilon_0 = 15.15$, $\varepsilon_\infty = 12.25$, $E_g = 418$ meV, and $\hbar \Omega_{LO} = 29.5$ meV [33]. For simplicity, we neglect the transitions between polaron-like states by setting $\xi_{\nu\nu'} = 0$. We also assume that the vibrational resonance takes place in the valence band, in which case Eq. (5) acquires the form

$$V_{P_2:\nu}^{(q)} = e \Phi^{(q)}_{l_1l_2m_1m_2} \delta_{\nu_2:2l_2} \delta_{\nu_1:2l_1} \delta_{\nu_2:2m_2} \delta_{\nu_1:2m_1},$$

where $\Phi^{(q)}_{l_1l_2m_1m_2}$ is given by Eq. (6).

In the strong confinement regime, the energy spectrum of noninteracting electrons and holes inside a spherical quantum dot is given by [1, 2]

$$E_{nlm,nlm_0} = E_g + E_{nlm,m} + E_{nlm_0} = E_g + \frac{\hbar^2 \xi_{nlm}^2}{2m_e R^2} + \frac{\hbar^2 \xi_{nlm_0}^2}{2m_h R^2},$$

where effective masses $m_e$ and $m_h$ are expressed through free-electron mass $m_0$ as $m_e = 0.0219 m_0$ and $m_h = 0.43 m_0$. It should be recorded that the energies of the electron-hole pairs are actually independent on the angular momentum projections $m_e$ and $m_h$. As follows from Eqs. (20), (21), and (23), only the states with $n_e = n_h = n$, $l_e = l_h = l$, and $m_e = m_h = m$ appear in the spectra of the quasi-elastic secondary emission. The last expression then reduces to

$$E_{nlm,nlm} = E_g + \frac{\hbar^2 \xi_{nlm}^2}{2\mu R^2},$$

where $\mu = m_e m_h / (m_e + m_h)$.

4.1. Resonance with nondegenerate electronic states

As a first application of the developed theory, we consider the vibrational resonance coupling a pair of orbitally nondegenerate electronic states of the lowest possible energies

$$E_{P_2} \equiv E_{200,200} = E_g + \frac{\hbar^2 (2\pi)^2}{2\mu R^2}$$

and

$$E_{P_1} \equiv E_{200,100} = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{4}{m_e} + \frac{1}{m_h} \right).$$

The detuning from the resonance in this instance is characterized by the parameter

$$\chi = E_{P_2} - E_{P_1} - \hbar \Omega_{LO} = \frac{3\hbar^2 \pi^2}{2m_e R^2} + \frac{\alpha e^2}{e^* R} - \hbar \Omega_{LO},$$

in which $\alpha \approx 0.0549$ is calculated using Eqs. (9a) and (25). For the exact resonance, equation $\chi = 0$ is readily solved to obtain the radius of the quantum dot wherein the resonance occurs

$$R_{res} = \frac{\alpha e^2}{2e^* \hbar \Omega_{LO}} + \frac{1}{2} \left[ \left( \frac{\alpha e^2}{e^* \hbar \Omega_{LO}} \right)^2 + \frac{6\hbar^2 \pi^2}{m_e \Omega_{LO}} \right]^{1/2} \approx 9.5 \text{ nm}.$$
We see that at the exact resonance, $R_\text{res}$ (where green and orange lines meet), the initially 3-fold degenerate state of energy $E_{200,100}$ splits into three nondegenerate states separated from each other in energy by $\hbar \Omega_{\text{LO}} = 29.5$ meV. For other parameters refer to text.

materially couple the states $|p_2\rangle = |200;200\rangle$ and $|p_1\rangle = |200;100\rangle$, and hence we deal with the second problem considered in Subsection 2.3. The energies of the polaron-like states in this situation are given according to Eq. (14) by

$$E^{(2)}_{\pm} = \frac{1}{2} [2E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{8}{m_e} + \frac{5}{m_v} \right) - \frac{\alpha e^2}{\epsilon^* R} + \hbar \Omega_{\text{LO}} \pm \delta_2],$$

(26a)

$$E^{(2)}_3 = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{4}{m_e} + \frac{1}{m_v} \right) - \frac{\alpha e^2}{\epsilon^* R} + \hbar \Omega_{\text{LO}},$$

(26b)

where

$$\delta_2 = \sqrt{\chi^2 + 4V_2^2}, \quad V_2 = \left( \frac{\beta e^2 \hbar \Omega_{\text{LO}}}{\epsilon^* R} \right)^{1/2},$$

and $\beta \approx 0.1346$.

The anticrossing behavior of the polaron-like states given by Eq. (26) is shown in Fig. 2(a). We see that at the exact resonance, $R = R_\text{res}$ (where green and orange lines meet), the initially 3-fold degenerate state of energy $E_{200,100} = \tilde{E}_{200,100} + \hbar \Omega_{\text{LO}}$ splits into three nondegenerate states separated from each other in energy by $V_2$. Figure 2(b) shows the size dependence of probability amplitudes

$$c^{(2)}_1 = \frac{\chi + \delta_2}{\sqrt{(\chi + \delta_2)^2 + 4V_2^2}}, \quad c^{(2)}_2 = \frac{2V_2}{\sqrt{(\chi + \delta_2)^2 + 4V_2^2}},$$

whose values directly affect the intensity of the quasi-elastic secondary emission.

In Fig. 3, we plot the spectra of the secondary emission given by Eq. (21) for the following five excitation frequencies in the vicinity of, or coinciding with, the electron-hole states exhibiting resonant coupling:

$$\omega_r = \omega_1^{(2)} - \omega_2, \quad \omega_2^{(2)} = \omega_2, \quad \omega_3^{(2)} + \omega_2, \quad \omega_4^{(2)} + \omega_2, \quad \omega_5^{(2)} + \omega_2,$$
where $\omega_2 = V_2/\hbar \approx 3.1$ meV. In the calculations, we assume that the quantum dot has radius $R_{\text{res}}$ and use the relaxation parameters of Table 1, chosen in accordance with the experimental data of Ref. [47]. The spectra corresponding to the set of parameters $S_1$ [panel (a)] represent the intensity of the resonant quasi-elastic scattering, while the spectra for the parameters of the set $S_2$ [panels (b)-(d)] show the total signal of the secondary emission, which contains contributions from both scattering and luminescence. The structure of Eq. (21) enables clear interpretation for the peculiarities of these spectra.

Different curves in Fig. 3(a) originate as follows. The upper two peaks correspond to the scattering upon resonant excitation of the polaron-like states at frequencies $\omega_\pm^{(2)} \approx 1223$ and 1229.1 meV. The left and right spectra in the middle represent the scattering excited nonresonantly, at frequencies $\omega_\pm^{(2)} \pm \omega_2 \approx 1219.9$ and 1232.2 meV. Finally, the lower peak shows the signal of scattering emerging upon nonresonant excitation of the quantum dot at frequency $\omega_\pm^{(2)} + \omega_2 \approx 1226$ meV, which lies right in the middle between the two polaron-like states exhibiting the vibrational resonance. This peak is much less intense than the other four, due to the destructive interference between the different terms under the modulus in Eq. (21). The widths of all peaks in Fig. 3(a) are equal to the bandwidth of the filter function, $\Gamma_F = 0.04$ meV. Such a small value of $\Gamma_F$ is typical for optical experiments on a single quantum dot [48].

The green spectrum in Fig. 3(b) is excited at frequency $\omega_\pm^{(2)} - \omega_2$. Its left peak represents scattering (which masks the weak signal of the resonant luminescence), while the middle and right peaks correspond to the luminescence from the lower and upper polaron-like states. The situation is somewhat similar for the wine-color spectrum, in which case both excitation and scattering occur at frequency $\omega_\pm^{(2)} + \omega_2$, whereas the two peaks of luminescence arise on the left, at frequencies $\omega_\pm^{(2)}$. The orange curve is the spectrum of secondary emission excited at frequency $\omega_\pm^{(2)} + \omega_2$. Again, it has a strong scattering peak centered at the excitation frequency, and the two luminescence maxima located symmetrically at both its sides and marking the energies of the polaron-like excitations. The widths of the luminescence peaks are determined by the parameters $\gamma_2$ and $\gamma_3$, because they are ten times larger than the parameter $\Gamma_F/2$. The widths of the scattering peaks are set by the bandwidth $\Gamma_F$.

Figure 3(c) shows the two spectra of the resonant secondary emission. We see that, in addition to the main maxima whose intensities are determined by the processes of scattering and luminescence, these spectra contain two small peaks owing to the luminescence from the polaron-like states. The spectra of secondary emission plotted in Fig. 3(d) are obtained for the same excitation conditions as the spectra in Fig. 3(b), but with a smaller spectral resolution of the detection system, $\Gamma_F = 0.4$ meV. Therefore the luminescence peaks in Fig. 3(d) are twice as wide as in Fig. 3(b), and the scattering peaks are wider by a factor of ten. Yet they are all still rather distinct to be used for studying the quantum dot’s polaron-like spectrum. It should also be noted that the decrease in spectral resolution leads to the increase of the luminescence contribution to the spectrum of the total secondary emission, and redistribution of the energy within the spectra.

Table 1. Relaxation Parameters (in $\mu$eV) used in Figs. 3 and 4

<table>
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<tr>
<th></th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\hat{\gamma}_2$</th>
<th>$\hat{\gamma}_3$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\zeta_{23}$</th>
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<td>0</td>
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<td>100</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>$S_2$</td>
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<td>200</td>
<td>100</td>
<td>100</td>
<td>200</td>
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<td>0</td>
</tr>
<tr>
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<td>20</td>
<td>0</td>
<td>0</td>
<td>10</td>
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<tr>
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<td>20</td>
<td>10</td>
<td>10</td>
<td>20</td>
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</tr>
</tbody>
</table>
Fig. 3. Spectra of the quasi-elastic secondary emission from a single quantum dot of radius $R_{\text{res}} \approx 9.5$ nm (see Fig. 2) for the excitation frequencies $\omega_L \approx 1219.9, 1223, 1226, 1229.1,$ and $1232.2$ meV shown by vertical ticks. (a) Resonant scattering and (b) total secondary emission for relaxation parameters $S_1$ and $S_2$ (see Table 1), respectively, and $\Gamma_F = 0.04$ meV. Total secondary emission for relaxation parameters $S_2$, (c) $\Gamma_F = 0.04$ meV, and (d) $\Gamma_F = 0.4$ meV. Legends in panels (c) and (d) show excitation frequencies for all spectra of the same color; $\omega_2 = V_2/h$. For other parameters refer to text.

The excitation spectra of the secondary emission are plotted in Figure 4. As before, the spectra are modeled for the quantum dot of radius $R_{\text{res}}$, and the same set of detection frequencies as the one we used for the purpose of excitation, $\omega_F = \omega_2^{(2)} \pm \omega_2, \omega_2^{(2)}$, and $\omega_2^{(2)} + \omega_2$. We also assume that $\Gamma_F = 0.4$ meV and employ the last two sets of the relaxation parameters in Table 1.

Figures 4(a) and 4(b) show the excitation spectra of the quasi-elastic scattering ($\hat{\gamma}_{12} = \hat{\gamma}_{13} = 0$). The green curve is obtained with a detector tuned to frequency $\omega_2^{(2)} - \omega_2$. Its left peak represents nonresonant scattering, since the excitation light in this case is out of resonance with any of the polaron-like energy levels. The full width at half maximum (FWHM) of the peak is determined by the bandwidth of the filter function, $\Gamma_F$. By contrast, the second and third peaks of the green spectrum correspond to the resonant excitation of the lower and upper polaron-like states. Their widths are equal to the coherence relaxation rates $\gamma_{12}$ and $\gamma_{13}$. The same features are seen for the orange and wine-color spectra in Fig. 4(a), which are detected at frequencies $\omega_2^{(2)} + \omega_2$, as well as for the blue and red spectra in Fig. 4(b), detected at frequencies $\omega_2^{(2)}$. The peaks of resonant scattering at $\omega_2^{(2)}$ have widths set by the relaxation parameters, while the width of the nonresonant scattering peak is equal to $\Gamma_F$. The central dips present in all five spectra are due to the destructive interference of the scattered waves.

The excitation spectra of the total secondary emission are presented in Figs. 4(c) and 4(d).
Fig. 4. Excitation spectra of the quasi-elastic secondary emission from a single quantum dot of radius $R_{\text{res}} \approx 9.5$ nm (see Fig. 2) for relaxation parameters [(a) and (b)] $S_3$ and [(c) and (d)] $S_4$ (see Table 1); $\Gamma_F = 0.4$ meV. Detection frequencies $\omega_F \approx 1219.9, 1223, 1226, 1229.1,$ and $1232.2$ meV, labeled in panels (a) and (b), are shown by vertical ticks; $\omega_2 = V_2/\hbar$. For other parameters refer to text.

The origins of different peaks and their spectral widths are evident from the above discussion. However, at this time, resonant peaks are formed by both scattering and luminescence. Note that, in general, the developed stationary theory does not allow us to separate the contributions of these two processes to the intensity of the total secondary emission. The regime of nonstationary excitation of the secondary emission from a quantum dot exhibiting vibrational resonance will be analyzed in a subsequent paper.

4.2. Resonance with degenerate electronic states

Let us now consider the situation discussed in Subsection 3.3, in which LO phonons couple a pair of orbitally degenerate electronic states. Without loss of generality, we shall look at the lowest states of such kind, with quantum numbers $n_e = n_h = 1$. Their energies are given by

$$E_{p_2} = E_{11m,11m} = E_g + \frac{\hbar^2}{2\mu R^2} \xi_{11}^2,$$

$$E_{p_1} = E_{11m,100} = E_g + \frac{\hbar^2}{2R^2} \left( \frac{\xi_{11}^2}{m_e} + \frac{\pi^2}{m_v} \right),$$

where $m = -1, 0, +1$ and $\xi_{11} \approx 4.4934$. As stated in connection with Eq. (24), the diagonal part of the polar electron-phonon interaction does not affect the upper electronic state, but modifies the lower one. As a result, the lower state splits into two,

$$\tilde{E}_{11 \pm 1,100} = E_g + \frac{\hbar^2}{2R^2} \left( \frac{\xi_{11}^2}{m_e} + \frac{\pi^2}{m_v} \right) - \frac{\alpha e^2}{\varepsilon^* R}. $$
Fig. 5. Size dependence of (a) polaron-like energy levels, (b) renormalization coefficients, and (c) level splitting $\Delta_{\pm} = \tilde{E}_{\pm} - E_{\pm}$ for vibrational resonance between the degenerate electron-hole states $|p_2\rangle = |11m;11m\rangle$ and $|p_1\rangle = |11m,100\rangle$ ($m = 0, \pm 1$) of a spherical quantum dot in the regime of strong confinement. In panels (a) and (b), the energies are reckoned from the lower state in the electron-hole doublet. For other parameters refer to text.

and

$$\tilde{E}_{110,100} = E_g + \frac{\hbar^2}{2R^2} \left( \xi_{11}^2 + \frac{\pi^2}{m_e} \right) - \frac{\alpha e^2}{\varepsilon^* R}$$

where $\alpha \approx 0.0513$ and $\alpha' \approx 0.0974$. These states exhibit the exact vibrational resonances (through phonons of energy $\hbar\Omega_{LO}$) with the upper electronic state inside the quantum dots of radii

$$R_{\text{res}} \approx \frac{\alpha e^2}{2\varepsilon^* \hbar \Omega_{LO}} + \left[ \frac{\hbar (\xi_{11}^2 - \pi^2)}{2m_e \Omega_{LO}} \right]^{1/2} \approx 5.59 \text{ nm}$$

and

$$R'_{\text{res}} \approx \frac{\alpha' e^2}{2\varepsilon^* \hbar \Omega_{LO}} + \left[ \frac{\hbar (\xi_{11}^2 - \pi^2)}{2m_e \Omega_{LO}} \right]^{1/2} \approx 5.61 \text{ nm}.$$ 

The detunings from the two resonances are:

$$\chi = \frac{\hbar^2 (\xi_{11}^2 - \pi^2)}{2m_e R^2} - \hbar \Omega_{LO} + \frac{\alpha e^2}{\varepsilon^* R}, \quad \chi' = \frac{\hbar^2 (\xi_{11}^2 - \pi^2)}{2m_e R^2} - \hbar \Omega_{LO} + \frac{\alpha' e^2}{\varepsilon^* R}.$$

Estimates show that only one LO phonon at a time contributes predominantly to the coupling of any pair of the electronic states. Specifically, states $|11+1;11+1\rangle$ and $|11+1;100\rangle$ are
mainly coupled via the phonon mode with quantum numbers $q_1 = \{1,1,1\}$, states $|110;100\rangle$ and $|110;100\rangle$ are coupled via the phonon mode $q_2 = \{1,0\}$, and states $|111;111\rangle$ and $|111;111\rangle$ via the phonon mode $q_3 = \{1,1,1\}$. The relevant off-diagonal matrix elements of the electron-phonon interaction are equal to each other and are given by

$$
|V_{11+1,11+1;11+1,100}\rangle = |V_{11+1,11+1;11+1,100}\rangle = |V_{11+1,11+1;11+1,100}\rangle = V_1 = \frac{\beta e^2 h \Omega_{LO}}{e^2 R} \right)^{1/2},
$$

where $\beta \approx 0.1265$. With this result, we can write the energies of the six optically allowed polaron-like states in the following form:

$$
\Sigma_1^{(1)} = \Sigma_3^{(1)} = \delta_+^1, \quad \Sigma_5^{(1)} = \Sigma_6^{(1)} = \delta_-^1, \quad \Sigma_4^{(1)} = \delta_+^0, \quad \Sigma_7^{(1)} = \delta_-^0,
$$

\begin{align}
\delta_\pm &= \frac{1}{2} \left[ 2E_g + \frac{h^2}{2 \mu R^2} \left( \frac{\delta_{11}}{m_+} + \frac{\pi^2}{m_+} \right) - \frac{\alpha e^2}{e^2 R} + h \Omega_{LO} \pm \delta_1 \right], \\
\delta_{\pm}^0 &= \frac{1}{2} \left[ 2E_g + \frac{h^2}{2 \mu R^2} \left( \frac{\delta_{11}}{m_+} + \frac{\pi^2}{m_+} \right) - \frac{\alpha e^2}{e^2 R} + h \Omega_{LO} \pm \delta_1 \right],
\end{align}

where $\delta_1 = (\chi^2 + 4V_1^2)^{1/2}$. The parameters $d_\alpha$ in Eq. (24) are explicitly given by

$$
d_2 = d_3 = \frac{\chi + \delta_1}{\sqrt{(\chi + \delta_1)^2 + 4V_1^2}}, \quad d_5 = d_6 = \frac{2V_1}{\sqrt{(\chi + \delta_1)^2 + 4V_1^2}},
$$

$$
d_4 = \frac{\chi' + \delta_1'}{\sqrt{(\chi' + \delta_1')^2 + 4V_1^2}}, \quad d_1 = \frac{2V_1}{\sqrt{(\chi' + \delta_1')^2 + 4V_1^2}}.
$$

The energies defined in Eq. (27) and parameters $d_\alpha$ are plotted in Figs. 5(a) and 5(b). Magnifying insets reveal the two pairs of closely spaced polaron-like states. The splitting, $\Delta_\pm = \delta_\pm^1 - \delta_\pm^0$, of the fine-structure levels is shown in Fig. 5(c). One can see that the quantum dot of radius $R_{\text{res}} \approx R_{\text{res}}^* \approx 5.6$ nm is the best for the simultaneous observation of the upper and lower energy doublets. The splitting of the doublets near the exact vibrational resonance is about $92 \mu$eV. For the upper pair of states, the maximal splitting of approximately $137 \mu$eV is achieved in the quantum dot of radius $\approx 6.9$ nm. In contrast, the splitting of the lower doublet grows monotonously with the decrease of $R$, as the constituent electronic states keep diverging due to the nonresonant electron-phonon interaction.

In Fig. 6, we plot the spectra of the secondary emission given by Eq. (24), assuming that $\gamma_n = \gamma_n = 2 \gamma_n = 20 \mu$eV for $n = 2,3,\ldots,7$. In order to be able to resolve the four energy levels of the polaron-like spectrum, the condition $\Gamma_F \leq \Delta_\pm$ needs to be satisfied. We shall meet this condition in the quantum dot of radius $R_{\text{res}}$, by setting $\Gamma_F = 40 \mu$eV. Figures 6(a)–6(c) show the five excitation spectra of the secondary emission detected at frequencies $\omega_n^{(1)} - \omega_1$, $\omega_n^{(1)} \equiv \delta_+/\hbar$, $\omega_n^{(1)} + \omega_1$, $\omega_n^{(1)} \equiv \delta_-/\hbar$, and $\omega_n^{(1)} + \omega_1$, where $\omega_1 = V_1 / \hbar$. The large-scale structure of these spectra and the spectra in Figs. 4(c) and 4(d) are similar. However, the spectra maxima that previously corresponded to the resonant excitation of the lower and upper polaron-like states are now distinctly split into two peaks each (see magnified portions of the spectra in the insets). The first and second low-energy peaks can be interpreted as resonant scattering and luminescence from the polaron-like states of the lower doublet; they appear at frequencies $\delta_+^1 / \hbar$ and $\delta_-^1 / \hbar$. Analogously, the first and second high-energy peaks are located at frequencies $\delta_+^1 / \hbar$ and $\delta_-^1 / \hbar$. 
Fig. 6. Excitation spectra of the quasi-elastic secondary emission from a single quantum dot of radius [(a)–(c)] \( R_{\text{res}} \approx 5.59 \text{ nm} \) and (d) \( R \approx 3.54 \text{ nm} \) [see Fig. 5(c)], for the vibrational resonance between a pair of orbitally degenerate electronic states. Detection frequencies are: \( \omega_F \approx 1592.7, 1596.6, 1600.5, 1604.4, \) and 1608.2 meV in panels (a)–(c); and 3322.6, 3332.3, and 3377.4 meV in panel (d); \( \Gamma_F = 0.04 \text{ meV} \). For other parameters refer to text.

and \( \omega_{+}^{(1)} \) and represent the secondary emission mediated by the scattering and luminescence from the upper doublet. The difference in the intensities of the first and second fine-structure peaks in Figs. 4(a)–4(c) is explained by the fact that the exact vibrational resonance occurs only for the higher-energy polaron-like states in each doublet, whereas the lower-energy states are slightly off resonance with the phonon modes.

Figure 6(d) shows how the spectra of the secondary emission in Fig. 6(a) are modified for a quantum dot of radius \( R \approx 3.5 \text{ nm} \) \( (R^{-2} = 0.08 \text{ nm}^{-2}) \). As the spectra suggest, and as is seen from Fig. 5(c), the level splitting in the lower doublet of the polaron-like states increases up
to $\approx 290 \mu$eV. At the same time, the splitting of the upper doublet becomes negligible and cannot be observed in the real spectra. The relative intensities of the two fine-structure peaks are now determined by the proximity of the corresponding polaron-like states to the vibrational resonance. Notice also a strong scattering peak, which occurs where the detection and excitation frequencies coincide. It is not suppressed by the destructive interference as in Fig. 6(a), since the contributions from the polaron-like states are not symmetrical.

5. Conclusions

This paper is intended to lay the foundation for the optical spectroscopy of the semiconductor quantum dots with electron and phonon subsystems strongly coupled due to the resonant polar electron-phonon interaction. Based on the generalized model for renormalization of the quantum dot's energy spectrum and using the density matrix technique, we have developed a new theory of the quasi-elastic secondary emission from a single quantum dot, while assuming that several LO-phonon modes may resonantly couple a pair of electron-hole states. We considered two examples of special simplicity and practical interest, namely, where the vibrational resonance involves either orbitally nondegenerate electron-hole states and two degenerate LO-phonon modes, or orbitally degenerate electron-hole states and three degenerate phonon modes. The derived analytical expressions for the differential cross section of the secondary emission provide an intuitive, yet accurate description of the quantum dot's optical response, and may prove useful in retrieving the coherence relaxation rates of the polaron-like states from the experimentally measured spectra.

Acknowledgments

The work of I. D. Rukhlenko and M. Premaratne was sponsored by the Australian Research Council through its Discovery Grant scheme under grants DP0877232 and DP110100713. The work of A. V. Fedorov and A. S. Baymuratov was supported by the Russian Foundation for Basic Research, project Nos. 09-02-00333-a and 09-02-01439-a, and the Ministry of Education of the Russian Federation [state contract No. P2324, Federal Target Program “Scientific and Scientific–Pedagogical Personnel of Innovative Russia” (2009–2013)].