Excitonic Polarons in Semiconductor Quantum Dots

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The discretization of the electronic spectrum in semiconductor quantum dots implies a strong coupling behavior between the optical phonons and the electron-hole pairs, despite the fact that a pair is electrically neutral. The excitonic polarons strongly modify the optical spectra. In particular, the ground excitonic polaron contains one or two phonon components, which leads to the existence of phonon replicas in the luminescence. The population and coherence decay times of the optical transition associated with the ground excitonic polaron are calculated.

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It has recently been shown theoretically and experimentally [1,2] that in InAs/GaAs self-organized quantum dots the electrons and optical phonons enter a strong coupling regime due to the discretization of the electronic continuum; i.e., they form polarons. These quantum dot polarons arise from the resonant mixing of different electronic states with energy separation comparable to the optical phonons [1–4]. Many optical experiments performed on quantum dots involve interband rather than intraband transitions, i.e., deal with interacting electron-hole pairs. Such pairs are electrically neutral. Since the coupling between carriers and optical phonons is electrical in nature (Fröhlich term), one could believe that the coupling between optical phonons and excitons (a shorthand notation for interacting electron-hole pairs in dots) will be small and that the strong coupling effects will disappear. In this Letter, we instead show that an exciton in a quantum dot does strongly couple to optical phonons in spite of its electrical neutrality. The eigenstates of the interacting exciton and phonon systems, the excitonic polarons, are the most accurate way to represent the strongly coupled excitons and phonons. We show the appearance of large anticrossings when two exciton-phonon factorized states have close enough energies and have phonon occupations which differ by one. This resonant mixing has very deep consequences on our understanding of the behavior of excited quantum dots. First, the existence of robust excitonic polarons calls for a reappraisal of the energy relaxation paths of excited quantum dots. Second, a novel scheme for understanding the decoherence effects when excitons and optical phonons are in the strong coupling regime is also needed: since there is no longer any possible phonon absorption or emission by an exciton, the decoherence effects should arise from the damping of the excitonic polarons as a whole entity. We provide in this work the first evaluation of these effects.

Let us consider a lens-shaped InAs/GaAs quantum dot. We model it as a truncated cone (basis radius: R, height: h) which floats on a 1 monolayer thick wetting layer. We adopt the same material parameters as found operative for electronic polarons in doped InAs dots [2]. We take an electron mass of $0.07m_0$, an anisotropic hole mass of $0.34m_0$ along z (growth direction), and $0.11m_0$ in the x-y direction. The conduction (valence) band discontinuities are taken as 550 meV (228 meV). We neglect piezoelectric field effects and take dispersionless bulklike longitudinal optical (LO) phonons to describe the phonons ($\hbar\omega_{\mathrm{LO}} = 37$ meV). Note that the existence of a strong coupling between excitons and phonons is to a large extent independent of the choice of these material parameters but relies only on the discrete nature of the quantum dot excitonic states.

The exciton states in this cylindrically symmetrical problem can be classified in terms of L_z, the z projection of the total angular momentum of the pair (spin effects are neglected). The Coulomb term $-e^2/4\pi\epsilon_0\kappa r_{eh}$ ($\kappa = 14.1$) mixes uncorrelated electron pairs with the same L_z, e.g., the $L_z = 0$ states $|S_e, S_h\rangle$, $|P_{e+}, P_{h-}\rangle$, and $|P_{e-}, P_{h+}\rangle$. A typical diagonal Coulomb effect is $\approx$20 meV. Note also the formation of the symmetrical/antisymmetrical combinations of $|P_{e+}, P_{h-}\rangle$ and $|P_{e-}, P_{h+}\rangle$, only the symmetrical one being optically active.

We next move to the Fröhlich coupling at $T = 0$ K of an exciton with optical phonons. It is the difference between the electronic and hole couplings (since the electron and the hole have opposite charges). This means that there exist direct Fröhlich couplings only between factorized exciton-phonon states which differ by one phonon and which are such that either the electron or the hole quantum number changes:

$$\langle n'_e, n'_h| \otimes \langle n'_{\mathbf{q}}|H_{\text{e-ph}} - H_{\text{h-ph}}|n_e, n_h\rangle \otimes |n_{\mathbf{q}}\rangle \propto \delta_{n'_{\mathbf{q}}, n_{\mathbf{q}}\pm 1}[\delta_{n'_h,n_h}\langle n'_e|e^{\mp i\mathbf{q}\cdot\mathbf{r}_e}|n_e\rangle - \delta_{n'_e,n_e}\langle n'_h|e^{\mp i\mathbf{q}\cdot\mathbf{r}_h}|n_h\rangle]\,. \quad (1)$$

We have diagonalized the Fröhlich terms between the zero phonon states $|S_e, S_h, 0\rangle$, $|S_e, P_{h\pm}, 0\rangle$, $|P_{e\pm}, S_h, 0\rangle$, $|P_{e\pm}, P_{h\pm}, 0\rangle$, the one phonon continuums $|S_e, S_h, 1_{\mathbf{q}}\rangle$, $|S_e, P_{h\pm}, 1_{\mathbf{q}}\rangle$, $|P_{e\pm}, S_h, 1_{\mathbf{q}}\rangle$, $|P_{e\pm}, P_{h\pm}, 1_{\mathbf{q}}\rangle$, and the two phonon continuums $|S_e, S_h, 1_{\mathbf{q}}, 1_{\mathbf{q}'}\rangle$, $|S_e, P_{h\pm}, 1_{\mathbf{q}}, 1_{\mathbf{q}'}\rangle$, $|P_{e\pm}, S_h, 1_{\mathbf{q}}, 1_{\mathbf{q}'}\rangle$, $|P_{e\pm}, P_{h\pm}, 1_{\mathbf{q}}, 1_{\mathbf{q}'}\rangle$. The numerical diagonalization generates entangled exciton-phonon states

(excitonic polaron states) which fall into five groups of orthogonal states. These five groups are most easily classified according to the symmetry of the factorized exciton-phonon component with zero phonon. There are $L_z = 0$ states, $L_z = \pm 1$ states, $L_z = \pm 2$ states. Of course, each state of the $L_z = +1$ $(+2)$ group is degenerate with a state of the $L_z = -1$ (-2) group. Let us first describe the $L_z = \pm 1$ part of the spectrum [Fig. 1(a)]. One recognizes the picture of a double anticrossing between $|S_e, P_{h\pm}, 0\rangle$, $|P_{e\pm}, S_h, 0\rangle$ and $|S_e, S_h, 1_{\mathbf{q}}\rangle$ as a function of the dot size. Note the size of the anticrossings: $\approx$7 and 10 meV. This had to be expected because for each of the anticrossings one of the two particles of the exciton is a spectator and the polaron problem is reminiscent of the electronic polaron one [2]. It is possible to split the $L_z = 0$ excitonic polarons into symmetrical and antisymmetrical states under the transformation ($\theta_{e,h} \rightarrow -\theta_{e,h}$; $\phi_{\mathbf{q}} \rightarrow -\phi_{\mathbf{q}}$), where $\theta_{e,h}$ and $\phi_{\mathbf{q}}$ are the polar angles of the electron or hole position vector and phonon wave vector, respectively (note that in the absence of exciton-phonon interaction only symmetrical states are optically active). Figure 1(b) shows part of the symmetrical states versus the dot size. Again one recognizes large anticrossings ($\approx$7 meV) when a factorized symmetrical state with zero phonon is degenerate with a factorized one phonon continuum. On the other hand, weaker anticrossings take place when a factorized symmetrical state with zero phonon crosses a factorized two phonon continuum. Since the Fröhlich interaction couples states which differ by one phonon, the anticrossings take place through relays: the one phonon continuum $|S_e, S_{h\pm}, 1_{\mathbf{q}}\rangle$ and $|P_{e\pm}, S_h, 1_{\mathbf{q}}\rangle$. Features similar to those shown in Fig. 1(b) take place for the antisymmetrical states $L_z = 0$ or for the $L_z = \pm 2$ states (not shown). The excitonic polaron ground state, which has a dominant $|S_e, S_h, 0\rangle$ component, is redshifted by about 0.9 meV with respect to the unperturbed factorized state $|S_e, S_h, 0\rangle$. For this ground state the electron and hole envelope functions are very similar. Hence, the exciton almost behaves as a neutral particle and displays a weak polaronic shift. This would not be the case in other materials or geometries: in GaN/AlN dots, the larger Fröhlich coupling joined to the huge internal electric field which separates the electron and the hole would enhance the ground polaronic corrections, while in InAs pyramidal dots [5] the piezoelectrical field again dissymetrizes the electron and hole wave functions and would lead again to a larger polaron shift of the ground state.

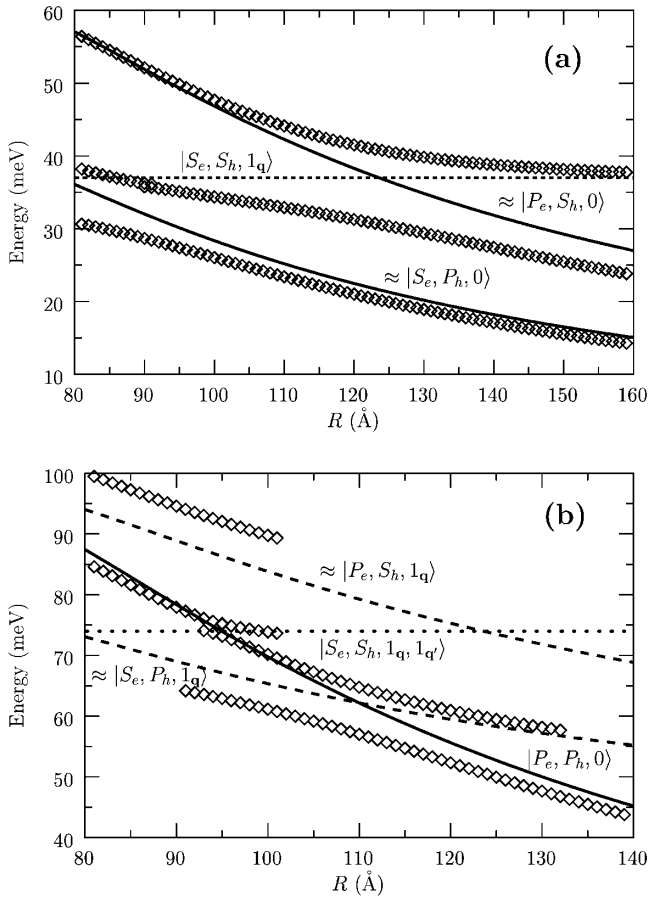

FIG. 1. Excitonic polaron energies versus R ($h/R = 0.1$) in InAs/GaAs quantum dots. (a) $L_z = \pm 1$ states. (b) Symmetrical $L_z = 0$ states. Only those states with more than 10% of zero phonon parts are shown. The energy zero is taken at the energy of the factorized $|S_e, S_h, 0\rangle$ state. Solid lines: zero phonon factorized state. Dashed lines: one phonon factorized states. Dotted lines: two phonon factorized states. Symbols: excitonic polaron energies.

Optical properties of InAs dots have often revealed complex series of lines in isolated dots [6–8] and dot ensembles [9–11]. In the latter, the size dispersion broadens the optical features. Signatures of the participation of optical phonons have often been reported in either the luminescence or excitation spectra. Phonon replicas in absorption and luminescence of quantum dots were calculated by Fomin *et al.* [12] and Gladilin *et al.* [13]. Let us first describe the absorption which is the simpler to predict since there are no relaxation effects. Since we assume $T = 0$ K, the initial state is the vacuum with zero phonon. The final states should therefore comprise a zero phonon optically active component. Figure 2 shows how the excitonic polaron absorption peaks strikingly differ from the purely excitonic predictions. Qualitatively, there are in general more absorption lines in the former formalism than in the latter. In the investigated R range the purely excitonic framework predicts only two lines of comparable intensities corresponding to the $L_z = 0$ excitons ($\approx |S_e, S_h\rangle$ and the symmetrical combination of $\approx |P_e, P_h\rangle$). The excitonic polaron absorption instead may display up to five lines of uneven strengths. Except the ground transition (mostly $|S_e, S_h, 0\rangle$ related), their energies have not a smooth variation versus R while the intensities and energy positions of the purely excitonic lines vary smoothly with R. The microscopic origin of the excitonic polaron lines can readily be seen in Fig. 1(b). The excitonic polaron picture also predicts an absorption line located at $\hbar\omega_{\mathrm{LO}}$ above

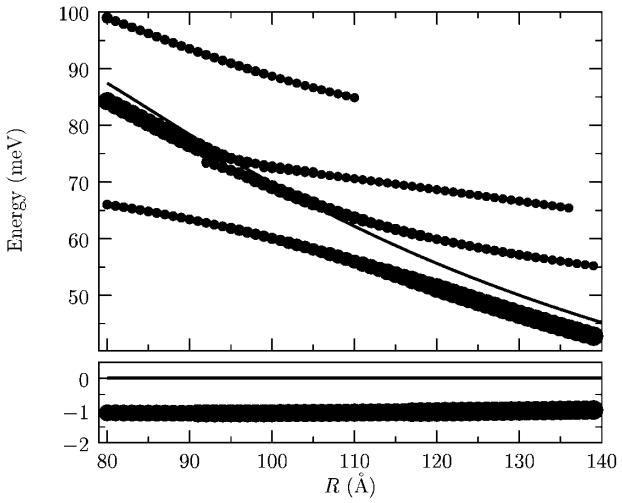

FIG. 2. Calculated energies and intensities of interband optical transitions in InAs/GaAs quantum dots versus R ($h/R = 0.1$). Solid lines: excitonic picture. Symbols: excitonic polaron description. The radius of each symbol is proportional to the corresponding oscillator strength. Only symbols with radii larger than 5% of the ground transition one are displayed. The energy zero is taken at the ground excitonic transition.

the ground transition, but for the parameters we have used it is too small to show up in Fig. 2. Lemaitre *et al.* [14] and Hawrylak *et al.* [8] have reported a phonon replica in the excitation spectra of single quantum dots. Note also that the existence of several absorption lines in the energy range of the expected excited excitonic transitions was also reported by Toda *et al.* [6]. While we believe our model can explain some of the lines, it is too simple to account for all the observed features. In particular, it is restricted to a few bound states for the excitons and has no continuum which could account for Toda *et al.*'s [6] increasing background in the excitation spectra.

Luminescence spectra under nonresonant excitation are more difficult to predict than absorption to the extent that such spectra not only reflect the ability to recombine but also the relative efficiencies between radiative recombination, population, and depopulation. The striking difference between luminescence and absorption in the excitonic polaron picture is that, even at $T = 0$ K, there is a possibility to recombine to the vacuum state with $0, 1, 2, \ldots$ phonons. This gives rise to satellite lines which are redshifted by $\hbar\omega_{\mathrm{LO}}, 2\hbar\omega_{\mathrm{LO}}, \ldots$ from the zero phonon line. These features are well documented experimentally and are often explained by the Huang-Rhys formalism [15,16] or by Fomin *et al.* [12] and by Gladilin *et al.* [13]. Note that the Huang-Rhys approach explicitly requires the phonon energy to be negligible compared to the electronic spacing, which is certainly not true in most quantum dots. Our calculation of the luminescence associated with the ground excitonic polaron state reveals a strong zero phonon line compared with the one phonon replica (for $R = 8$ nm its strength is only 10^{-3} of the 0-phonon line) and the 2-phonon replica (7×10^{-5} of the 0-phonon line). It is remarkable that the 2-phonon replica is $\approx$100 times larger than predicted by the Huang-Rhys formula. This large enhancement, also predicted by Fomin *et al.* [12] and Gladilin *et al.* [13], can easily be shown to arise from the Fröhlich coupling between product states with different electron and/or hole state, an absent ingredient in the Huang-Rhys approach.

One of the most striking consequences of the strong coupling behavior between excitons and phonons in dots is the impossibility of using the notion of optical phonon emission or absorption by excitons, since the excitonic polarons are the stationary eigenstates of the interacting exciton-phonon system. What allows transitions within the excitonic polaron system is its coupling to the phonon thermostat which is triggered by the instability of the phonon part of its wave function. This genuine instability is associated with the anharmonicity of the lattice vibrations and is well documented in bulk materials (e.g., GaAs [17,18]), but little is known on phonon decay in quantum dots. The knowledge of decay times of the excitonic polarons in dots is of paramount importance for understanding the energy relaxation in excited quantum dots as well as ascertaining the use of dots in the buildup of quantum logics devices [19,20]. We have used a semiclassical approach [21] to evaluate the population decay time of excited excitonic polaron states. The decay frequency of an excited state $|e_i\rangle$ to the ground state $|g\rangle$ is equal to the decay frequency of the phonon Γ_{ph} times the square modulus $|\alpha_i|^2$ of the $|S_e, S_h, 1_{\mathbf{q}}\rangle$ component in $|e_i\rangle$. The nonradiative lifetime of the ground state population τ_g then follows via

$$\frac{1}{\tau_g} = \Gamma_g = \Gamma_{\mathrm{ph}} \sum_{e_i} |\alpha_i|^2 \exp\left(\frac{\varepsilon_{e_i} - \varepsilon_g}{k_B T}\right). \qquad (2)$$

To apply this rule the energy difference between the ground and excited states should be in a window compatible with the phonon decay due to anharmonicity [22,23]. Assuming that the phonon decay path is the same in quantum dots as in bulk GaAs, this energy window is [28 meV, 45 meV]. As seen from Fig. 1(a), there are always at least two dark $L_z = \pm 1$ excited polaron states in the required energy window. Since Γ_{ph} varies little with temperature (0.1 ps^{-1} at low T and 0.5 ps^{-1} at $T = 300$ K [17,18]), the emptying of the ground excitonic polaron population (besides the radiative decay) will be thermoactivated with an energy distance equal to the separation between the ground and the excited excitonic polarons (which may differ substantially from the excited exciton states). For $R = 10$ nm we have calculated $\tau_g \approx 4$ ns (7 ps) at $T = 77$ K (300 K). The coherence of the $|g\rangle \leftrightarrow$ vacuum optical transition decays at a rate $\Gamma_{\mathrm{coh}} = (\Gamma_{\mathrm{rad}} + \Gamma_g)/2$ besides its oscillations at the $\varepsilon_g/\hbar$ frequency. Borri *et al.* [24] and Cassabois *et al.* [25] have recently measured a thermoactivated loss of coherence of the ground optical transition. Flissikowski *et al.* [26] observed in CdSe/ZnSe dots that no measurable decoherence of the ground excitonic transition occurs during the exciton lifetime. This finding is consistent with

Borri *et al.* [24] and Cassabois *et al.* [25] and well explained by our model which shows that decoherence of the ground excitonic polaron is thermoactivated and inefficient at cryogenic temperatures. Therefore, the decoherence of the ground excitonic polaron should at low temperatures be dominated by acoustical phonons and/or electrostatic fluctuations. At room temperatures we have shown the LO phonon decay should limit this decoherence time to a few picoseconds.

In conclusion, we have shown theoretically that the excitons and LO phonons enter a strong coupling regime in quantum dots. This regime manifests itself in a multiplication of allowed optical transitions in the vicinity of the excited states due to the entanglement of exciton states with LO phonon states. This feature was also found by Fomin *et al.* [12] and Gladilin *et al.* [13] in their Green function analysis of the exciton-phonon system and explained in terms of the nonadiabaticity of the exciton-phonon coupling. The strong coupling regime joined to the intrinsic phonon instability provides a novel and consistent scheme for explaining quantum dot optical properties. Moreover, it is a prerequisite to the understanding of energy relaxation in excited quantum dots. Finally, we have shown that this excitonic polaron picture provides an upper limit to the population and coherence decay times of the fundamental optical transition in quantum dots.

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