Polaron contributions to the biexciton binding energies in self-assembled quantum dots

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The contribution to the biexciton binding energy in quantum dots resulting from the interaction with longitudinal optical phonons is estimated by performing the configuration–interaction calculation of the few-particle states in a simple model of the confining potential and including the phonon corrections by means of a perturbation theory. It is found that the polaron contribution tends to compensate the Coulomb-related biexciton shift (binding energy) and reduces its value by several to even 30%, depending on the material parameters of the system.

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The biexciton binding energy (also referred to as the biexciton shift) is one of the most important parameters determining the optical properties of quantum dots (QDs). For instance, the spectral shift between the exciton and biexciton transition makes it possible to independently address various degrees of freedom of the biexciton system which opens the way to a range of quantum optical control schemes. The magnitude of this shift is usually of the order of a few meV while its sign may be either positive or negative. Theoretically, the effects of Coulomb correlations in few-electron QDs, underlying the biexciton shift, can be calculated using a configuration-interaction scheme or built upon more realistic wave functions obtained within the multiple-band kp or pseudopotential theory.

One factor that is missing from all the existing calculations is the effect of the interaction between carriers and longitudinal optical (LO) phonon which is of particular importance in confined systems and leads, among other effects, to polaron shifts and resonant anticrossings. According to theoretical calculations, the magnitude of these features may be as large as a few meV for a single confined exciton in a self-assembled QD. Since this is comparable to the biexciton binding energy it seems interesting to study the phonon-related shift for a confined biexciton.

The purpose of this paper is to estimate the polaron contribution to the biexciton binding energy in a QD. This will be done by calculating the polaron correction to the exciton and biexciton states using the perturbation theory. The few-particle states themselves will be calculated within the usual configuration-interaction scheme with a simple parabolic model of confinement.

The quantum dot will be modeled by axially symmetric harmonic oscillator potentials for electrons and holes with a strong confinement in the growth direction. In order to mimic (in a simple way) the spatial charge separation observed in many QD structures, the minima of the potentials for electrons and holes are allowed to be displaced along the growth direction and located at different points \( z_e \) and \( z_h \), respectively. The single particle Hamiltonian is then

\[
H^{(e/h)} = -\frac{\hbar^2}{2m_e/h} \Delta + \frac{1}{2} m_e/h \omega_e^2 r_z^2 + \frac{1}{2} m_e/h \omega_e^2 (z - z_e)^2,
\]

where “e/h” corresponds to the electron and hole wave functions, \( m_e/h \) are the effective masses, and \( \omega_e/h \) are the harmonic oscillator frequencies for the confinement potential in the \( xy \) plane and along the \( z \) axis, respectively, with \( \omega_z/h \gg \omega_e/h \). The motion along the \( z \) axis (growth direction) will be restricted to the ground state. It will be assumed that the confinement width is the Fock–Darwin wave function of the 2-dimensional harmonic oscillator potential.

The biexciton binding energy is the difference between the biexciton and exciton transition energies, \( \Delta E_{\text{bi}} = E_{\text{exc}} - E_{\text{bi}} \). In order to approximate the biexciton energy \( E_{\text{bi}} \), one may use single-particle wave functions \( \psi_{n,m}^{(e/h)}(r) \) determined by minimizing the variational exciton ground state

\[
\psi_{n,m}^{(e/h)}(r) = \Phi(z) \psi_{n,m}^{(e/h)}(r_z),
\]

where \( \Phi(z) = \frac{1}{\pi^{1/4} \gamma_z^{1/2}} \exp \left[ -\frac{(z - z_e)^2}{2 \gamma_z^2} \right] \)

is the wave function in the \( z \) direction and

\[
\psi_{n,m}^{(e/h)}(r_z) = \frac{1}{\gamma_z^{1/2}} \sqrt{\frac{2n!}{(m + n)!}} L_n^{(m)} \left( \frac{r_z}{\gamma_z} \right)
\]

is the Fock–Darwin wave function of the 2-dimensional harmonic oscillator, where \( L_n^{(m)}(x) \) is the Laguerre polynomial. Here \( n = 0, 1, \ldots \) is the radial quantum number and \( m = 0, \pm 1, \ldots \) is the angular momentum quantum number. The length parameters \( \gamma_z \) and \( \gamma_e \) are determined by minimizing the variational exciton ground state

\[
E^{\text{var}} = \int d^3r \int d^3r' \Psi_{00}^{(e)}(r) \Psi_{00}^{(h)}(r') \left[ H^{(e)}(r) + H^{(h)}(r') - V(r, r') \right] \Psi_{00}^{(h)}(r') \Psi_{00}^{(e)}(r),
\]
where
\[ V(r, r') = \frac{e^2}{4\pi\varepsilon_0\varepsilon_s} \frac{1}{|r - r'|}, \]
\[ \varepsilon_0 \text{ is the vacuum permittivity, and } \varepsilon_s \text{ is the static relative dielectric constant. In the following, we will use a single Greek index } \alpha, \beta, \ldots \text{ to represent the pair of quantum numbers } (n, m). \]

The confined few-particle electron–hole subsystem is then described by the Hamiltonian
\[ H_{e-h} = \sum_{\alpha\beta\sigma} \varepsilon_{\alpha\beta} a_{\alpha\sigma}^\dagger a_{\beta\sigma} + \sum_{\alpha\beta\sigma'} \sum_{i,j} V_{e}(\alpha, \beta; \alpha', \beta') a_{\alpha\sigma}^\dagger a_{\beta^\prime\sigma'} a_{\alpha'\sigma'} a_{\alpha\sigma'}^\dagger \\
+ \sum_{\alpha\beta\alpha'\beta'} \sum_{\sigma\sigma'} V_{hh}(\alpha, \beta; \alpha', \beta') h_{\alpha\sigma}^\dagger h_{\beta\sigma'} h_{\beta\sigma'}^\dagger h_{\alpha\sigma} + \sum_{\alpha\beta\alpha'\beta'} \sum_{\sigma\sigma'} V_{eh}(\alpha, \beta; \alpha', \beta') a_{\alpha\sigma}^\dagger h_{\beta\sigma'}^\dagger h_{\beta\sigma'} h_{\alpha\sigma}, \tag{2} \]
with \( a_{\alpha\sigma}, a_{\beta\sigma}^\dagger \) and \( h_{\alpha\sigma}, h_{\beta\sigma}^\dagger \) being the annihilation and creation operators for electrons and holes, respectively, corresponding to the states described by the wave functions given by Eq. (1) and spin orientation \( \sigma \),
\[ \varepsilon_{\alpha\beta}^{(e/h)} = \int d^3r \bar{\psi}_{\alpha}^{(e/h)*} (r) H^{(e/h)} (r) \psi_{\beta}^{(e/h)} (r) \]
and
\[ V_{ij}(\alpha, \beta; \alpha', \beta') = \int d^3r \int d^3r' \bar{\psi}_{\alpha}^{(i)*} (r) \bar{\psi}_{\beta}^{(j)*} (r') V(r, r') \psi_{\alpha}^{(j)} (r') \psi_{\beta}^{(i)} (r), \]
with \( i, j = e, h \).

The interaction between the carriers and LO phonons is described by the Fröhlich Hamiltonian \[^{16} \]
\[ H_{e-ph} = \varepsilon \sum_{\alpha\beta\sigma} \sum_{\alpha'\beta'\sigma'} \left( \varepsilon_{\alpha\beta}^{(h)} h_{\alpha\sigma}^\dagger h_{\beta\sigma} + \varepsilon_{\alpha\beta}^{(e)} a_{\alpha\sigma}^\dagger a_{\beta\sigma} \right) \left( b_k + b_k^\dagger \right), \tag{3} \]
where \( \varepsilon = (1/\varepsilon_s - 1/\varepsilon_\infty)^{-1} \) is the effective dielectric constant (\( \varepsilon_\infty \) is the high-frequency relative dielectric constant), \( \Omega \) is the frequency of the LO phonons (assumed constant in the narrow range of the relevant wave vectors), \( b_k \) and \( b_k^\dagger \) are the annihilation and creation operators for the LO phonon with the wave vector \( k \), \( V \) is the normalization volume for phonons, and the form factors are given by
\[ \mathcal{F}^{(e/h)}_{\alpha\beta} (k) = \int d^3r \bar{\psi}_{\alpha}^{(e/h)*} (r) e^{ik \cdot r} \psi_{\beta}^{(e/h)} (r). \]

First, the Coulomb part of the biexciton shift \( \Delta E_C \) is determined. To this end, the Hamiltonian (2) is diagonalized in the truncated basis of one-pair states yielding the exciton energies \( E_n^{(1)} \) and the corresponding eigenstates
\[ |Xn\rangle = \sum_{\alpha\beta} c_{\alpha\beta}^{(n)} a_{\alpha\sigma}^\dagger h_{\beta\sigma'}^\dagger |0\rangle, \tag{4} \]
where \( |0\rangle \) is the empty dot state. The subtle fine structure effects are not included in the model, so the states are degenerate with respect to spin configurations. As both the Coulomb interaction and the carrier-phonon coupling conserves separately the electron and hole spins and we are interested in the ground state only it is sufficient to take into account the two-pair states with singlet spin configurations. The energies of the biexciton states are therefore found by diagonalizing the Hamiltonian \( H_{e-h} \) in the basis of two-pair spin-singlet states, from which one finds the energies \( E_n^{(2)} \) and the corresponding eigenstates
\[ |XXn\rangle = \sum_{\alpha\beta} \sum_{\alpha'\beta'} \eta_{\alpha\alpha'} \eta_{\beta\beta'} c_{\alpha\beta}^{(n)} a_{\alpha\sigma}^\dagger a_{\beta\sigma}^\dagger h_{\alpha'\sigma'}^\dagger h_{\beta'\sigma'}^\dagger |0\rangle, \tag{5} \]
where \( \uparrow \) and \( \downarrow \) denote spin orientations, \( \eta_{\alpha\beta} = (1 - \sqrt{2}) \delta_{\alpha\beta} + \sqrt{2} \), and comparing the labels \( \alpha, \beta \) is performed in the sense of an arbitrary but fixed ordering of the single-particle states. The Coulomb part of the ground state biexciton shift is then simply
\[ \Delta E_C = E_0^{(2)} - 2E_0^{(1)}. \]

Next, one has to compute the phonon-induced corrections to the exciton and biexciton states. Even though the polaron shifts for single carriers can be quite large, those appearing for globally neutral exciton states are smaller due to partial cancellation of the electron–phonon and hole–phonon interactions. Therefore, a reliable estimate of the polaron shift in the cases considered here can be obtained by means of the second order perturbation theory. The calculation is done again separately for the exciton and biexciton cases.

In the case of an exciton, one rewrites the carrier-phonon interaction in terms of the one-pair eigenstates [Eq. (4)] for an arbitrary, fixed spin configuration,
\[ H_{e-ph}^{(1)} = \varepsilon \sum_{\alpha\beta\sigma} \sum_{\alpha'\beta'\sigma'} \left( \varepsilon_{\alpha\beta}^{(h)} h_{\alpha\sigma}^\dagger h_{\beta\sigma'} + \varepsilon_{\alpha\beta}^{(e)} a_{\alpha\sigma}^\dagger a_{\beta\sigma'} \right) \left( b_k + b_k^\dagger \right), \tag{6} \]
where
\[ \mathcal{G}^{(1)}_{nm}(k) = \sum_{\alpha\beta\sigma\sigma'} \sum_{\alpha'\beta'\sigma'\sigma''} c_{\alpha\beta}^{(n)*} c_{\alpha'\beta'}^{(m)} \delta_{\alpha\alpha'} \delta_{\beta\beta'} \mathcal{F}^{(h)}_{\alpha\beta}, \delta_{\beta'\beta''} \mathcal{F}^{(e)}_{\alpha'\beta'}. \]
In an analogous manner, for the biexciton, one writes
\[ H_{e-ph}^{(2)} = \varepsilon \sum_{\alpha\beta\sigma\sigma'} \sum_{\alpha'\beta'\sigma'\sigma''} \left( \varepsilon_{\alpha\beta}^{(h)} h_{\alpha\sigma}^\dagger h_{\beta\sigma'} + \varepsilon_{\alpha\beta}^{(e)} a_{\alpha\sigma}^\dagger a_{\beta\sigma'} \right) \left( b_k + b_k^\dagger \right). \]
\[
\mathcal{G}_{nm}(^{(2)}k) = \frac{1}{2} \sum_{\mu' \geq \nu' \geq \mu \geq \nu} \sum_{\kappa \lambda} C^{(n)*}_{\kappa \lambda \mu \nu} C^{(m)}_{\kappa \lambda \mu' \nu'} \\
\times \left[ \mathcal{F}^{(h)}_{\mu' \mu}(k) \delta_{\nu' \nu} + \mathcal{F}^{(e)}_{\nu' \nu}(k) \delta_{\mu' \mu} \right] \\
+ \mathcal{F}^{(e)}_{\nu' \nu}(k) \delta_{\mu' \mu} + \mathcal{F}^{(e)}_{\mu' \mu}(k) \delta_{\nu' \nu} \\
- \frac{1}{2} \sum_{\mu' \geq \nu' \geq \mu \geq \nu} \sum_{\kappa \lambda} C^{(n)*}_{\kappa \lambda \mu' \nu'} C^{(m)}_{\mu \nu \kappa \lambda} \eta_{\mu \mu'} \eta_{\nu' \nu} \\
\times \left[ \mathcal{F}^{(h)}_{\mu' \mu}(k) \delta_{\nu' \nu} + \mathcal{F}^{(e)}_{\nu' \nu}(k) \delta_{\mu' \mu} \right] \\
+ \mathcal{F}^{(e)}_{\nu' \nu}(k) \delta_{\mu' \mu} + \mathcal{F}^{(e)}_{\mu' \mu}(k) \delta_{\nu' \nu}. \tag{7}
\]

The phonon-induced correction (polaron shift) to the ground state energy is then given by

\[
\delta E^{(i)} = -\frac{e^2 \hbar \Omega}{16 \pi^2 \varepsilon_0 \varepsilon} \sum_n \int \frac{d^3k}{k^2} \frac{|\mathcal{G}^{(i)}(k)|^2}{E_n^{(i)} - E_0^{(i)} + \hbar \Omega}. \tag{8}
\]

where \(i = 1, 2\) refers to the exciton and biexciton cases, respectively.

The phonon correction to the biexciton shift is

\[
\Delta E_{\text{ph}} = \delta E^{(2)} - 2\delta E^{(1)}. \tag{9}
\]

The total biexciton shift is \(\Delta E = \Delta E_C + \Delta E_{\text{ph}}\).

In the numerical calculations, two sets of parameters will be used, representing two groups of material systems: GaAs (a moderately polar III-V compound) and CdTe (a II-VI compound with a more polar character) (see Tab. I). The numerical computations are performed using the basis of 6 electron and hole shells (\(2|n|+n \leq 5\)), that is, 21 electron and hole wave functions. This is sufficient to assure the convergence of numerical results within \(\sim 0.1\) meV of possible error, which is sufficient in view of the much larger magnitude of the discussed effect (a few meV).

The results for the first set of parameters are shown in Fig. 1 where the dependence of the biexciton shift on the e-h displacement \(D = z_0 - z_1\) is shown for two lateral QD sizes. Although the polaron contribution does not essentially change the qualitative behavior of the biexciton shift it constitutes an important correction to the overall value. For this material system, the phonon-induced contribution amounts to roughly 15-17% of the Coulomb part over the whole range of e-h displacements \(D\) studied here, except for the region where the binding energy changes sign and this ratio is poorly defined. The relative value of the polaron part is very similar for both QD sizes even though the absolute magnitude of the total binding energy is larger for the smaller dot (larger \(\hbar \omega_0\)). It turns out that the phonon correction has the opposite sign to the Coulomb contribution and, therefore, reduces the absolute value of the binding energy. Interestingly, both these contributions change sign at almost the same value of \(D\).

In Fig. 2 analogous results for a more strongly polar system are shown. The magnitude of both the contributions to the binding energy is now much larger. Also the role of the phonon correction becomes more important and its value reaches almost 30% for both dot sizes. Again, the signs of the two contributions are opposite over most of the parameter range studied. In this case, the sign change still appears in the same region for both contributions but not as closely as in the previous case.

In the presented discussion, the wave functions along the growth direction were restricted to the ground state, that is, the charge distribution was supposed to be rigid with respect to axial shifts. However, for \(D > 0\), the Coulomb attraction will lead to an axial shift of the electron and hole charge distributions, which will contribute
to the biexciton shift. Accounting for this effect requires extending the computational basis by including the first excited state wave functions along $z$. By virtue of the Ritz theorem, the same goal (to the leading order) can be achieved by a variational minimization of the system energy with respect to the positions of the centers of the wave functions along $z$ for a given distance $D$ between the minima of the electron and hole confinement potentials. The gray dash-dotted line in Fig. 2 shows the biexciton shift for the CdTe-like system including the additional contribution from the axial shift obtained by such a procedure (with fixed $l_{eh}$ found earlier). The correction reaches almost 1 meV at $D = 2$ nm, which is noticeable, although not particularly large compared to the values without the correction. For a GaAs-like system, the correction does not exceed 0.2 meV and is therefore relatively much smaller. The shift of the charge distributions does not exceed 0.04 nm and 0.1 nm for the GaAs and CdTe system, respectively. Therefore, the correction to the phonon part, which is only sensitive to the geometry of the wave functions, will reach 0.03 meV and 0.25 meV, respectively, as can be deduced from the slopes of the phonon curves in Figs. 1 and 2. In both cases, this corrections is rather small compared to the overall values of the biexciton shift.

Finally, it can be argued that the results presented above are in a way nontrivial, at least in the sense that they cannot be reproduced using a simple model. Indeed, if one considers only exciton and biexciton wave functions in a product (Hartree) form and takes into account that the wave functions for the two electrons (or for the two holes) that differ only by their spin orientation must be the same then the resulting biexciton shift for the two holes) that differ only by their spin orientation must be the same then the resulting biexciton shift will reach 0.03 meV and 0.25 meV, respectively, as can be deduced from the slopes of the phonon curves in Figs. 1 and 2. In both cases, this corrections is rather small compared to the overall values of the biexciton shift.

For the phonon effect, it seems impossible to draw such a general conclusion since the polaron correction depends strongly on the charge cancellation and hence on the exact shape of the wave functions which can differ between the exciton and biexciton cases. However, if one restricts the discussion to a single-orbital model in which only one wave function is available for electrons and one for holes (the same in the exciton and biexciton configurations) then it can be seen from Eqs. (6) and (7) that

$$\mathcal{G}^{(2)}(k) = 2 \left[ \mathcal{F}^{(h)}(k) - \mathcal{F}^{(e)}(k) \right] = 2\delta E^{(1)}(k),$$

where the indices of the form factors have been omitted. As there is only one state, only one term ($n = 0$) remains in Eq. (5) and, clearly, $\delta E^{(2)} = 4\delta E^{(1)}$. Therefore, according to Eq. (9), $\Delta E_{\text{ph}} = 2\delta E^{(1)} < 0$, since the ground state polaron shift is negative. Clearly, this result is opposite to that obtained from the full model, where the phonon correction to the biexciton shift is positive for small $D$. Therefore, exact shape of the wave functions, including admixtures of higher single particle states is essential for correct modeling.

In summary, the LO phonon-related (polaronic) contribution to the biexciton shift (biexciton binding energy) in quantum dots has been calculated. It turns out that this correction is about 15% of the dominating Coulomb contribution in a typical III-V material and reaches almost 30% of the Coulomb term for a more strongly polar II-VI system. The phonon correction usually has an opposite sign to the Coulomb part and, hence, reduces the binding energy of a confined biexciton.

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