Optical absorption in semiconductor quantum dots: Nonlocal effects

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The optical absorption of a single spherical semiconductor quantum dot in an electrical field is studied taking into account the nonlocal coupling between the electric field of the light and the polarizability of the semiconductor. These nonlocal effects lead to a small size and field dependent shift and broadening of the excitonic resonance, which may be of interest in future precision experiments.

I. INTRODUCTION

In recent years, optical investigations on semiconductor quantum dots (QDs) have attracted much attention both from the physical and technological points of view. Such quasi zero dimensional systems display a discrete atomic–like density of states which is essentially different from that of higher dimensional systems, see e.g. textbooks [1, 2] and reviews [3–5]. In order to realize the full potential of QDs, it is very important to understand the basic physical properties of single QDs whose fabrication and spatially resolved optical spectroscopy became possible in the last decade, see e.g. [6–8].

Optical properties of semiconductor microstructures are usually described in the approximation of a homogeneous effective medium, which is applicable as long as the optical wave length in the structure is much larger than the relevant length scales in the system. This is a well accepted and frequently stated condition, e.g. Eq.(4) of Ref. [9]. Near a sharp excitonic resonance, however, this condition is violated and the homogeneous medium approximation breaks down. Hence, the nonlocal character of the relation between the electrical field of the light and the polarization of the QD comes into play. In particular, this holds if the dimensions of the QD become comparable with the exciton Bohr radius, see e.g. the discussion by Schmitt–Rink et al. [10].

In the bulk of a semiconductor, radiative decay of an exciton is forbidden by conservation of momentum. In a confined structure, however, such decay processes become possible and they are considered to be relevant to estimate the long intrinsic radiative lifetimes of excitons [11]. The nonlocal coupling leads to an additional size and polarization dependent line–shift and line width–which contributes to the radiative decay of an exciton in a confined system and, thus, should be taken into account in the analysis of precision experiments. Ultranarrow ($30 \ldots 60 \mu eV$) photoluminescence lines have been reported [6, 7] which, presumably, are still broader than the intrinsic line–width. We expect that the width of absorption lines is of the same order. However, with the exception of Refs. [9, 12], the nonlocal coupling between the polarization and the electric field of the light wave is generally omitted without giving reasons.

The physical motive of our paper is to formulate a sound theoretical basis of optical absorption (extinction) in a confined system with the inclusion of nonlocality and to give a reliable prediction of the corrections to the line–shift and line width. Following Ivchenko and Kavokin [12], we solve the scattering problem of an incident electromagnetic wave on a QD with inclusion of the spatial dependence of the polarizability in the vicinity of a single excitonic resonance line. In addition, we consider the influence of a (symmetry breaking) static electric field which uncovers nonlocal effects, Sec. II. Sec. III contains our numerical results and discussion for a $CdSe$ QD in an external electric field. Unexpectedly, the numerical values are rather small but the field induced line shift is of the same order of magnitude as the experimental line–width without field. Hence, the reported corrections may be relevant in future precision experiments.

II. THEORY OF NONLOCAL OPTICAL ABSORPTION

A. Nonlocal Susceptibility

In linear response theory the relation between the polarization and electric field reads [13]

$$\mathbf{P}(\mathbf{r},\omega) = \int \boldsymbol{\chi}(\mathbf{r},\mathbf{r}';\omega)\,\mathbf{E}(\mathbf{r}',\omega)\,d^3r' \,. \tag{1}$$

In a local approximation $\boldsymbol{\chi}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')\boldsymbol{\chi}(\omega)$. Nonlocality has different origins in the bulk and in a QD. In the homogeneous bulk $\boldsymbol{\chi}$ depends only on the relative coordinate $\mathbf{r}_1 = \mathbf{r}-\mathbf{r}'$ so that Eq.(1) becomes in Fourier–space $\mathbf{P}(\mathbf{q},\omega) = \boldsymbol{\chi}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega)$. The wave number dependence of $\boldsymbol{\chi}(\mathbf{q},\omega)$ is usually termed spatial dispersion and it originates from the delocalized nature of the excitations. On the other hand, in a QD $\boldsymbol{\chi}$ depends on both $\mathbf{r}$ and $\mathbf{r}'$ and nonlocality is governed by the confinement of the wave functions, see Eq. (2).

Near resonance the contribution of a single exciton line to the polarizability is given by [2, 13]

$$\chi_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega) = \left(\frac{e}{m_0}\right)^2 \frac{1}{\hbar\omega_0^2} \frac{p_\alpha^{cv} p_\beta^{cv}}{\omega_0 - \omega - i\Gamma} \times \Phi(\mathbf{r},\mathbf{r})\,\Phi^*(\mathbf{r}',\mathbf{r}')\,, \tag{2}$$

where, $\alpha, \beta \in \{x, y, z\}$, ω_0 is the exciton transition frequency, Γ is a phenomenological damping rate, $\mathbf{p}_{cv}$ is the interband momentum matrix element, and $\Phi(\mathbf{r}_e, \mathbf{r}_h)$ denotes the exciton envelope–function. In addition, we neglect optical anisotropy and approximate $\chi_{\alpha,\beta}$ by a diagonal matrix. As a result, we have

$$\mathbf{P}_{\rm ex}(\mathbf{r},\omega) = \epsilon_0 T(\omega)\, \Phi(\mathbf{r}) \mathbf{\Lambda}(\omega)\,, \tag{3}$$

$$\mathbf{\Lambda}(\omega) = \int d^3r'\, \Phi^*(\mathbf{r}')\, \mathbf{E}(\mathbf{r}',\omega)\,, \tag{4}$$

$$T(\omega) = T_0 \frac{\omega_0}{\omega_0 - \omega - i\Gamma}\,, \tag{5}$$

$$T_0 = \frac{e^2 |p_{cv}|^2}{\epsilon_0 m_0^2\, \hbar\, \omega_0^3}\,. \tag{6}$$

For shortness, $\Phi(\mathbf{r}) := \Phi(\mathbf{r},\mathbf{r})$. Clearly, the length scale of nonlocality is set by the exciton envelope function, and nonlocal corrections are expected to be particularily important for small QDs.

B. Scattering Problem

We consider a linearily polarized monochromatic electromagnetic wave propagating along the x–axis which is scattered by the QD centered at the origin. Following Jackson [14], the electric field is represented by

$$\mathbf{E}(\mathbf{r},\omega) = \hat{\mathbf{e}}_\eta E_i e^{ikx} + \mathbf{E}_s(\mathbf{r},\omega)\,, \tag{7}$$

$$\mathbf{E}_s(\mathbf{r},\omega) = \frac{k_0^2}{\epsilon_0} \int d^3r'\, \mathbf{G}(\mathbf{r}-\mathbf{r}')\, \mathbf{P}_{\rm ex}(\mathbf{r}',\omega)\,. \tag{8}$$

$\hat{\mathbf{e}}_\eta$ is the unit polarization vector in direction η, $k_0 = \omega/c$, $k^2 = \epsilon_b k_0^2$, ϵ_b is a "background" dielectric constant, which accounts for all non–resonant contributions at higher frequencies to the polarization which are not contained in Eq.(2), and $\mathbf{G}$ is the matrix Green function of the wave–equation

$$\begin{aligned} G_{\alpha\beta}(\mathbf{r}) &= \left(\delta_{\alpha\beta} + \frac{1}{k^2}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\right)\frac{e^{ikr}}{4\pi r} \\ &= \frac{e^{ikr}}{4\pi r}\left[\frac{2}{3}\delta_{\alpha\beta} + \left(3\frac{r_\alpha r_\beta}{r^2} - \delta_{\alpha\beta}\right)\right. \\ &\qquad \left.\times\left(\frac{1}{(kr)^2} - \frac{i}{kr} - \frac{1}{3}\right)\right]\,. \end{aligned} \tag{9}$$

$r = |\mathbf{r}|$. $\mathbf{P}_{\rm ex}$ implicitly depends on the unknown $\mathbf{E}$ field, Eq. (3,4), but, fortunately, the vector $\mathbf{\Lambda}(\omega)$, can be obtained directly [12]. Multiplying Eq. (7) by $\Phi^*(\mathbf{r})$ and integrating over $\mathbf{r}$, we obtain a linear vector equation

$$\mathbf{\Lambda}(\omega) = \hat{\mathbf{e}}_\eta E_i \Phi^*(k\hat{\mathbf{e}}_x) + \mathbf{\Xi}(\omega)\, \mathbf{\Lambda}(\omega) \tag{10}$$

which can be solved by matrix inversion

$$\mathbf{\Lambda}(\omega) = E_i\, \Phi^*(k\hat{\mathbf{e}}_x)\, [\mathbf{I} - \mathbf{\Xi}(\omega)]^{-1}\, \hat{\mathbf{e}}_\eta\,. \tag{11}$$

$\Phi(\mathbf{k})$ is the Fourier–transform of $\Phi(\mathbf{r})$, $\mathbf{\Xi}$ is a 3×3 matrix,

$$\Phi(\mathbf{k}) = \int d^3r\, \Phi(\mathbf{r})\, e^{-\imath \mathbf{k}\mathbf{r}}\,, \tag{12}$$

$$\mathbf{\Xi}(\omega) = k_0^2\, T(\omega)\, \mathbf{K}\,, \tag{13}$$

$$\mathbf{K} = \int d^3r \int d^3r'\, \mathbf{G}(\mathbf{r}-\mathbf{r}')\, \Phi^*(\mathbf{r})\, \Phi(\mathbf{r}')\,, \tag{14}$$

and $\mathbf{I}$ is the 3×3 unit matrix. Eq. (11), together with Eqs. (3,7,8) completes the solution of the electromagnetic scattering problem. The magnetic field of the wave is given by $\mathbf{H} = -\imath\nabla\times\mathbf{E}/(\mu_0\omega)$. Large nonlocal corrections are expected to occur if $\det[\mathbf{I} - \mathbf{\Xi}(\omega)] \approx 0$. (This condition is equivalent to Eq.(4) in Ref. [9]).

C. Optical Absorption

The optical absorption is determined by the time–averaged energy flux $\bar{\mathbf{S}}$ through a closed surface centered around the QD, where $\mathbf{S} = \mathbf{E}\times\mathbf{H}$. $\bar{\mathbf{S}} = \bar{\mathbf{S}}_i + \bar{\mathbf{S}}_s + \bar{\mathbf{S}}_{\rm ext}$ can be decomposed in an incident, scattered, and extinction contribution [14, 15]. In addition, we assume that the QD is surrounded by a nonabsorbing medium of the same background dielectric constant. As a result, the net absorbed energy flux becomes

$$W_a = -\oint_A \bar{\mathbf{S}}\cdot\hat{\mathbf{e}}_r\, dA = W_i - W_s + W_{\rm ext}\,. \tag{15}$$

$W_i = 0$, whereas $W_s, W_{\rm ext} > 0$. $W_{\rm ext} = W_a + W_s$ gives the missing energy flux out of the incident wave.

To calculate the optical absorption of the QD we only need the scattered field in the far field, $r \gg R \geq r'$. In leading order, we obtain

$$\mathbf{E}_s(\mathbf{r},\omega) = E_i\, \frac{e^{ikr}}{4\pi r}\, \mathbf{F}(\hat{\mathbf{e}}_r,\omega)\,, \tag{16}$$

$$\mathbf{F}(\hat{\mathbf{e}}_r,\omega) = -k_0^2\, T(\omega)\, \Phi^*(k\hat{\mathbf{e}}_x)\, \Phi(k\hat{\mathbf{e}}_r)\, \hat{\mathbf{e}}_r\times[\hat{\mathbf{e}}_r\times\boldsymbol{\xi}]\,, \tag{17}$$

$$\mathbf{H}_s(\mathbf{r},\omega) = \sqrt{\frac{\epsilon_0\epsilon_b}{\mu_0}}\, \hat{\mathbf{e}}_r \times \mathbf{E}_s(\mathbf{r},\omega)\,, \tag{18}$$

$$\boldsymbol{\xi}(\omega) = [\mathbf{I} - \mathbf{\Xi}(\omega)]^{-1}\, \hat{\mathbf{e}}_\eta\,. \tag{19}$$

$\mathbf{F}(\hat{\mathbf{e}}_r,\omega)$ is the scattering amplitude of the wave in direction $\mathbf{r}$. Eqs.(16-19) can be considered as a nonlocal generalization of Mie–scattering.

The scattered energy flux is easy to obtain as the respective electric and magnetic fields are transversal

$$\begin{aligned} W_s = I_i \left|\frac{k_0^2\, T(\omega)}{4\pi}\, \Phi(k\hat{\mathbf{e}}_x)\right|^2 \\ \times \int |\Phi(k\hat{\mathbf{e}}_r)|^2 \left(|\boldsymbol{\xi}|^2 - |\hat{\mathbf{e}}_r\cdot\boldsymbol{\xi}|^2\right)\, d\Omega_r\,. \end{aligned} \tag{20}$$

$I_i = \sqrt{\epsilon_0\epsilon_b/\mu_0}\, E_i^2/2$ is the intensity of the incident light wave and $d\Omega_r$ is the surface element of the unit sphere.

For $kR \ll 1$ the integration is trivial so that Eq. (20) simplifies to

$$W_s = I_i \, \frac{k_0^4}{6\pi} \left| T(\omega) \, \boldsymbol{\xi}(\omega) \, \Phi(k\hat{\mathbf{e}}_x) \, \Phi(\mathbf{k}=0) \right|^2 . \qquad (21)$$

The extinction is conveniently calculated from the optical theorem which relates $W_{\rm ext}$ to the imaginary part of the scattering amplitude in forward direction [14, 15]

$$\begin{aligned} W_{\rm ext} &= \frac{I_i}{k} \Im \, \hat{\mathbf{e}}_\eta \, \mathbf{F}(\hat{\mathbf{e}}_x, \omega) \\ &= \frac{I_i}{k} |\Phi(k\hat{\mathbf{e}}_x)|^2 \, \Im \left\{ k_0^2 \, T(\omega) \, \left([\mathbf{I} - \boldsymbol{\Xi}(\omega)]^{-1} \right)_{\eta\eta} \right\} . \qquad (22) \end{aligned}$$

For typical material parameters ($E_g \approx 2$ eV, $R \approx 5$nm, $\Gamma = 0.1 \ldots 1$meV) $|\Xi_{\alpha\beta}(\omega_0)| \lesssim 0.1$ so that an expansion of $(\mathbf{I} - \boldsymbol{\Xi})^{-1}$ is reasonable. For a rough estimate, we consider the zeroth–order and assume $kR \ll 1$, where $\boldsymbol{\xi} = \hat{\mathbf{e}}_\eta$ so that $W_s / W_{\rm ext} \approx 10^{-4}$, i.e. the optical absorption is dominated by the extinction. Our numerical results indicate that this estimate holds for other reasonable parameters, too.

Up to first order $[\mathbf{I} - \boldsymbol{\Xi}]^{-1} = \mathbf{I} + \boldsymbol{\Xi} + O(\boldsymbol{\Xi}^2)$ the optical cross section $\sigma_a = \sigma_{\rm ext} = W_{\rm ext}/I_i$ is given by

$$\begin{aligned} \sigma_a(\omega, R) &= \frac{\omega_0}{c\sqrt{\epsilon_b}} \, T_0 \, |\Phi(\mathbf{k}=0)|^2 \\ &\times \Im \left\{ \frac{\omega_0}{(\omega_0 + \Delta\omega_0) - \omega - \imath(\Gamma + \Delta\Gamma)} \right\} , \qquad (23) \\ \Delta\omega_0 - \imath\Delta\Gamma &= -k_0^2 T_0 K_{\eta\eta} . \qquad (24) \end{aligned}$$

$\Delta\omega_0$ and $\Delta\Gamma$ respectively denote the shift and broadening of the excitonic resonance which are caused by the nonlocality, and $|\Phi(\mathbf{k}=0)|^2$ is a measure of the oscillator strength of the excitonic line.

For the first order nonlocal correction of the line–width and line–shift, only the diagonal elements of Eq. (14) are needed. According to Eq. (9) (second line), the Green function is made up of an isotropic and a traceless term, $\mathbf{G} = \mathbf{G}^{(1)} + \mathbf{G}^{(2)}$. Therefore, $K_{\eta\eta} = K^{(1)} + K^{(2)}_\eta$, where $K^{(1)}$ is independent of the polarization η and $K^{(2)}_x + K^{(2)}_y + K^{(2)}_z = 0$. Moreover, in the ground state we still have rotational symmetry around the z–axis, thus $K^{(2)}_x = K^{(2)}_y = -K^{(2)}_z/2$, and, in addition, $K_{\alpha\beta} = 0$, $\alpha \neq \beta$, so that the inversion of $[I - \boldsymbol{\Xi}]$, Eq.(22), is trivial. For $F_z = 0$ the ground state exciton wave function is isotropic which implies $K^{(2)}_\eta = 0$ for all η.

D. Exciton States

In a spherical QD with infinite confinement the electron/hole Hamiltonians (without external field) read

$$H_j = -\frac{\hbar^2}{2m_j^*} \Delta , \qquad (25)$$

where $r \leq R$, j=e/h, and m_j^* are the respective effective masses. The eigenstates of H_j (omitting the indices j=e/h) are well known from textbooks, e.g. Ref. [16]

$$\begin{aligned} \psi^{(0)}_{nlm}(\mathbf{r}) &= F_{nl}(r) \, Y_l^m(\theta, \varphi) , \qquad (26) \\ F_{nl}(r) &= \sqrt{\frac{2}{R^3}} \, \frac{j_l(a_{ln} \frac{r}{R})}{j_{l+1}(a_{ln})} , \qquad (27) \\ E^{(0)}_{nl} &= \frac{\hbar^2 a_{ln}^2}{2m^* R^2} . \qquad (28) \end{aligned}$$

Electron/hole energies count from their respective band edges, quantum numbers n, l, m have their usual meaning and a_{ln}, $n = 1, 2, \ldots$ denotes the n^{th} positive zero of the spherical Bessel function $j_l(x)$ [17].

Next, we consider noninteracting electron–hole pair states which are the eigenstates of $H_e + H_h$,

$$\begin{aligned} \Psi^{(0)}_{\lambda_e\lambda_h}(\mathbf{r}_e, \mathbf{r}_h) &= \psi^{(0)}_{\lambda_e}(\mathbf{r}_e) \psi^{(0)}_{\lambda_h}(\mathbf{r}_h) , \qquad (29) \\ E^{(0)}_{\lambda_e\lambda_h} &= E^{(0)}_{\lambda_e} + E^{(0)}_{\lambda_h} , \qquad (30) \end{aligned}$$

where $\lambda_j = (n_j, l_j, m_j)$ label the electron/hole states. For shortness, the pair states and energies, Eqs. (29,30), will be denoted by $|\lambda>$ and E_p, where $\lambda = (\lambda_e, \lambda_h)$. For a discussion of pair and exciton states in QDs see, e.g. Chapter 3 of Ref. [4].

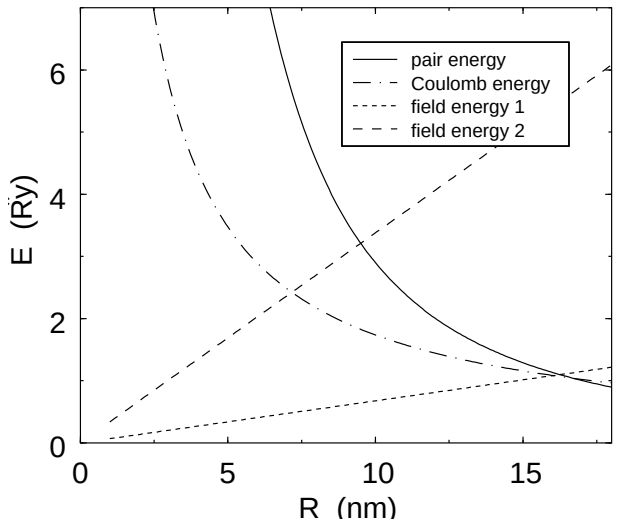

FIG. 1. Different energy scales which are set by the confinement: pair energy Eq.(30), Coulomb energy in first–order pertubation theory for $F_z = 0$, and field–energy, eF_zR, for (1) $F_z = 1$ and (2) 5MeV/m. Ry^* denote the excitonic Rydberg–energy [2].

In the final step we have to include the Coulomb interaction between the electron and the hole inside the QD as well as the interaction with the electrical field (in z–direction) F_z. For QD sizes of $R = 2 \ldots 20$nm the localization energy, Coulomb–energy, and relevant field–energies eRF_z are approximately of the same magnitude, see Fig. 1.

Therefore, we found it convenient to expand the exciton states in the QD directly in terms of the pair states Eqs. (29, 30), rather than first constructing exciton states for $F_z = 0$. Total angular momentum of the electrons and holes is not conserved but there is still rotational symmetry around the z–axis so that the z–component of total electron–hole angular momentum $M = m_e + m_h$ is a good quantum number.

$$|\kappa, M\rangle = \sum_{\lambda} C_{\lambda}^{\kappa,M} |\lambda\rangle \,. \tag{31}$$

κ is an additional exciton quantum number. Expansion (31) leads to the algebraic eigenvalue problem

$$\sum_{\lambda'} C_{\lambda'}^{\kappa,M} \Big(E_{\lambda'} \delta_{\lambda\lambda'} + eF_z \langle\lambda| z_e - z_h |\lambda'\rangle - \frac{e^2}{4\pi\epsilon_0\epsilon_b} \langle\lambda| \frac{1}{|\mathbf{r}_e - \mathbf{r}_h|} |\lambda'\rangle \Big) = E_{\kappa}^{M} C_{\lambda}^{\kappa,M} \,, \tag{32}$$

where E_{κ}^{M} is the exciton energy in a QD as measured with respect to the gap. (For shortness it will be sometimes referred to by $E_{\rm ex}$). The z– and Coulomb matrix elements can be obtained analytically and some details are listed in Appendix A.

III. RESULTS AND DISCUSSION

Numerical studies have been performed for an optical transition to the excitonic ground state and the parameters are appropriate for $CdSe$: $m_e^* = 0.11 m_0, m_h^* = 0.44 m_0$, $E_g = 1.9$eV, $\epsilon_b \approx 9.8$ [18]. This implies $T_0 = 0.3\text{nm}^3$ and $Ry = 13$meV. For a QD radius of $R = 5$nm the pair energy is $E_p = 170$meV and the exciton binding energy is $E_b = 60$meV so that in total the exciton energy (as measured from the gap) becomes $E_{\rm ex} = E_p - E_b = 110$meV. Even for the narrowest excitonic lines which have been observed so far, $\hbar\Gamma \approx 30\mu$eV [6–8], the linear approximation Eq.(23) is still reasonable, $|\Xi_{\eta\eta}| \approx 10^{-5}\omega_0/\Gamma < 0.3$. Although these experiments refer to photoluminescence rather than to optical absorption similar results for the line–shift and line–width are expected.

There are two sources which cause the excitonic resonance frequency to change with the radius or applied field: change of the "atomic" transition frequency ω_0 in the dot (=difference of energy levels which is not explicitely considered here) and the radiation induced shift and damping $\Delta\Gamma$, $\Delta\omega_0$ which originate from the (nonlocal) coupling to the electromagnetic field, see Figs. 2,3.

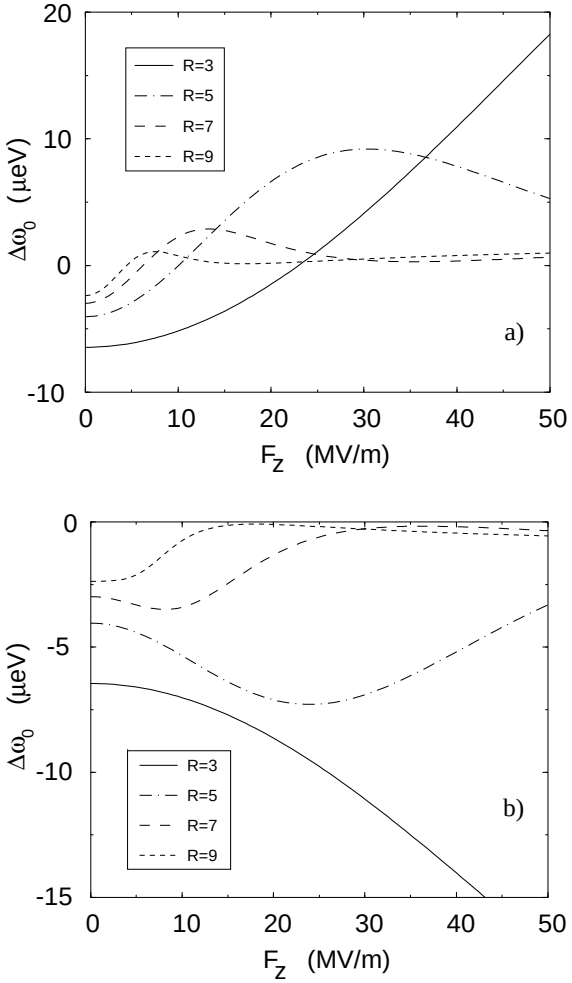

FIG. 2. Nonlocal contribution to the exciton line shift. (a) Light polarization parallel and (b) perpendicular to the applied field. (R in nm).

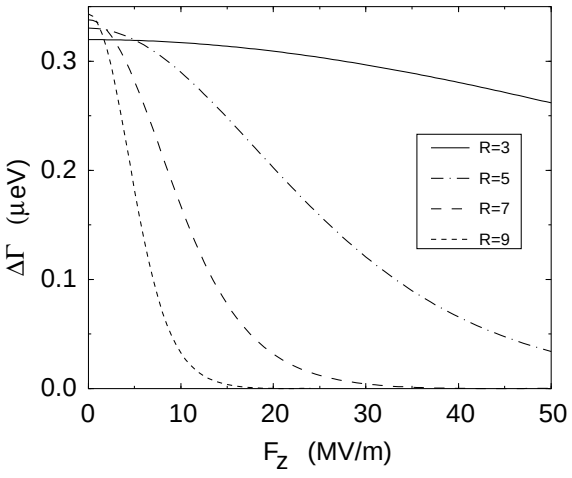

FIG. 3. Nonlocal contribution to the exciton line–width as a function of the applied field. (Polarization dependence not resolved. R in nm).

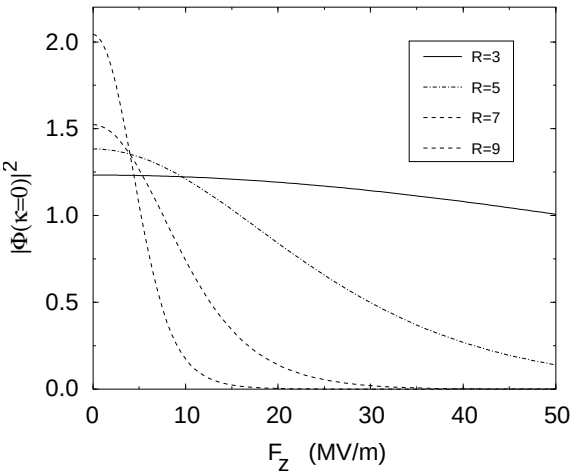

FIG. 4. Relative oscillator strength in the exciton ground state as a function of the applied field (R in nm).

For $F_z = 0$: $K_\eta^{(2)} = 0$, hence, $\Delta\Gamma$ and $\Delta\omega_0$ are both independent of the polarization direction η. With applied field, $K_\eta^{(2)} \neq 0$ but $|\Im K_\eta^{(2)}| \ll |\Im K^{(1)}|$, hence $\Delta\Gamma$ is (almost) independent of η. With increasing field, $|\Re K_\eta^{(2)}| > |\Re K^{(1)}|$, so that $\Delta\omega_0$ displays a pronounced polarization dependence. For large applied fields, the electron and hole states become spatially separated so that both $K^{(1)}$ and $K_\eta^{(2)}$ tend to zero. Therefore, $\Delta\omega_0$, $\Delta\Gamma$ as well as the oscillator strength, Fig. 4, tend to zero. Therefore, $\Delta\omega_0$ runs over an extremum when the pair energy approximately equals field energy, see Fig. 1. Because of the different signs of $K_y^{(2)}$ and $K_z^{(2)}$, $\Delta\omega_0$ display a maximum/minimum for y/z polarization.

Eventually we list some general results: (i) Smaller dot radii require larger fields to generate comparable changes of the electronic states, (ii) the importance of nonlocal corrections increases with decreasing dot radii and deviations from spherical symmetry, (iii) the nonlocal contributions are rather insensitive with respect to the electron–hole Coulomb interaction, and (iv) the leakage of the exciton wave function in the host material may be incorporated using an effective radius $R_{eff} = R + \lambda$, where λ is aproximately the decay length of the (electron) wave function, $\lambda \approx 1nm$.

Although the reported influence of the nonlocal coupling between the light and the polarization of the semiconductor is unexpectedly small, such corrections may be of increasing importance for the analysis of future precision experiments on single QDs, in particular in an external field or in non–spherical shaped structures. To the best of our knowledge, the smallest line width reported so far is that of localized biexciton states in a $GaAs/AlGaAs$ structure at low temperatures which is 30μeV [6]. The field dependence may come into play for QDs sandwiched between two metallic leads similar to those which have been fabricated recently, e.g. [19, 20].

IV. ACKNOWLEDGEMENTS

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APPENDIX A: MATRIXELEMENTS

The z–matrix elements can be obtained analytically,

$$\langle n'l'm'|z|nlm\rangle = \langle n'l'|r|nl\rangle\langle l'm|\cos\theta|lm\rangle\delta_{m,m'}\,, \quad \text{(A1)}$$

where the angular part is listed in C_X of Ref. [16].

$$\langle n'l'|r|nl\rangle = \frac{2R}{j_{l+1}(\alpha)j_{l'+1}(\beta)} I_{l,l'}(\alpha,\beta) \quad \text{(A2)}$$

with abbreviations $\alpha = a_{ln}$, $\beta = a_{l'n'}$, and

$$I_{l,l'}(\alpha,\beta) = \int_0^1 d\rho\,\rho^3\, j_l(\alpha\rho)\, j_{l'}(\beta\rho)\,. \quad \text{(A3)}$$

In particular, for $l' = l+1$, Eq. (A3) can be rewritten by using the recursion formula for $j_{l+1}(x)$ in terms of $j_l(x)$, and $j_l'(x)$, as given by (10.1.22) in Ref. [17]

$$I_{l,l+1}(\alpha,\beta) = \left(\frac{l}{\beta} + \frac{\partial}{\partial\beta}\right)\int_0^1 \rho^2\, j_l(\alpha\rho)\, j_l(\beta\rho)\, d\rho\,. \quad \text{(A4)}$$

The remaining integral is a special case of (11.3.29) with (10.1.1) in Ref. [17] when $j_l(\alpha) = 0$ and $\alpha \neq \beta$ are used. For $l' = l-1$ we have only to interchange the role of α, β.

The Coulomb matrix elements are calculated by first expanding $|\mathbf{r}_e - \mathbf{r}_h|^{-1}$ in terms of spherical harmonics [14], and subsequently performing angular integrations of triple products of spherical harmonics in terms of Clebsch–Gordan coefficients [16]

$$\big\langle\lambda'\big|\frac{1}{|\mathbf{r}_e - \mathbf{r}_h|}\big|\lambda\big\rangle = \sum_{l=0}^{\infty}\frac{1}{2l+1} W_{\lambda,\lambda'}\, Z_{\lambda,\lambda'}\,. \quad \text{(A5)}$$

$W_{\lambda,\lambda'}$ summarizes the result of r–integrations, and $Z_{\lambda,\lambda'}$ contains a sum on m of products of matrix elements of the angular part of the wave–functions. $Z_{\lambda,\lambda'}$ is only nonzero if $l_e + l_e' + l_h + l_h =$ even and $\max\{|l_e - l_e'|, |l_h - l_h'|\} \leq l \leq \min\{l_e + l_e', l_h + l_h'\}$. The remaining integrations have been done numerically with Mathematica [21].

APPENDIX B: EVALUATION OF K

Expanding $\Phi(\mathbf{r}_e, \mathbf{r}_h)$ in terms of pair states, Eq. (31), we obtain

$$K_{\alpha\beta} = \sum_{\lambda_1\lambda_1'\lambda_2\lambda_2'} C^*_{\lambda_1\lambda_1'}\, C_{\lambda_2\lambda_2'}\, (\lambda_1\lambda_2|G_{\alpha\beta}|\lambda_1'\lambda_2')\,, \qquad \text{(B1)}$$

$$(\lambda_1\lambda_2|G_{\alpha\beta}|\lambda_1'\lambda_2') = \int d^3r_1 \int d^3r_2\, G_{\alpha\beta}(\mathbf{r}_1-\mathbf{r}_2) \times\psi^*_{\lambda_1}(\mathbf{r}_1)\psi_{\lambda_2}(\mathbf{r}_2)\psi^*_{\lambda_1'}(\mathbf{r}_1)\psi_{\lambda_2'}(\mathbf{r}_2)\,. \qquad \text{(B2)}$$

Electron and hole wave functions are identical, hence the labels e/h have been dropped. The definition used in Eq.(B2) looks skew but it is useful for the evaluation in analogy with the Coulomb matrix elements. The diagonal elements are split into two parts: $K_{\eta\eta} = K^{(1)} + K^{(2)}_\eta$, where $K^{(1)}$ is independent of the light polarization.

The numerical evaluation of $K^{(1)}$ is conveniently done by first expanding $\exp(ik|\mathbf{r}_1-\mathbf{r}_2|)/|\mathbf{r}_1-\mathbf{r}_2|$ in terms of spherical harmonics [14], and then follow closely the evaluation of the Coulomb matrix elements. If $kR < 0.3$, the expansion of the exponential function in $(\lambda_1\lambda_2|G^{(1)}_{\alpha\beta}|\lambda_1'\lambda_2')$ leads to fast converging series and, to leading order, we have

$$R\left|\Re\left\{(\lambda_1\lambda_2|G^{(1)}|\lambda_1'\lambda_2')\right\}\right| \lesssim 10^{-1}\,,$$
$$R\left|\Im\left\{(\lambda_1\lambda_2|G^{(1)}|\lambda_1'\lambda_2')\right\}\right| \lesssim (\lambda_1\lambda_2|\frac{kR}{6\pi}|\lambda_1'\lambda_2')\,. \qquad \text{(B3)}$$

Therefore, the imaginary part of $K^{(1)}$ is proportional to the oscillator strength, Eq(23),

$$\Im\left\{K^{(1)}\right\} = \frac{k}{6\pi}\,|\Phi(\mathbf{k}=0)|^2 + O\big((kR)^2\big)\,. \qquad \text{(B4)}$$

The evaluation of $K^{(2)}_\eta$ is more difficult than that of $K^{(1)}$ as it depends on the polarization direction and $G^{(2)}_\eta \sim r^{-3}$ is singular at $r=0$. The latter problem, however, can be circumvented by doing the angular integrations first. In addition, the parity of the spherical harmonics, $(-1)^l$, implies that the matrix elements of $\mathbf{G}^{(2)}$ obeys the same angular momentum selection rules as $\mathbf{G}^{(1)}$. For $kR < 0.3$, we estimate the $G^{(2)}$ matrix elements as

$$R|\Re\left(\lambda_1\lambda_2|G^{(2)}_\eta|\lambda_1'\lambda_2'\right)| \lesssim \frac{0.2}{(kR)^2}\,, \qquad \text{(B5)}$$

$$R|\Im\left(\lambda_1\lambda_2|G^{(2)}_\eta|\lambda_1'\lambda_2'\right)| \lesssim \frac{0.002}{(kR)^2}\,. \qquad \text{(B6)}$$

Therefore, contributions of $G^{(2)}$ to $\Im K$ are expected to be small even in an applied field. For the real part, however, the situation is opposite. Without the electrical field, the excitonic ground state is mainly made up of electron/hole pair states of the type $|n00;n'00>$, with $\sum |C_{n00;n'00}|^2 > 0.96$, if $R > 5$nm, so that the $G^{(2)}$–elements almost vanish for small fields.

The final expression for the numerical evaluation of the $G^{(2)}$–elements becomes a sum of two five–dimensional integrals, which have been performed numerically. To calculate the optical properties, the lowest 30 pair states were used which lead to 140 independent integrals. The estimated numerical accuracy is 0.5%.

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