Electrodynamical treatment of the electron-hole long-range exchange interaction in semiconductor nanocrystals

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We show that the contribution to the fine structure of the ground exciton level in a semiconductor nanocrystal due to the long-range part of the electron-hole exchange interaction can be equivalently described as arising from the mechanical exciton interaction with the exciton-induced macroscopic longitudinal electric field. Particular cases of nanocrystals with cubic and wurtzite crystal lattice in the strong confinement regime are studied taking into account the complex structure of the valence band. A simplified model accounting for the exciton ground-level splitting and exploiting an effective local scalar succeptibility is established.

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The electron-hole exchange interaction in excitons confined in semiconductor nanocrystals (NCs) of radius R less than the bulk exciton Bohr radius a_B has attracted much attention in recent years. Such interest stems from the fact that, due to the strong size quantization of the electron and the hole, the exchange-induced exciton-level splittings become very large compared with those in bulk semiconductors. These splittings were observed in CdSe NCs embedded in glassy matrices and polymer films and were intensively studied by a number of experimental groups [1–6].

The electron-hole exchange interaction is usually divided into the long-range (non-analytical) and short-range (analytical) parts [7–9] and can be accounted for in different ways. According to Agranovich and Ginzburg [10] (see also Ref. [11]), the term „mechanical exciton“ stands for the case where only the direct Coulomb interaction between the electron and the hole is taken into account. The „Coulomb exciton“ is obtained by the further inclusion of the short-range exchange interaction plus either the long-range electron-hole exchange interaction or, equivalently, the mechanical-exciton interaction with the exciton-induced macroscopic longitudinal electric field. In bulk direct-gap semiconductors the short-range exchange leads to the splitting of the ground-state exciton level into several sublevels. The number of these sublevels corresponds to the number of irreducible representations contained in the direct product $\Gamma_c \times \Gamma_v$, where Γ_c and Γ_v are the irreducible representations according to which the electron states at the bottom of the conduction band and at the top of the valence band transform under symmetry operations. The long-range electron-hole exchange interaction, or, alternatively, the mechanical exciton interaction with the exciton-induced macroscopic longitudinal electric field, leads to a further splitting of the optically active exciton states to the longitudinal and transverse components with respect to the direction of the exciton wave vector. This is the case of the Coulomb exciton which will be studied in the present paper. Speaking more generally, the linear part of the light-metter interaction in semiconductors for the near-absorption-edge spectral region can be accounted for either by the interatction of the Coulomb exciton with the transverse part of the electromagnetic field (scheme [A] in terms of Ref. [12] which we adopt here) or by the interaction of the mechanical exciton (split by the short-range exchange) with the full Maxwell field (scheme [B]). The detailed analysis of the relation between these two schemes was recently performed by Cho [12].

The theoretical study of the electron-hole exchange interaction for both bulk materials and NCs was mainly performed following the scheme [A]. In the framework of the effective-mass approximation the theory of electron-hole exchange interaction for excitons in bulk semiconductors was constructed by Pikus and Bir [7,8] and by Denisov and Makarov [9]. For the case of NCs of spherical shape it was generalized by one of the present authors and Ivchenko [13,14], who for the first time outlined the crucial role of the long-range exchange interaction in the fine structure of excitonic levels in quantum dots (see also Ref. [15]). A reasonable agreement with experimental data was obtained for the case of CdSe NCs [14]. Franceschetti et al. performed calculations of the electron-hole exchange interaction in CdSe NCs based on atomistic pseudopotential wave functions [16]. By expanding the Coulomb potential between two points located in the vicinities of different atomic sites in powers of the reciprocal separation between the sites, they obtained the multipole decomposition of the long-range exchange interaction in a NC and showed numerically that the monopole-monopole term of this expansion is predominant. It is worth noting, however, that the scale of the long-range exchange interaction with the NC size reported in Ref. [16] contradicts that obtained in the framework of the effective-mass approximation [13,14]. Another treatment alternative to the effective-mass approximation is the method of expansion via Wannier functions (see [17,18] and references therein). For the case of quantum dots this method was adopted by Takagahara [19]. He showed that, for excitons confined in NCs of spherical shape, the matrix elements of the long-range exchange Hamiltonial in this method vanish identically in the case of simple (two-fold degenerate at the Γ point) valence band. The work of Takagahara served as the basis for Refs. [1–3], which entirely neglected the long-range exchange interaction in its interpretation of the experimental data even for the case of the complex structure of the valence band.

Very recently one of the present authors and Ivchenko considered the long-range exchange interaction in a bulk semiconductor in the framework of the orthogonal empirical tight-binding model [20]. They analytically formulated the problem in terms of the inter- and intra-atomic matrix elements of the velocity operator and showed that these give nonequivalent contributions to the long-range exchange. Expanding the Coulomb potential between two points located in the vicinities of different atomic sites in powers of the reciprocal separation between the sites up to the dipole approximation, they found that the contribution of the monopole-monopole term of this expansion to the long-range exchange is due to inter-atomic transtitions. If the latter are ignored, only the contribution of the dipole-dipole ferm governed by intra-atomic transitions survives if the long-rangle exchange Hamiltonian. In the general case, there is also the contribution of the monopole-dipole term which is due to both inter- and intra-atomic transitions [21]. It was also shown that the effective-mass approximation corresponds to neglecting the intra-atomic transitions while the method of the expansion via Wannier functions applied in Refs. [17–19] ignores the inter-atomic ones. The theory was naturally generalized for the case of NCs of spherical shape. The contribution of the monopole-monopole term to the matrix element of the long-range exchange interaction on the size-quantized functions was represented both in the form similar to that of Ref. [16] and via the effective-mass envelope functions. Although the effective-mass method ignores both contributions of the monopole-dipole and dipole-dipole terms, it was found to be a good approximation in case of CdSe NCs since according to Ref. [16] the contribution of the monopole-monopole term dominates over all other contributions. The importance of the monopole-monopole contribution was also recently confirmed by Lee et al. [22] who performed numerical calculations of the electron-hole exchange interaction in CdSe NCs in the framework of the empirical tight-binding model formulated in terms of Coulomb and exchange integrals on atomic orbitals. The method of expansion via Wannier functions, however, seems to be a good approach for the specific case of CuCl NCs where the bulk exciton Bohr radius is very small, so that the weak confinement regime ($R \gg a_B$) is always realized [23].

The scheme $[B]$ was successfully applied in Refs. [24,25] to the case of CuCl NCs where $R \gg a_B$, the bulk longitudinal-transverse splitting is very large, and the lowest-energy exciton state is formed by the hole from the simple (two-fold degenerate at the Γ point) valence band.

In the first part of the present paper we will show that, in case of excitons formed by the hole from the complex (four-fold degenerate at the Γ point) valence band in semiconductor NCs of the radius less that the bulk exciton Bohr radius ($R \ll a_B$), the exchange-induced splittings of the ground-state exciton level can be also obtained following the scheme $[B]$. We will derive the expression for the polarized-light-induced linear macroscopic polarization of the semiconductor NC in terms of the effective-mass approximation. Once the polarization is written, only the Maxwell equations will be used to obtain the frequency renormalization of the exciton resonance. Note that to solve the same problem following the scheme $[A]$, one has to deal with 8×8 Hamiltonian [13,14]. The difficulty of this problem is reflected in the scheme $[B]$ by the fact that the linear nonlocal susceptibility has a tensor character. Therefore, the question arises if the nonlocal tensor susceptibility can be replaced by some effective local scalar one, thus in practice greatly simplifying the problem. In the second part of this paper we will present such an effective susceptibility, which leads to the same frequence renormalization of the exciton resonance as the rigorous treatment presented in the first part, and discuss a simple physical picture associated with this model.

We conclude our article by showing how the formalism developed in the first two parts can be applied to the case of NCs with wurtzite crystal lattice. In all previous works addressing this case [13,14,26] the long-range-exchange-induced corrections were first found for the cubic structure NCs and then the crystal-field-induced corrections due to the wurtzite structure of the material were added. We show that within the scheme $[B]$ the wurtzite structure of the NC can be introduced from the very beginning. To that end we consider two close-lying resonances simultaneously excited by the monochromatic light. We show how the results previously obtained within the scheme $[A]$ can be derived in the framework of the scheme $[B]$.

1. Exciton size quantization

In this section we will specify the model describing the electron and the hole states in a quantum dot to be used throughout the present paper.

Let us consider a spherical NC of a cubic semiconductor whose valence band may be described by the spherical Luttinger Hamiltonian, i. e., it is assumed that the Luttinger parameters $\gamma_2 = \gamma_3 \equiv \gamma$. In the strong confinement limit ($R \ll a_B$) the wave function of the electron-hole pair is determined primarily by the reflections of the electron and the hole from the quantum-dot walls, while the Coulomb interaction between them is merely a weak perturbation. Then, to a zeroth-order approximation in the Coulomb interaction, the mechanical exciton (or rather elecrtron-hole pair) two-particle wave function can be written as the product of the electron and the hole single-particle wave functions. We will accept here the model of the spherical quantum dot with infinitely high barriers. A simple boundary condition of the electron and the hole envelope functions vanishing at the NC–matrix interface will be applied.

The electronic states in a spherical quantum dot are characterized by the electron orbital angular momentum l_e. The lowest-energy electron state corresponds to $l_e = 0$. For an infinitely high barrier, the electron wave function has the form

$$\psi_m^{(e)}(\mathbf{r}_e) \equiv \phi(r_e)|m\rangle = \frac{1}{\sqrt{2\pi R}} \frac{\sin(\pi r_e/R)}{r_e} |m\rangle, \qquad (1)$$

where the spin index m assumes the values $\pm 1/2$.

The state of a confined hole from the four-fold spin-degenerate band of Γ_8 symmetry (the hole spin $J_h = 3/2$, its projection $n = \pm 3/2, \pm 1/2$) cannot be characterized by any definite value of the hole orbital angular momentum L. In the spherical approximation for the Luttinger Hamiltonian ($\gamma_2 = \gamma_3 \equiv \gamma$), this is the total hole angular momentum $\mathbf{F}_h = \mathbf{J}_h + \mathbf{L}$ which serves as a good quantum number [27]. The hole state is, therefore, $(2F_h + 1)$-fold degenerate due to the projection F_z of the angular momentum $\mathbf{F}_h$ along an arbitrary axis, z.

For the ground state we have $F_h = 3/2$, $F_z = \pm 3/2, \pm 1/2$. The wave function of the hole in this state can be written as [3,14]

$$\psi_{F_z}^{(h)}(\mathbf{r}_h) = \sum_n \mathscr{R}_{n,F_z}(\mathbf{r}_h)\,|n\rangle, \qquad (2)$$

where the components of the matrix $\hat{\mathscr{R}}(\mathbf{r})$ can be expressed through Wigner $3jm$ symbols,

$$\mathscr{R}_{n,F_z}(\mathbf{r}) = R^{-3/2} \sum_{L=0,2} f_L\left(\frac{r}{R}\right)(-1)^{3/2-L/2+F_z}$$

$$\times 2 \sum_M \begin{pmatrix} 3/2 & L & 3/2 \\ n & M & -F_z \end{pmatrix} Y_{LM}\left(\frac{\mathbf{r}}{r}\right), \qquad (3)$$

Y_{LM} are the normalized spherical harmonics defined as in Ref. [28],

$$f_L(x) = C\left[j_L(\phi^{(h)}x) + (-1)^{L/2} \frac{j_2(\phi^{(h)})}{j_2\left(\sqrt{\beta}\phi^{(h)}\right)} \right.$$

$$\left. \times\, j_L\left(\sqrt{\beta}\,\phi^{(h)}x\right)\right], \qquad (4)$$

j_L are the spherical Bessel functions, $\beta = (\gamma_1 - 2\gamma)/(\gamma_1 + 2\gamma)$ is the light-to-heavy hole mass ratio, γ_1 and γ are the Luttinger parameters in the spherical approximation, $\phi^{(h)}$ is the first root of the equation

$$j_0(x)\, j_2\left(\sqrt{\beta}\,x\right) + j_2(x)\, j_0\left(\sqrt{\beta}\,x\right) = 0, \qquad (5)$$

and C is determined by the normalization condition

$$\int_0^1 [f_0^2(x) + f_2^2(x)]x^2 dx = 1.$$

Note that the definition of the functions $f_L(x)$ should be consistent with those of spherical harmonics. To keep for $f_L(x)$ the definition of Ref. [14] we introduced the factor of $(-1)^{L/2}$ in Eq. (3).

The wave function of the mechanical exciton with the total exciton engular momentum $\mathscr{F}_{exc} = 1$ and its projection $\mathscr{F}_z = F_z + m$ can be composed of the electron (1) and the hole (2) wave functions using the summation rule for angular momenta

$$|exc, 1\mathscr{F}_z\rangle = (-1)^{1+\mathscr{F}_z}\sqrt{3} \sum_m \begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -\mathscr{F}_z \end{pmatrix}$$

$$\times\, \psi_m^{(e)}(\mathbf{r}_e)\, \psi_{\mathscr{F}_z - m}^{(h)}(\mathbf{r}_h). \qquad (6)$$

Substituting Eqs. (1) and (2) we obtain

$$|exc, 1\mathscr{F}_z\rangle = (-1)^{1+\mathscr{F}_z}\sqrt{3} \sum_{m,n} \begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -\mathscr{F}_z \end{pmatrix}$$

$$\times\, \phi(r_e)\, \mathscr{R}_{n,\mathscr{F}_z - m}(\mathbf{r}_h)\, |mn\rangle. \qquad (7)$$

Using Eq. (7) we can derive an expression for the complex conjugated covariant spherical σ-component ($\sigma = \pm 1, 0$) of the NC ground state–exciton transition dipole moment density matrix element in the form

$$\langle 0|\, \hat{d}_\sigma^*(\mathbf{r})\, |exc, 1\mathscr{F}_z\rangle = -\sum_{m,n} \frac{ie\hbar}{m_0 E_g} \langle \bar{n}|\, p_\sigma^*\, |m\rangle\, \Phi_{mn}^{1\mathscr{F}_z}(\mathbf{r}), \quad (8)$$

where e is the electron charge, m_0 is the free-electron mass, E_g is the band gap energy, $\langle \bar{n}|p_\sigma^*|m\rangle$ is the matrix element of the complex conjugated covariant spherical σ-component of the momentum operator calculated between the electron Bloch function $|m, \mathbf{k} = 0\rangle$ and $|\bar{n}, \mathbf{k} = 0\rangle$ (the hole state n, $\mathbf{k}$

and the electron state $\bar{n}, -\mathbf{k}$ are related through time-reversal operation), and

$$\Phi_{mn}^{1\mathscr{F}_z}(\mathbf{r}) = (-1)^{1+\mathscr{F}_z}\sqrt{3}\,\phi(r)\begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -\mathscr{F}_z \end{pmatrix} \times \mathscr{R}_{n,\mathscr{F}_z - m}(\mathbf{r}). \quad (9)$$

In what follows it will be convenient to recast Eq. (9) in the form

$$\Phi_{mn}^{1\mathscr{F}_z}(\mathbf{r}) = 2\sqrt{3}\,\phi(r)\,R^{-3/2}\sum_{L=0,2} D_{L,m,n}^{\mathscr{F}_z}\,f_L(r/R) \times Y_{L,\mathscr{F}_z - m - n}(\mathbf{r}/r), \quad (10)$$

where we used Eq. (3) and introduced the coefficients

$$D_{L,m,n}^{\mathscr{F}_z} = (-1)^{1/2-m-L/2}\begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -\mathscr{F}_z \end{pmatrix} \times \begin{pmatrix} 3/2 & L & 3/2 \\ n & \mathscr{F}_z - m - n & m - \mathscr{F}_z \end{pmatrix}. \quad (11)$$

2. Macroscopic linear polarization

In this section we will derive an expression for the resonant exciton contribution to the macroscopic linear polarization density. A similar derivation for the exciton resonance in a quantum well was carried out in Ref. [29].

Suppose that circularly- or linearly-polarized light excites from the NC ground state an exciton with the total angular momentum $\mathscr{F} = 1$ and its projection in an arbitrary direction $\mathscr{F}_z$. In the first order of the perturbation theory we can write for the time-dependent wave function of the NC

$$|t\rangle = |0\rangle + C_{\mathscr{F}_z}(t)\,|exc,\,1\mathscr{F}_z\rangle\,e^{-i\omega_0 t}, \quad (12)$$

where $|0\rangle$ is the wave function of the NC ground state, and ω_0 is the frequency of the resonance corresponding to the mechanical exciton (with the short-range part of the exchange interaction taken into account). The resonant exciton contribution to the macroscopic linear polarization density is given by the matrix element of the dipole moment operator density on the functions (12). For its covariant spherical σ-component we have

$$P_{exc,\sigma}(\mathbf{r},t) = \langle t|\,\hat{d}_\sigma(\mathbf{r})\,|t\rangle = C_{\mathscr{F}_z}(t)\,e^{-i\omega_0 t}\langle 0|\,\hat{d}_\sigma(\mathbf{r})\,|exc,\,1\mathscr{F}_z\rangle + C^*_{\mathscr{F}_z}(t)\,e^{i\omega_0 t}\langle exc,\,1\mathscr{F}_z|\,\hat{d}_\sigma(\mathbf{r})\,|0\rangle. \quad (13)$$

Here we omit the superscript in $\mathbf{P}_{exc}^{(\mathscr{F}_z)}(\mathbf{r},t) \equiv \mathbf{P}_{exc}(\mathbf{r},t)$, although it is understood. Substituting Eq. (12) into the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\,|t\rangle = (\hat{H}_0 + \hat{V})\,|t\rangle, \quad (14)$$

where $\hat{H}_0$ is the Hamiltonian of the unperturbed electronic system and $\hat{V}$ describes the mechanical exciton interaction with the Maxwell electric field, we obtain

$$i\hbar\frac{dC_{\mathscr{F}_z}(t)}{dt} = \langle exc,\,1\mathscr{F}_z|\,\hat{V}\,|0\rangle\,e^{i\omega_0 t} = -e^{i\omega_0 t}\int d\mathbf{r}\sum_\mu\langle exc,\,1\mathscr{F}_z|\,\hat{d}_\mu(\mathbf{r})\,|0\rangle \times \left(E^\mu(\mathbf{r})\,e^{-i\omega t} + E^{\mu *}(\mathbf{r})\,e^{i\omega t}\right). \quad (15)$$

Here $E^\mu(\mathbf{r})$ is the contravariant μ-component of the amplitude of the Maxwell electric field. The solution of Eq. (15) is given by

$$C_{\mathscr{F}_z}(t) = i\hbar^{-1}\int_{-\infty}^{t} dt'\int d\mathbf{r}\sum_\mu\langle exc,\,1\mathscr{F}_z|\,\hat{d}_\mu(\mathbf{r})\,|0\rangle \times \left(E^\mu(\mathbf{r})\,e^{i(\omega_0-\omega)t'} + E^{\mu *}(\mathbf{r})\,e^{i(\omega_0+\omega)t'}\right). \quad (16)$$

Taking into account that the resonant frequency ω_0 has a negative imaginary part (adiabatic switching), performing integration and omitting the non-resonant term, we obtain

$$C_{\mathscr{F}_z}(t) = \hbar^{-1}\frac{e^{i(\omega_0-\omega)t}}{\omega_0 - \omega}\,\Lambda, \quad (17)$$

where

$$\Lambda = \int d\mathbf{r}\sum_\mu\langle exc,\,1\mathscr{F}_z|\,\hat{d}_\mu(\mathbf{r})\,|0\rangle\,E^\mu(\mathbf{r}).$$

Substituting Eq. (17) into Eq. (13) we finally obtain

$$P^\sigma_{exc}(\mathbf{r},t) = P^*_{exc,\sigma}(\mathbf{r},t) = \hbar^{-1}\frac{\exp(-i\omega t)}{\omega_0 - \omega}\,\langle 0|\,\hat{d}^*_\sigma(\mathbf{r})\,|exc,\,1\mathscr{F}_z\rangle\,\Lambda + \hbar^{-1}\frac{\exp(i\omega t)}{\omega_0 - \omega}\langle exc,\,1\mathscr{F}_z|\,\hat{d}^*_\sigma(\mathbf{r})\,|0\rangle\,\Lambda^*. \quad (18)$$

Eq. (18) gives an expression for the resonant exciton contribution to the macroscopic linear polarization density. Note that, since we accepted the model of the spherical quantum well with infinitely high barriers, the macroscopic polarization density (18) satisfies the boundary condition $\mathbf{P}_{exc}(r = R, t) = 0$.

3. Principal equations

In this section we will show how the exciton-induced macroscopic longitudinal electric field affects the energy of the optically active excitonic states. Since the NC radius is much less than the wavelength of light, we can naglect the effect of retardation within the NC. In the non-retarded limit the Maxwell electric field does not include the field re-emitted by the polarization and, therefore, its transverse part is represented by the electric field of incident light $\mathbf{E}^{(0)}(\mathbf{r},t)$ $(\boldsymbol{\nabla}\cdot\mathbf{E}^{(0)}(\mathbf{r},t) \equiv 0)$. The longitudinal part of the Maxwell electric field may be expressed through the gradient of a scalar potential, $\varphi(\mathbf{r},t)$. For this polentail from the Maxwell equation $\boldsymbol{\nabla}\cdot\mathbf{D}=0$, we have

$$\varepsilon_b(r)\Delta\varphi(\mathbf{r},t)=\sum_\mu \nabla_\mu 4\pi P^\mu_{exc}(\mathbf{r},t)$$
$$=\frac{4\pi\Lambda\exp(-i\omega t)}{\hbar(\omega_0-\omega)}\sum_\mu \nabla_\mu\langle 0|\,\hat{d}^*_\mu(\mathbf{r})\,|exc,1\mathscr{F}_z\rangle$$
$$+\frac{4\pi\Lambda^*\exp(i\omega t)}{\hbar(\omega_0-\omega)}\sum_\mu \nabla_\mu\langle exc,1\mathscr{F}_z|\,\hat{d}^*_\mu(\mathbf{r})\,|0\rangle, \quad (19)$$

where $\varepsilon_b(r)=\varepsilon_b^{(1)}\theta(R-r)+\varepsilon_b^{(2)}\theta(r-R)$, $\varepsilon_b^{(1)}$ and $\varepsilon_b^{(2)}$ are respectively the NC and the host medium background permittivities, and $\theta(x)$ is the Heaviside step function. In order to avoid the second term in the right-hand side of Eq. (19), let us made a rotating-wave approximation about ω, i.e. we multiply both sides of Eq. (19) be $\exp(i\omega t)$ and average over time. Then we obtain

$$\varepsilon_b(r)\Delta\varphi(\mathbf{r})=\sum_\mu \nabla_\mu 4\pi P^\mu_{exc}(\mathbf{r})$$
$$=\frac{4\pi\Lambda}{\hbar(\omega_0-\omega)}\sum_\mu \nabla_\mu\langle 0|\,\hat{d}^*_\mu(\mathbf{r})\,|exc,1\mathscr{F}_z\rangle, \quad (20)$$

where $P^\mu_{exc}(\mathbf{r})$ is the contravariant μ-component of the time-averaged linear polarization density. We can write the latter as

$$P^\mu_{exc}(\mathbf{r})=\sum_\sigma\int d\mathbf{r}'\chi^\mu_\sigma(\mathbf{r},\mathbf{r}')\,E^\sigma(\mathbf{r}'), \quad (21)$$

where

$$\chi^\mu_\sigma(\mathbf{r},\mathbf{r}')=\frac{\langle 0|\,\hat{d}^*_\mu(\mathbf{r})\,|exc,1\mathscr{F}_z\rangle\langle exc,1\mathscr{F}_z|\,\hat{d}_\sigma(\mathbf{r}')\,|0\rangle}{\hbar(\omega_0-\omega)} \quad (22)$$

is the time-averaged linear susceptibility of the scheme $[B]$ relating the Maxwell electric field to the macroscopic linear polarization density. Here we omit the superscript at $\hat{\chi}^{(\mathscr{F}_z)}(\mathbf{r},\mathbf{r}')\equiv\hat{\chi}(\mathbf{r},\mathbf{r}')$ to simplify the notation.

Introducing the Green function $G(\mathbf{r},\mathbf{r}')$ of Eq. (20) for the scalar potential as

$$\varepsilon_b(r)\,\Delta G(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}') \quad (23)$$

and integrating by parts [30] we can rearrange it in the form

$$\varphi(\mathbf{r})=\varphi_0(\mathbf{r})+\frac{4\pi\Lambda}{\hbar(\omega_0-\omega)}$$
$$\times\sum_\mu\int d\mathbf{r}'\langle 0|\,\hat{d}^*_\mu(\mathbf{r}')\,|exc,1\mathscr{F}_z\rangle\nabla'_\mu G(\mathbf{r},\mathbf{r}'), \quad (24)$$

where $\varphi_0(\mathbf{r})$ is an arbitrary solution of the homogeneous Laplace equation satisfying boundary conditions. Thus, for the contravariant component of the total Maxwell electric field we obtain

$$E^\sigma(\mathbf{r})=E^{\sigma(0)}(\mathbf{r})-\frac{4\pi\Lambda}{\hbar(\omega_0-\omega)}(-1)^\sigma$$
$$\times\int d\mathbf{r}'\sum_\mu G_{-\sigma\mu}(\mathbf{r},\mathbf{r}')\,\langle 0|\,\hat{d}^*_\mu(\mathbf{r}')\,|exc,1\mathscr{F}_z\rangle, \quad (25)$$

where

$$E^{\sigma(0)}(\mathbf{r})=E^{\mathscr{F}_z(0)}(\mathbf{r})\,\delta_{\sigma,\mathscr{F}_z}\approx E^{\mathscr{F}_z(0)}\,\delta_{\sigma,\mathscr{F}_z}$$

stands for the amplitude of the incident light, and

$$G_{-\sigma\mu}(\mathbf{r},\mathbf{r}')=\nabla_{-\sigma}\nabla'_\mu\,G(\mathbf{r},\mathbf{r}'). \quad (26)$$

Comparing Eqs. (24) and (25) we note that in the long wave-length limit one can formally consider the full Maxwell field to be longitudinal by letting $\varphi_0(\mathbf{r})=-(\mathbf{r}\cdot\mathbf{E}^{(0)})$. Multiplying both sides of Eq. (25) by $\langle exc,1\mathscr{F}_z|\,\hat{d}_\sigma(\mathbf{r})\,|0\rangle$, integrating over $\mathbf{r}$, and summing over σ we obtain

$$\Lambda=\Lambda^{(0)}-\frac{\Lambda\delta\omega^{(1\mathscr{F}_z)}}{\omega_0-\omega}, \quad (27)$$

or

$$\Lambda=\frac{\Lambda^{(0)}(\omega_0-\omega)}{\omega_0+\delta\omega^{(1\mathscr{F}_z)}-\omega}, \quad (28)$$

where

$$\Lambda^{(0)}=\int d\mathbf{r}\,E^{\mathscr{F}_z(0)}(\mathbf{r})\,\langle exc,1\mathscr{F}_z|\,\hat{d}_{\mathscr{F}_z}(\mathbf{r})\,|0\rangle,$$

and

$$\delta\omega^{(1\mathscr{F}_z)}=4\pi/\hbar\int d\mathbf{r}\int d\mathbf{r}'\sum_{\sigma,\mu}(-1)^\sigma G_{-\sigma\mu}(\mathbf{r},\mathbf{r}')$$
$$\times\langle exc,1\mathscr{F}_z|\,\hat{d}_\sigma(\mathbf{r})\,|0\rangle\langle 0|\,\hat{d}^*_\mu(\mathbf{r}')\,|exc,1\mathscr{F}_z\rangle. \quad (29)$$

Substituting Eq. (28) in Eq. (18) we see that the exciton-induced linear polarization which is responsible for all the exciton-related linear optical properties of the system has the pole at $\omega=\omega_0+\delta\omega^{(1\mathscr{F}_z)}$. The expression for the Maxwell electric field (25) naturally contains this pole as well. Thus, $\delta\omega^{(1\mathscr{F}_z)}$ is the renormalization of the exciton resonant frequency due to the long-range exchange interaction. The latter can be also expressed via the averaged linear susceptibility (22)

$$\delta\omega^{(1\mathscr{F}_z)}=4\pi(\omega_0-\omega)$$
$$\times\int d\mathbf{r}\int d\mathbf{r}'\sum_{\sigma,\mu}(-1)^\sigma G_{-\sigma\mu}(\mathbf{r},\mathbf{r}')\,\chi^\mu_\sigma(\mathbf{r}',\mathbf{r}). \quad (30)$$

Eqs. (29) and (30) give the difference in energy (divided by $\hbar$) between the optically active states of the Coulomb and the mechanical (with the short-range exchange interaction taken into account) excitons confined in a semiconductor NC.

To conclude this section let us write the contravariant μ-component of the time-averaged linear polarization density in the form

$$P^{\mu}_{exc}(\mathbf{r}) = \int d\mathbf{r}'\alpha^{\mu}_{\mathscr{F}_z}(\mathbf{r},\mathbf{r}')\,E^{\mathscr{F}_z(0)}(\mathbf{r}'). \tag{31}$$

Here

$$\alpha^{\mu}_{\mathscr{F}_z}(\mathbf{r},\mathbf{r}') = \frac{\langle 0|\,\hat{d}^{*}_{\mu}(\mathbf{r})\,|exc,\,1\mathscr{F}_z\rangle\langle exc,\,1\mathscr{F}_z|\,\hat{d}_{\mathscr{F}_z}(\mathbf{r}')\,|0\rangle}{\hbar(\omega_0+\delta\omega^{(1\mathscr{F}_z)}-\omega)} \tag{32}$$

is the linear susceptibility of the scheme $[A]$ relating the incident electric field to the time-averaged linear polarization density. It is the susceptibility most directly related to optical spectroscopy and, as one can see, it contains the renormalized resonant pole.

4. Green function

The Green function for the scalar potential defined by Eq. (23), for both $\mathbf{r}$ and $\mathbf{r}'$ within the sphere ($r < R$, $r' < R$), consists of two terms

$$G(\mathbf{r},\mathbf{r}') = G^0(\mathbf{r},\mathbf{r}') + G^1(\mathbf{r},\mathbf{r}'). \tag{33}$$

The first term

$$G^0(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi\varepsilon^{(1)}_b|\mathbf{r}-\mathbf{r}'|} \tag{34}$$

represents the Green function for the case $\varepsilon^{(1)}_b = \varepsilon^{(2)}_b$ while the second one

$$G^1(\mathbf{r},\mathbf{r}') = \frac{\varepsilon^{(1)}_b-\varepsilon^{(2)}_b}{\varepsilon^{(1)}_b}\sum_{l=0}^{\infty}\frac{1}{2l+1}\,\frac{l+1}{\varepsilon^{(1)}_b l+\varepsilon^{(2)}_b(l+1)}\,\frac{r'r'^{l}}{R^{2l+1}} \times \sum_{l_z=-l}^{l} Y_{ll_z}(\mathbf{r}/r)\,Y^{*}_{ll_z}(\mathbf{r}'/r') \tag{35}$$

allows for a difference in the NC and the host medium background permittivities.

5. Resonant frequency renormalization due to electron-hole long-range exchange interaction

In this section we will consider the resonant frequency renormalization arising due to the first term in Eq. (33).

Substituting Eqs. (26), (33), and (34) into Eq. (29) and integrating by parts [30] we can rewrite the latter in the form

$$\hbar\,\delta\omega^{(1\mathscr{F}_z)}_0 = \int d\mathbf{r}\int d\mathbf{r}'\,\frac{\rho(\mathbf{r})\,\rho^{*}(\mathbf{r}')}{\varepsilon^{(1)}_b|\mathbf{r}-\mathbf{r}'|}, \tag{36}$$

where $\rho(\mathbf{r}) = -\big(\boldsymbol{\nabla}\cdot\langle exc,\,1\mathscr{F}_z|\,\hat{\mathbf{d}}(\mathbf{r})\,|0\rangle\big)$ may be interpreted as an effective charge density induced by the optical transition. In Refs. [12,23,25,26] Eq. (36) was interpreted as the Coulomb energy of this effective induced charge density. This interpretation is misleading. In fact, if we have a given charge density and intend to calculate its Coulomb energy, we should exclude domains where $\mathbf{r}=\mathbf{r}'$ while evaluating the integrals in Eq. (36) unless they make infinitesimal contributions to the integrals. It means that, if it turns out that the integrand of Eq. (36) contains contributions proportional to $\delta(\mathbf{r}-\mathbf{r}')$, then the latter must be excluded from further consideration. Comparing Eq. (36) with Eqs. (26), (29), and (34) one can see that the integrand of Eq. (36) does in fact contain a term proportional to the Dirac δ-function, since it always arises when one takes the second derivative of the Coulomb potential. This term makes the main contribution to the resonant frequency renormalization [14]. In Sec. VIII we will show that the same δ-function appears during a formal solution of electrostatic boundary problems. However, in practice it is convenient to compute the exciton resonant frequency renormalization due to the first term in Eq. (33) by tranformation into the $\mathbf{k}$-spase [14].

Below we will apply the general equations derived in Secs. 3 and 4 to the concrete model introduced in Secs. 1 and 2. Substituting Eq. (34) in Eq. (29) we get

$$\delta\omega^{(1\mathscr{F}_z)}_0 = \frac{1}{2\pi^2\hbar\varepsilon^{(1)}_b}\int d\mathbf{k}\sum_{\sigma,\mu}\frac{k^{\sigma}k_{\mu}}{k^2} \times \langle exc,\,1\mathscr{F}_z|\,\hat{d}_{\sigma}(\mathbf{k})\,|0\rangle\langle 0|\hat{d}^{*}_{\mu}(\mathbf{k})\,|exc,\,1\mathscr{F}_z\rangle, \tag{37}$$

where

$$\langle 0|\,\hat{d}^{*}_{\sigma}(\mathbf{k})\,|exc,\,1\mathscr{F}_z\rangle = \int d\mathbf{r}\,e^{-i\mathbf{k}\cdot\mathbf{r}}\langle 0|\,\hat{d}^{*}_{\sigma}(\mathbf{r})\,|exc,\,1\mathscr{F}_z\rangle \tag{38}$$

is the Fourier transform of the dipole moment density operator matrix element. By the use of Eq. (8) and the exponent espansion via spherical harmonics, Eq. (38) may be further recast in the form

$$\langle 0|\,\hat{d}^{*}_{\sigma}(\mathbf{k})\,|exc,\,1\mathscr{F}_z\rangle = -2\sqrt{3}\,\frac{ie\hbar}{m_0E_g} \times \sum_{L=0,2}\sum_{m,n} D^{\mathscr{F}_z}_{L,m,n}\langle\overline{n}|\,p^{*}_{\sigma}\,|m\rangle\,I_L(kR)\,Y_{L,\mathscr{F}_z-m-n}(\mathbf{k}/k), \tag{39}$$

where the function

$$I_L(y) = 2\sqrt{2\pi}\,(-1)^{L/2}\int_0^1 dx\,x\,f_L(x)\sin(\pi x)\,j_L(xy)$$

was introduced in Ref. [14], and the coefficients $D^{\mathscr{F}_z}_{L,m,n}$ are defined by Eq. (11). Substituting Eq. (39) into Eq. (37) we obtain

$$\delta\omega^{(1\mathscr{F}_z)}_0 = \frac{6e^2\hbar}{\pi^2\varepsilon^{(1)}_b m_0^2E_g^2}\sum_{\substack{L=0,2\\ L'=0,2}}\sum_{\substack{m,n\\ m',n'}} D^{\mathscr{F}_z}_{L,m,n}\,D^{\mathscr{F}_z}_{L',m',n'}\,A^{\mathscr{F}_zLL'}_{\substack{m,\ n\\ m',\ n'}} \times \int_0^{\infty} dk\,k^2 I_L(kR)\,I_{L'}(kR), \tag{40}$$

where

$$A^{\mathscr{F}_z LL'}_{\substack{m,\ n\\ m',\ n'}} = \sum_{\sigma,\mu} \langle m'|\, p_\sigma\, |\overline{n}'\rangle \langle \overline{n}|\, p^*_\mu\, |m\rangle \int d\Omega_{\mathbf{k}} Y^*_{L',\mathscr{F}_z - m' - n'}(\Omega_{\mathbf{k}}) \times Y_{L,\mathscr{F}_z - m - n}(\Omega_{\mathbf{k}})\, \frac{k^\sigma k_\mu}{k^2}. \quad (41)$$

Using the technique developed in the quantum theory of angular momentum [28], we can perform the angular integration in Eq. (41) and obtain

$$A^{\mathscr{F}_z LL'}_{\substack{m,\ n\\ m',\ n'}} = \sum_{\sigma,\mu} \sum_{l,M} (2l+1)\sqrt{(2L+1)(2L'+1)} \times \begin{pmatrix} 1 & L' & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & L & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & L' & l \\ \sigma & \mathscr{F}_z - m' - n' & -M \end{pmatrix} \times \begin{pmatrix} 1 & L & l \\ \mu & \mathscr{F}_z - m - n & -M \end{pmatrix} \langle m'|\, p_\sigma\, |\overline{n}'\rangle\, \langle \overline{n}|\, p^*_\mu\, |m\rangle. \quad (42)$$

Using Eq. (42) we can further recast Eq. (40) in the form

$$\delta\omega_0^{(1\mathscr{F}_z)} = \frac{6e^2\hbar}{\pi^2 \varepsilon_b^{(1)} m_0^2 E_g^2} \times \sum_{\substack{L=0,2\\ L'=0,2}} \sum_{l,M} (2l+1)\sqrt{(2L+1)(2L'+1)}\, B^{\mathscr{F}_z}_{L,l,M}\, B^{\mathscr{F}_z}_{L',l',M'} \times \begin{pmatrix} 1 & L' & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & L & l \\ 0 & 0 & 0 \end{pmatrix} \int\limits_0^\infty dk\, k^2 I_L(kR)\, I_{L'}(kR), \quad (43)$$

where

$$B^{\mathscr{F}_z}_{L,l,M} = \sum_{m,n,\mu} D^{\mathscr{F}_z}_{L,m,n}\, \langle \overline{n}|\, p^*_\mu\, |m\rangle \begin{pmatrix} 1 & L & l \\ \mu & \mathscr{F}_z - m - n & -M \end{pmatrix}. \quad (44)$$

Recalling that, for the canonical basis of the Bloch functions $|m\rangle$, $|n\rangle$ [31],

$$\langle m|\, p_\mu\, |\overline{n}\rangle = \langle \overline{n}|\, p^*_\mu\, |m\rangle = 2p_{cv}(-1)^{1-\mu} \begin{pmatrix} 1/2 & 3/2 & 1 \\ m & n & -\mu \end{pmatrix}, \quad (45)$$

where $p_{cv} = i\langle S|\, \hat{p}_x\, |X\rangle$ is the interband matrix element of the momentum operator, we can perform summation in Eq. (44) and express $B^{\mathscr{F}_z}_{L.l,M}$ through a Wigner $6j$ symbol as (see e.g. Ref. [28])

$$B^{\mathscr{F}_z}_{L,l,M} = (-1)^{L/2+1-\mathscr{F}_z}\, 2/3\, p_{cv} \begin{Bmatrix} 1/2 & 3/2 & 1 \\ L & 1 & 3/2 \end{Bmatrix} \delta_{l1}\, \delta_{M\mathscr{F}_z}. \quad (46)$$

Introducing the longitudinal-transverse splitting for a bulk exciton by

$$\hbar\omega_{\mathrm{LT}} = \frac{4}{\varepsilon_b^{(1)} a_B^3} \left(\frac{e\hbar p_{cv}}{m_0 E_g}\right)^2, \quad (47)$$

and substituting Eq. (46) into Eq. (43) we obtain

$$\delta\omega_0^{(1\mathscr{F}_z)} = \frac{2\omega_{\mathrm{LT}}}{\pi^2} \left(\frac{a_B}{R}\right)^3 \times \sum_{\substack{L=0,2\\ L'=0,2}} (-1)^{(L+L')/2} \sqrt{(2L+1)(2L'+1)} \times \begin{Bmatrix} 1/2 & 3/2 & 1 \\ L & 1 & 3/2 \end{Bmatrix} \begin{Bmatrix} 1/2 & 3/2 & 1 \\ L' & 1 & 3/2 \end{Bmatrix} \times \begin{pmatrix} 1 & L' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & L & 1 \\ 0 & 0 & 0 \end{pmatrix} \int\limits_0^\infty dy\, y^2 I_L(y)\, I_{L'}(y). \quad (48)$$

Substituting explicit values of the $3jm$ and $6j$ Wigner symbols [28], we finally obtain the renormalization of the exciton resonant frequency

$$\delta\omega_0^{(1\mathscr{F}_z)} = \frac{4\pi}{9}\, \xi(\beta)\, \omega_{\mathrm{LT}} \left(\frac{a_B}{R}\right)^3, \quad (49)$$

where the function

$$\xi(\beta) = \frac{1}{(2\pi)^3} \int\limits_0^\infty dy\, y^2 \big[I_0(y) + I_2(y)\big]^2 \quad (50)$$

was introduced in Ref. [14]. The exchange splitting given by Eq. (49) coincides with that extracted from the corresponding exchange spin Hamiltonian

$$-\frac{\pi}{9}\, \xi(\beta)\, \hbar\omega_{\mathrm{LT}} \left(\frac{a_B}{R}\right)^3 (\boldsymbol{\sigma} \cdot \mathbf{J}) \quad (51)$$

obtained in Refs. [13,14]. Here $\sigma_x, \sigma_y, \sigma_z$ and J_x, J_y, J_z are respectively the Pauli matrices and the matrices of the projections of the angular momentum $J = 3/2$ which refers to the total angular momentum of the quantized hole. Note that, once we know the resonant frequency renormalization (49), we can readily reconstruct the exchange spin Hamiltonian. One can see from Eq. (49) that the exciton resonant frequency renormalization does not depend on the value of $\mathscr{F}_z$. That is what one would expect, since the exchange interaction (51) splits the exciton ground state into sublevels characterized by different values of the total exciton angular momentum and degenerate with respect to its projections.

6. Inclusion of difference in the background permittivities of the nanocrystal and the host

In this section we will study the effect of difference in the background permittivities of the NC and the host on the frequency renormalization of the excitonic resonance.

Substituting Eq. (35) in Eq. (26) we obtain

$$G^1_{-\sigma\mu}(\mathbf{r},\mathbf{r}') = \frac{\varepsilon_b^{(1)}-\varepsilon_b^{(2)}}{\varepsilon_b^{(1)}} \sum_{l=0}^{\infty} \frac{R^{-(2l+1)}}{2l+1} \frac{l+1}{\varepsilon_b^{(1)} l + \varepsilon_b^{(2)}(l+1)} \times \sum_{l_z=-l}^{l} \nabla_{-\sigma}\big[r^l Y_{ll_z}(\mathbf{r}/r)\big] \nabla'_\mu \big[r'^l Y^*_{ll_z}(\mathbf{r}'/r')\big]. \quad (52)$$

Further substituting Eq. (52) into Eq. (29) we have

$$\delta\omega_1^{(1\mathscr{F}_z)} = \frac{4\pi}{\hbar} \frac{\varepsilon_b^{(1)}-\varepsilon_b^{(2)}}{\varepsilon_b^{(1)}} \sum_{l=0}^{\infty} \frac{R^{-(2l+1)}}{2l+1} \frac{l+1}{\varepsilon_b^{(1)} l + \varepsilon_b^{(2)}(l+1)} \times \sum_{l_z=-l}^{l} W^*_{\mathscr{F}_z l l_z} W_{\mathscr{F}_z l l_z}, \quad (53)$$

where

$$W_{\mathscr{F}_z l l_z} = \int d\mathbf{r} \sum_\sigma (-1)^\sigma \langle exc, 1\mathscr{F}_z | \hat{d}_\sigma(\mathbf{r}) | 0 \rangle \times \nabla_{-\sigma}\big[r^l Y_{ll_z}(\mathbf{r}/r)\big]. \quad (54)$$

Using Eqs. (8) and (9), it results

$$W_{\mathscr{F}_z l l_z} = (-1)^{1+\mathscr{F}_z} \frac{ie\hbar}{m_0 E_g} \times \sqrt{3} \sum_m \begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -\mathscr{F}_z \end{pmatrix} I^{(l,l_z)}_{m,\mathscr{F}_z - m}, \quad (55)$$

where the coefficients

$$I^{(l,l_z)}_{m,\mathscr{F}_z-m} = \sum_n \int d\mathbf{r}\, \phi(r)\, \mathscr{R}_{\mathscr{F}_z-m,n}(\mathbf{r}) (\mathbf{p}_{m\bar{n}}) \big[r^l Y_{ll_z}(\mathbf{r}/r)\big] \quad (56)$$

were introduced in Ref. [14] and $\mathbf{p}_{m\bar{n}} \equiv \langle m | \mathbf{p} | \bar{n} \rangle$. Using Eqs. (3) and (45) and applying the technique described in Ref. [28], we can perform the angular integration in Eq. (56) to obtain

$$I^{(l,l_z)}_{m,\mathscr{F}_z-m} = (-1)^{l+\frac{l+1}{2}+l_z} \sqrt{l}\,(2l+1)\, 4p_{cv} \times \begin{pmatrix} 3/2 & 1/2 & l \\ \mathscr{F}_z - m & m & -l_z \end{pmatrix} \begin{Bmatrix} 1/2 & l & 3/2 \\ l-1 & 3/2 & 1 \end{Bmatrix} \times R^{-3/2} \int_0^R f_{l-1}(r/R)\, \phi(r)\, r^{l+1}\, dr, \quad (57)$$

where l can assume the values 1 or 3. Noting that for $l = 3$ the Wigner $3jm$ symbol in Eq. (57) vanishes identically and substituting the explicit expression for $\phi(r)$ from Eq. (1) we obtain [14]

$$I^{(l,l_z)}_{m,\mathscr{F}_z-m} = \frac{(-1)^{l_z+1}\sqrt{6}\, p_{cv}\delta_{l1}}{\sqrt{\pi}} \begin{pmatrix} 3/2 & 1/2 & 1 \\ \mathscr{F}_z - m & m & -l_z \end{pmatrix} \times \int_0^1 f_0(x) \sin(\pi x)\, x\, dx. \quad (58)$$

Substituting Eq. (58) in Eq. (55) we get

$$W_{\mathscr{F}_z l l_z} = \frac{ie\hbar}{m_0 E_g} \frac{\sqrt{2} p_{cv} \delta_{l1} \delta_{l_z \mathscr{F}_z}}{\sqrt{\pi}} \int_0^1 f_0(x) \sin(\pi x)\, x\, dx. \quad (59)$$

Combining Eqs. (47), (53), and (59) we finally obtain

$$\delta\omega_1^{(1\mathscr{F}_z)} = \frac{4}{3}\omega_{\mathrm{LT}} \left(\frac{a_B}{R}\right)^3 \frac{\varepsilon_b^{(1)}-\varepsilon_b^{(2)}}{\varepsilon_b^{(1)}+2\varepsilon_b^{(2)}} \times \left[\int_0^1 f_0(x)\sin(\pi x)\, x\, dx\right]^2. \quad (60)$$

This result can be alternatively derived from the corresponding part of the exchange spin Hamiltonian obtained in Ref. [14].

7. Effective local scalar susceptibility

In this section we will construct an effective local scalar susceptibility describing an excitonic resonance in a spherical semiconductor nanocrystal. We will show that even in such a simple model it is possible to account for the fine structure of excitonic levels due to the long-range electron-hole exchange interaction.

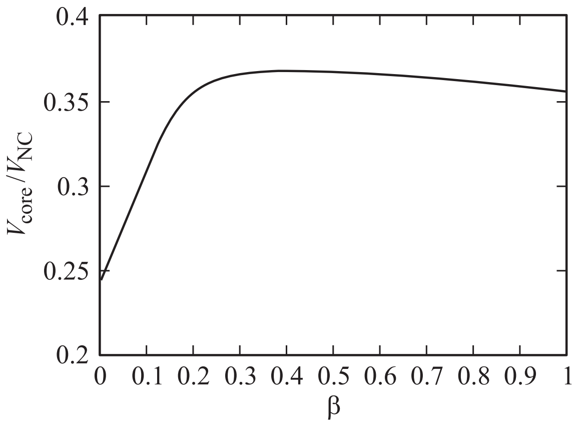
The attempts to derive the long-range exchange induced splitting using the local scalar susceptibility were first made by one of the authors led by his physical intuition [32]. Below we show how it can be carried out correctly.

Consider a sphere of the volume $V_{\mathrm{NC}} = 4\pi R^3/3$ and the background dielectric permittivity $\varepsilon_b^{(1)}$ surrounded by the medium with the background dielectric permittivity $\varepsilon_b^{(2)}$. Suppose that inside the sphere there is a concentric core sphere of the volume V_{core} whose dielectric constant $\varepsilon_{\mathrm{core}}(\omega)$ contains a resonant contribution

$$\varepsilon_{\mathrm{core}}(\omega) = \varepsilon_b^{(1)} + \frac{\varepsilon_b^{(1)}\omega_{\mathrm{NC}}}{\omega_0 - \omega}, \quad (61)$$

where ω_0 is the frequency of the optically active mechanical exciton (with the short-range part of the exchange interaction taken into account) in the spherical NC of the radius R, and ω_{NC} characterizes the oscillator strength of the exciton transition. V_{core} and ω_{NC} are the effective parameters of this model. To obtain the frequency renormalization of the excitonic resonance due to the mechanical exciton interaction with the exciton-induced macroscopic longitudinal electric field we can proceed as in Sec. 3. To that end we will suppose that the electric field inside the core sphere is homogeneous, i.e. in Eq. (21) $E^\sigma(\mathbf{r}') \equiv E^\sigma$. Then we obtain that the time-averaged linear susceptibility

$$\tilde{\chi}^\mu_\sigma(\mathbf{r},\mathbf{r}') \equiv \tilde{\chi}^\mu_\sigma = \frac{\varepsilon_b^{(1)}\omega_{\mathrm{NC}}}{4\pi(\omega_0-\omega)V_{\mathrm{core}}} \delta_{\mu\sigma}\, \delta_{\mu\mathscr{F}_z} \quad (62)$$



The ratio of the effective core sphere volume V_{core} to the NC volume V_{NC} as a function of the light-to-heavy hole effective mass ratio β.

for $\mathbf{r}$ and $\mathbf{r}'$ inside the core sphere and zero outside. Strictly speaking, to use equations of Sec. 3, the function $\tilde{\chi}^{\mu}_{\sigma}(\mathbf{r},\mathbf{r}')$ should be continuous at the points $r = R_{core}$, $r' = R_{core}$, where R_{core} is the radius of the core sphere. To satisfy this condition we can assume that, when $r \to R_{core}$, $r' \to R_{core}$, $\tilde{\chi}^{\mu}_{\sigma}(\mathbf{r},\mathbf{r}')$ continuously approches zero within very small vicinities of the points $r = R_{core}$, $r' = R_{core}$. Substituting Eq. (62) into Eq. (30) we have

$$\delta\omega^{(1\mathcal{F}_z)} = \frac{\varepsilon_b^{(1)}\omega_{NC}}{V_{core}} \int d\mathbf{r} \int d\mathbf{r}' (-1)^{\mathcal{F}_z} G_{-\mathcal{F}_z\mathcal{F}_z}(\mathbf{r},\mathbf{r}'), \quad (63)$$

where the integration is performed within the core sphere ($r, r' < R_{core}$). Taking into account that [14]

$$(-1)^{\mathcal{F}_z} G^0_{-\mathcal{F}_z\mathcal{F}_z}(\mathbf{r},\mathbf{r},') = \frac{1}{3\varepsilon_b^{(1)}}\delta(\mathbf{r}-\mathbf{r}'), \quad (64)$$

$$(-1)^{\mathcal{F}_z} G^1_{-\mathcal{F}_z\mathcal{F}_z}(\mathbf{r},\mathbf{r}') = \frac{\varepsilon_b^{(1)}-\varepsilon_b^{(2)}}{\varepsilon_b^{(1)}} \times \sum_{l=0}^{\infty} \frac{l(l+1)(2l+1)}{\sqrt{2l-1}} \frac{1}{\varepsilon_b^{(1)} l + \varepsilon_b^{(2)}(l+1)} \frac{r^{l-1}r'^{l-1}}{R^{2l+1}} \times \sum_{l_z,M,M'} (-1)^M \begin{pmatrix} 1 & l-1 & l \\ \mathcal{F}_z & M' & l_z \end{pmatrix} \begin{pmatrix} 1 & l-1 & l \\ -\mathcal{F}_z & M & -l_z \end{pmatrix} \times Y_{l-1,M}(\mathbf{r}/r)\, Y_{l-1,M'}(\mathbf{r}'/r'), \quad (65)$$

and

$$\int Y_{l-1,M}(\mathbf{r}/r)\, d\Omega_{\mathbf{r}} = (4\pi)^{-1/2}\delta_{l1}\,\delta_{M0},$$

we immediately obtain

$$\delta\omega^{(1\mathcal{F}_z)} = \frac{\omega_{NC}}{3}\left(1 + 2\,\frac{\varepsilon_b^{(1)}-\varepsilon_b^{(2)}}{\varepsilon_b^{(1)}+2\varepsilon_b^{(2)}}\,\frac{V_{core}}{V_{NC}}\right). \quad (66)$$

The δ-function entering Eq. (64) and hidden in Eqs. (29) and (30) was mentioned at the beginning of Sec. 5. It also appears while proceeding following the scheme [A] where it enters the matrix element of the long-range exchange interaction Hamiltonian [14,20]. In Ref. [20] it was highlighted that this δ-function has a macroscopic meaning unlike the short-range exchange interaction associated with characteristic distances of the order of the crystal lattice constant. This statement is further supported by the present consideration in the framework of the scheme [B] where the above-mentioned δ-function appears during a formal solution of a macroscopic electrostatic problem. Below we also present an alternative and more traditional derivation of Eq. (66) which does not apply any singular functions.

Comparing Eq. (66) with Eqs. (49) and (60), we can determine the parameters of the model developed in this section

$$\omega_{NC} = \frac{4\pi}{3}\,\xi(\beta)\,\omega_{LT}\left(\frac{a_B}{R}\right)^3, \quad (67)$$

$$V_{core} = V_{NC}\,\frac{3\left[\int_0^1 f_0(x)\sin(\pi x)\,x\,dx\right]^2}{2\pi\,\xi(\beta)} = R^2\,\frac{2\left[\int_0^1 f_0(x)\sin(\pi x)\,x\,dx\right]^2}{\xi\beta}. \quad (68)$$

The ratio V_{core}/V_{NC} is plotted in Figure as a function of the light-to-heavy hole effective mass ratio β. One can see that $V_{core} < V_{NC}$ for any value of β. We can further combine Eqs. (67) and (68) to obtain

$$\omega_{NC} = \frac{8\pi\omega_{LT}a_B^3}{3V_{core}}\left[\int_0^1 f_0(x)\sin(\pi x)\,x\,dx\right]^2 = \frac{4\pi}{\hbar\varepsilon_b^{(1)}V_{core}}\left|\int \langle exc, 1\mathcal{F}_z|\,\hat{d}_{\mathcal{F}_z}(\mathbf{r})\,|0\rangle\,d\mathbf{r}\right|^2. \quad (69)$$

Note that the parameter ω_{NC} characterizing the oscillator strength of the NC ground state-exciton transition within the present model is equal to the analogous bulk-exciton parameter ω_{LT} multiplied by the square of the electron and the hole envelope functions overlap integral and by the ratio of the bulk-exciton volume $4\pi a_B^3/3$ to the core sphere volume V_{core}. Substituting Eq. (69) into Eq. (62) we have

$$\tilde{\chi}^{\mu}_{\sigma} = \frac{\left|\int\langle exc, 1\mathcal{F}_z|\,\hat{d}_{\mathcal{F}_z}(\mathbf{r})\,|0\rangle\,d\mathbf{r}\right|^2}{V_{core}^2\hbar(\omega_0-\omega)}\,\delta_{\mu\sigma}\,\delta_{\mu\mathcal{F}_z}. \quad (70)$$

Comparing this expression with Eq. (22) we see that

$$\tilde{\chi}^{\mu}_{\sigma} = V_{core}^{-2}\,\delta_{\mu\sigma}\,\delta_{\mu\mathcal{F}_z}\int d\mathbf{r}\int d\mathbf{r}'\chi^{\mathcal{F}_z}_{\mathcal{F}_z}(\mathbf{r},\mathbf{r}'). \quad (71)$$

Equation [71] establishes the relation between the rigorous treatment developed in the first part of the present paper and the simplified model of this section. It shows that we can suppose that the only component of the electric field different from zero is that in the direction of the polarization of the incident light and, thus, we can use the space-averaged linear susceptibility. At the same time we must assume that the exciton is confined within an effective volume given by Eq. (68) which is less than the real NC volume.

We will conclude this section by noting that, along with a rather formal derivation of Eq. (66) given above, another very simple derivation may be presented. The latter is based on the fact that, as was already mentioned in Sec. 3, in the long-wavelength limit the full Maxwell field may be treated as longitudinal. Then we can write the electrostatic potential as [33,34]

$$\varphi(r) = \begin{cases} -(\mathbf{r}\mathbf{E}^{(0)})(1 - A/r^3), & \text{when} \quad r > R, \\ -C(\mathbf{r}\mathbf{E}^{(0)})(1 - D/r^3), & \text{when} \quad R_{\text{core}} < r < R, \\ -B(\mathbf{r}\mathbf{E}^{(0)}), & \text{when} \quad r < R_{\text{core}}, \end{cases} \tag{72}$$

where A, B, C and D are constants to be determined from the boundary conditions. Requiring that φ and $\varepsilon\,\partial\varphi/\partial r$ be continous at the interfaces, we obtain [34]

$$B = \frac{9V_{\text{NC}}\varepsilon_b^{(1)}\varepsilon_b^{(2)}}{V_{\text{NC}}\left(\varepsilon_{\text{core}}(\omega) + 2\varepsilon_b^{(1)}\right)\left(\varepsilon_b^{(1)} + 2\varepsilon_b^{(2)}\right) + 2V_{\text{core}}\left(\varepsilon_{\text{core}}(\omega) - \varepsilon_b^{(1)}\right)\left(\varepsilon_b^{(1)} - \varepsilon_b^{(2)}\right)}. \tag{73}$$

Substituting Eq. (61) into Eq. (73) we find that B, and, therefore, the electric field inside the core sphere, contains a pole whose frequency is different from ω_0 by the value of $\delta\omega^{(1\mathscr{F}_z)}$ given by Eq. (66).

8. Application to wurtzite structure nanocrystals

In this section we will show how the formalism developed above may be applied to NCs of semiconductors with wurtzite crystal lattice. This case is quite important since the most widely used for experimental studied [1–6] CdSe NCs possess wurtzite crystal structure.

To describe the states near the top of the valence band in bulk hexagonal crystals with wurtzite structure, one can add a perturbative term responsible for the crystal-field splitting [35] to the spherical Luttinger Hamiltonian,

$$\hat{\mathscr{H}}_{cr} = -\frac{\Delta_{cr}}{2}\left(J_z^2 - 5/4\right),$$

where Δ_{cr} is the energy of the crystal-field induced splitting in a bulk semiconductor and J_z now refers to the hole spin. As a result, the valence band splits into two bands characterized by the absolute values of the hole spin projections in the C_6 axis.

Hence, the ground level of the mechanical exciton confined in a spherical wurtzite structure NC is split into two four-fold degenerate sublevels. The upper level state is a superposition of two states with $\mathscr{F}_z = 0$ and two states with $\mathscr{F}_z = \pm 1$, where $\mathscr{F}_z$ stands for the mechanical exciton total angular momentum projection in the C_6 axis. We will denote the latter two states as $\pm 1^{\tilde{U}}$. The lower level state is a superposition of states with $\mathscr{F}_z = \pm 2$ and those with $\mathscr{F}_z = \pm 1$ which will be denoted as $\pm 1^{\tilde{L}}$. The energy difference between the upper and the lower sublevels of the mechanical exciton will be denoted as Δ. Since Δ is quite small compared with the unperturbed resonant exciton energy, the circularly polarized light propagating along the C_6 axis would excite states with $\mathscr{F}_z = \pm 1$ from both the upper and the lower sublevels. Below we will show how to account for this case.

The wave function of either the $+1^{\tilde{U}}$ or the $+1^{\tilde{L}}$ state is given by

$$\begin{aligned} |exc, +1^{\tilde{U},\tilde{L}}\rangle &= \tilde{C}_{1/2}^{\tilde{U},\tilde{L}}\,\psi_{1/2}^{(e)}(\mathbf{r}_e)\,\psi_{1/2}^{(h)}(\mathbf{r}_h) \\ &\quad + \tilde{C}_{-1/2}^{\tilde{U},\tilde{L}}\,\psi_{-1/2}^{(e)}(\mathbf{r}_e)\,\psi_{3/2}^{(h)}(\mathbf{r}_h) \\ &\equiv \sum_m \tilde{C}_m^{\tilde{U},\tilde{L}}\psi_m^{(e)}(\mathbf{r}_e)\,\psi_{1-m}^{(h)}(\mathbf{r}_h), \end{aligned} \tag{74}$$

where $-\tilde{C}_{1/2}^{\tilde{U}} = \tilde{C}_{-1/2}^{\tilde{L}} = 1$, $\tilde{C}_{-1/2}^{\tilde{U}} = \tilde{C}_{1/2}^{\tilde{L}} = 0$. In what follows we will not first take into account the short-range part of the exchange interaction. However, it is worth noting that in the present formalism it would only affect the values of the constants $\tilde{C}_m^{\tilde{U},\tilde{L}}$ and the initial energy difference between the $\pm 1^{\tilde{U}}$ and $\pm 1^{\tilde{L}}$ states.

Comparing Eqs. (74) and (6) and using Eqs. (8), (10), and (11) we obtain

$$\langle 0|\,\hat{d}_\sigma^*(\mathbf{r})\,|exc, +1^{\tilde{U},\tilde{L}}\rangle = -\sum_{m,n}\frac{ie\hbar}{m_0E_g}\,\langle \bar{n}|\,p_\sigma^*\,|m\rangle\,\tilde{\Phi}_{mn}^{\tilde{U},\tilde{L}}(\mathbf{r}), \tag{75}$$

where

$$\tilde{\Phi}_{mn}^{\tilde{U},\tilde{L}}(\mathbf{r}) = 2\sqrt{3}\,\phi(r)\,R^{-3/2} \times \sum_{L=0,2} D_{L,m,n}^{\tilde{U},\tilde{L}}\,f_L(r/R)Y_{L,1-m-n}(\mathbf{r}/r), \tag{76}$$

$$D_{L.m,n}^{\tilde{U},\tilde{L}} = \frac{1}{\sqrt{3}}\,(-1)^{1/2-m-L/2}\,\tilde{C}_m^{\tilde{U},\tilde{L}} \times \begin{pmatrix} 3/2 & L & 3/2 \\ n & 1-m-n & m-1 \end{pmatrix}. \tag{77}$$

Suppose that the circularly polarized light propagating along the C_6 axis excites from the NC ground state an exciton with projection in this axis $\mathscr{F}_z = +1$. Then, instead of Eq. (12), for the time-dependent wave function of the NC we will have

$$|t\rangle = |0\rangle + C^{\tilde{L}}(t)\,|exc, +1^{\tilde{L}}\rangle\,e^{-i\omega_{\tilde{L}}t} + C^{\tilde{U}}(t)\,|exc, +1^{\tilde{U}}\rangle\,e^{-i\omega_{\tilde{U}}t}, \tag{78}$$

where $\omega_{\tilde{L}}$ and $\omega_{\tilde{U}}$ are the frequencies of the lower and the upper levels of the mechanical exciton ground state, respectively. Repeating the derivation of Sec. 2 we will find

$$C^{\tilde U,\tilde L}(t) = \hbar^{-1}\,\frac{e^{i(\omega_{\tilde U,\tilde L}-\omega)t}}{\omega_{\tilde U,\tilde L}-\omega}\,\Lambda^{\tilde U,\tilde L}, \tag{79}$$

where

$$\Lambda^{\tilde U,\tilde L} = \int d\mathbf{r} \sum_{\mu} \langle exc, +1^{\tilde U,\tilde L}|\,\hat d_\mu(\mathbf{r})\,|0\rangle\, E^{\mu}(\mathbf{r}).$$

Then, instead of Eq. (20) we will have

$$\varepsilon_b(r)\Delta\varphi(\mathbf{r}) = \frac{4\pi\Lambda^{\tilde L}}{\hbar(\omega_{\tilde L}-\omega)} \sum_{\mu} \nabla_\mu\,\langle 0|\,\hat d^{*}_\mu(\mathbf{r})\,|exc, +1^{\tilde L}\rangle$$

$$+\frac{4\pi\Lambda^{\tilde U}}{\hbar(\omega_{\tilde U}-\omega)} \sum_{\mu} \nabla_\mu\,\langle 0|\,\hat d^{*}_\mu(\mathbf{r})\,|exc, +1^{\tilde U}\rangle. \tag{80}$$

In deriving Eq. (80) and averaging over time, we assumed $\omega_{\tilde U} \approx \omega_{\tilde L} \approx \omega_0$. If we further proceed as in Sec. 3, then instead of Eq. (27) we will find a system of two coupled equations

$$\begin{cases} \Lambda^{\tilde L} = \Lambda^{\tilde L(0)} - \frac{\Lambda^{\tilde L}\Xi^{\tilde L\tilde L}}{\omega_{\tilde L}-\omega} - \frac{\Lambda^{\tilde U}\Xi^{\tilde L\tilde U}}{\omega_{\tilde U}-\omega} \\ \Lambda^{\tilde U} = \Lambda^{\tilde U(0)} - \frac{\Lambda^{\tilde L}\Xi^{\tilde U\tilde L}}{\omega_{\tilde L}-\omega} - \frac{\Lambda^{\tilde U}\Xi^{\tilde U\tilde U}}{\omega_{\tilde U}-\omega}. \end{cases} \tag{81}$$

Here

$$\Xi^{\tilde\alpha\tilde\beta} = 4\pi \int d\mathbf{r} \int d\mathbf{r}' \sum_{\sigma,\mu} (-1)^{\sigma} G_{-\sigma\mu}(\mathbf{r},\mathbf{r}')$$

$$\times\,\langle exc, +1^{\tilde\alpha}|\,\hat d_\sigma(\mathbf{r})\,|0\rangle\langle 0|\,\hat d^{*}_\mu(\mathbf{r}')\,|exc, +1^{\tilde\beta}\rangle \tag{82}$$

and $\tilde\alpha, \tilde\beta = \tilde U, \tilde L$. From Eq. (81) for e.g. $\Lambda^{\tilde L}$ we find

$$\Lambda^{\tilde L}\Big[(\omega_{\tilde U} - \omega + \Xi^{\tilde U\tilde U})(\omega_{\tilde L} - \omega + \Xi^{\tilde L\tilde L}) - \Xi^{\tilde L\tilde U}\Xi^{\tilde U\tilde L}\Big]$$

$$= \Lambda^{\tilde L(0)}(\omega_{\tilde U} - \omega + \Xi^{\tilde U\tilde U})(\omega_{\tilde L} - \omega) - \Xi^{\tilde L\tilde U}\Lambda^{\tilde U(0)}(\omega_{\tilde L} - \omega). \tag{83}$$

The zeros of the expression in the square brackets in the left-hand side of Eq. (83) give the new renormalized frequencies of the exciton states

$$\omega_{1,2} = \frac{\omega_{\tilde U} + \omega_{\tilde L} + \Xi^{\tilde U\tilde U} + \Xi^{\tilde L\tilde L}}{2}$$

$$\pm\,1/2\sqrt{\begin{matrix}(\omega_{\tilde U} + \omega_{\tilde L} + \Xi^{\tilde U\tilde U} + \Xi^{\tilde L\tilde L})^2 - 4(\omega_{\tilde U}\omega_{\tilde L} + \Xi^{\tilde U\tilde U}\omega_{\tilde L} + \\ + \Xi^{\tilde L\tilde L}\omega_{\tilde U} + \Xi^{\tilde L\tilde L}\Xi^{\tilde U\tilde U} - \Xi^{\tilde L\tilde U}\Xi^{\tilde U\tilde L})\end{matrix}}\,. \tag{84}$$

If we neglect, for the sake of brevity, the difference in the NC and the host matrix background permittivities, then for $\Xi^{\tilde\alpha\tilde\beta}$ we will have (the derivation is similar to that of Eq. (49) in Sec. 5)

$$\Xi^{\tilde\alpha\tilde\beta} = \sum_{m,m'} \tilde C^{\tilde\alpha}_{m}\,\tilde C^{\tilde\beta}_{m'} \begin{pmatrix} 3/2 & 1/2 & 1 \\ m-1 & -m & 1 \end{pmatrix} \begin{pmatrix} 3/2 & 1/2 & 1 \\ m'-1 & -m' & 1 \end{pmatrix}$$

$$\times\,\frac{4\pi}{3}\,\xi(\beta)\,\omega_{\mathrm{LT}} \left(\frac{a_B}{R}\right)^3. \tag{85}$$

Substituting the explicit values of the Wigner $3jm$-symbols and $-\tilde C^{\tilde U}_{1/2} = \tilde C^{\tilde L}_{-1/2} = 1$, $\tilde C^{\tilde U}_{-1/2} = \tilde C^{\tilde L}_{1/2} = 0$ we obtain

$$\Xi^{\tilde U\tilde U} = \frac{\pi}{9}\,\xi(\beta)\,\omega_{\mathrm{LT}} \left(\frac{a_B}{R}\right)^3 \equiv \tilde\eta,$$

$$\Xi^{\tilde L\tilde L} = 3\tilde\eta,$$

$$\Xi^{\tilde L\tilde U} = \Xi^{\tilde U\tilde L} = \sqrt{3}\,\tilde\eta. \tag{86}$$

Choosing the zero of energy in the middle of the upper and the lower sublevels so that $\omega_{\tilde U} = \Delta/2$, $\omega_{\tilde L} = -\Delta/2$ and substituting Eq. (86) into Eq. (84) we find

$$\omega_{1,2} = 2\tilde\eta \pm \sqrt{4\tilde\eta^2 - \Delta^2/4 - \tilde\eta\Delta}. \tag{87}$$

The summetry of the problem dictates that the short-range and the long-range parts of the exchange interaction lead to additive contributions to the resonant frequencies renormalization. It means that the short-rangle part can be taken into account if we simply substitute the value of $\tilde\eta$ by the magnitude of $\bar\eta$ which was introduced in Refs. [13,14] adn takes into account both parts of the exchange interaction. However, it is possible to introduce the short-range induced splitting initially. If we denote the parameter responsible for the short-rangle exchange interaction in a NC by $\eta \equiv \bar\eta - \tilde\eta$ then we will have

$$\omega^{\tilde U,\tilde L} = 2\eta \pm \sqrt{4\eta^2 + \Delta^2/4 - \eta\Delta}$$

and

$$\tilde C^{\tilde U,\tilde L}_{1/2} = \mp\sqrt{\frac{\sqrt{f^2+d} \pm f}{2\sqrt{f^2+d}}},$$

$$\tilde C^{\tilde U,\tilde L}_{-1/2} = \sqrt{\frac{\sqrt{f^2+d} \mp f}{2\sqrt{f^2+d}}},$$

where $f = -\eta + \Delta/2$, $d = 3\eta^2$. One can chek that Eqs. (84) and (85) lead in this case to Eq. (87), where $\tilde\eta$ should be substituted by $\bar\eta$, i.e.

$$\omega_{1,2} = 2\bar\eta \pm \sqrt{4\bar\eta^2 + \Delta^2/4 - \bar\eta\Delta}. \tag{88}$$

This result coincides with that obtained in the scheme [*A*] [13,14].

Light linearly polarized along the C_6 axis would excite one of the states with $\mathscr{F}_z = 0$. The other one possessing lower energy due to the short-rangle exchange interaction is optically inactive [1–3,13,14]. Thus, this case in quite similar to that of cubic structure NCs and needs no special consideration.

The energy-level diagrams for excitons confined in wurtzite structure NCs as well as a comparison of calculated splittings with available experimental data can be found in Ref. [14].

Generalization of the treatment developed in Sec. 7 for the case of wurtzite structure NCs becomes straightforward by using Eq. (71).

We have provided an explicit demonstration that the contribution to the fine structure of the ground exciton level in a semiconductor NC due to the long-range part of the electron-hole exchange interaction can be equivalently described as arising from the mechanical exciton interaction with the exciton-induced longitudinal electric field. Proceeding in this manner we reproduced all the results initially obtained as long-range exchange induced splittings [13,14] in the framework of the effective mass approximation. However, the present treatment is more instructive, since it enables one to understand better the limits of validity of the calculation (such as those imposed by the necessity of taking into account the retardation effect) and some pecularities of the Coulomb interaction (such as those leading to the term in the long-range exchange Hamiltonian proportional to the Dirac δ-function). We also established a simplified model which allows to use a scalar linear susceptibility averaged over shace in order to account for the effect under consideration. The price of this simplification is the supposition that the exciton is confined within some effective core volume which is less than the real NC volume. This effective volume constitutes a new parameter. However, once the parameter is found and the model itself is proved for a particular case of a cubic structure NC, it can be used, e. g., in order to account for the case of a wurtzite structure NC [36]. Nevertheless, we gave the rigorous treatment of the latter case, since it costed us few space and allowed to demonstrate the power of the developed formalism.

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