PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Short-range versus long-range electron-hole exchange interactions in semiconductor quantum dots

A. Franceschetti, L. W. Wang, H. Fu, and A. Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 25 August 1998)

Using a many-body approach based on atomistic pseudopotential wave functions we show that the electron-hole exchange interaction in semiconductor quantum dots is characterized by a large, previously neglected long-range component, originating from *monopolar* interactions of the transition density between different unit cells. The calculated electron-hole exchange splitting of CdSe and InP nanocrystals is in good agreement with recent experimental measurements. [S0163-1829(98)51144-7]

One of the most intriguing features of the spectroscopy of semiconductor quantum dots is the energy shift between the zero-phonon absorption and emission peaks observed in size-selective spectroscopies of monodispersed samples.[1–7] The redshift of the emission peak, of the order of 10 meV, has been measured in Si,[1] CdSe,[2–5] InP,[6] and InAs (Ref. 7) nanocrystals grown with different techniques. Although several models have been proposed to explain the redshifted emission, recent measurements and calculations for CdSe (Refs. 2–5) and InP (Refs. 6 and 8) nanocrystals indicate that, as first proposed by Calcott *et al.*,[1] the redshift originates from the exciton splitting induced by the electron-hole (e-h) *exchange* interaction. According to this model, absorption takes place in a spin-allowed state, while emission occurs from a lower energy spin-forbidden state.

There are four open issues regarding the e-h exchange interaction in semiconductor quantum dots.

(i) *The magnitude of the long-range exchange interaction.* In general, the effective exchange interaction contains a short-range (SR) component, which decays exponentially with an effective length comparable with the bulk lattice constant, and a long-range (LR) component, which decays instead as a power law and extends over several lattice constants.[9] In bulk periodic semiconductors the LR interaction is responsible for the nonanalytic behavior of the exciton dispersion as the exciton wave vector approaches zero,[10] which is observed spectroscopically as a longitudinal-transverse splitting. However, the magnitude of LR exchange interactions in zero-dimensional quantum dots is still an open question.

(ii) *The physical origin of the LR exchange interaction.* Conventional wisdom[2–4,11] suggests that the LR exchange interaction in quantum dots originates, as in bulk semiconductors, from *dipole-dipole* coupling of the transition density between unit cells. Under this assumption, the LR contribution to the exchange splitting of *s*-like excitons in spherical quantum dots vanishes.[11] It is not obvious, however, that only dipolar LR interactions exist in quantum dots.

(iii) *The screening of the LR exchange interaction.* The effects of dielectric screening on the e-h exchange interaction are quite controversial.[12–14] It is generally understood that in *bulk semiconductors* the SR exchange interaction should be unscreened, while the LR exchange interaction should be screened by the bulk dielectric tensor.[14] It is not clear, however, to what extent the exchange interaction in *quantum dots* is affected by dielectric screening. Recent direct calculations[8,15] for InP and CdSe nanocrystals revealed that the unscreened exciton splitting is significantly larger than the measured redshift, suggesting that the screening of the LR interaction may be important.

(iv) *How to calculate the exchange splitting.* In standard approaches based on the effective-mass approximation (EMA) the e-h exchange interaction is described by a *short-range* phenomenological Hamiltonian acting on the exciton envelope function:[2–4]

$$H_{exch}^{EMA} = -\xi a_x^3 \Delta E_x \delta(\mathbf{r}_h - \mathbf{r}_e)\sigma \cdot J, \tag{1}$$

where ξ is a structure-dependent parameter ($\xi = \pi/4$ for cubic lattice structure and $\xi = \pi/3$ for hexagonal lattice structure), σ and J are the electron and hole spin operators, a_x is the bulk exciton radius, and ΔE_x is the bulk exchange splitting. This model relies heavily on the knowledge of a_x and ΔE_x [~ 0.1 meV,[2] 0.001 meV (Ref. 7)], which are often subject to large experimental uncertainties. The solutions of the model Hamiltonian (1) fit well the observed redshift in CdSe nanocrystals,[2–4] but in the case of spherical zinc-blende quantum dots Eq. (1) predicts a $1/R^3$ scaling of the redshift with size,[3] which is not observed in either InP (Ref. 6) or InAs (Ref. 7) nanocrystals where a $\sim R^{-2}$ dependence is seen. While the prefactor of Eq. (1) has been recently questioned,[16] the inability of the conventional EMA to reproduce the correct scaling law is particularly troublesome.

In this work we investigate the nature of the e-h exchange interaction in semiconductor quantum dots using a many-body approach based on atomistic pseudopotential wave functions having a degree of accuracy comparable to *ab initio* wave functions. We find the following.

(i) For direct excitons the e-h exchange interaction has a sizable LR contribution, comparable in magnitude (even after screening) with the SR contribution. The LR and SR components have distinct dependencies on the quantum dot size.

(ii) The LR component *does not* originate from dipole-dipole interactions between unit cells, as in the case of bulk excitons, but from monopole-monopole interactions that are peculiar to quantum-confined systems.

 ©1998 The American Physical Society

(iii) Using a phenomenological, distance-dependent dielectric constant, we show that the LR component of the exchange interaction in quantum dots is significantly reduced by screening effects.

(iv) We are able to calculate the exciton splitting of semiconductor quantum dots without any *a priori* empirical information on the bulk exchange splitting or exciton radius. Our results are in good agreement with the experimentally measured redshift in a number of systems.

The low-lying excited states of a quantum dot are calculated by a configuration-interaction expansion of the many-particle wave function in terms of single-substitution Slater determinants $\{\Phi_{vc}\}$, obtained from the ground state Φ_0 by exciting an electron from the occupied single-particle state $\psi_v(\mathbf{x})$ of energy ϵ_v to the unoccupied single-particle state $\psi_c(\mathbf{x})$ of energy ϵ_c [here $\mathbf{x}\equiv(\mathbf{r},\sigma)$, where $\sigma=\uparrow,\downarrow$ is the spin variable]. By taking the ground-state energy as energy zero, the matrix elements of the many-particle Hamiltonian $\mathcal{H}$ in the representation $\{\Phi_{vc}\}$ are

$$\langle\Phi_{vc}|\mathcal{H}|\Phi_{v'c'}\rangle=(\epsilon_c-\epsilon_v)\,\delta_{v,v'}\delta_{c,c'}-J_{vc,v'c'}+K_{vc,v'c'}\,, \tag{2}$$

where J and K are the Coulomb and exchange integrals:

$$J_{vc,v'c'}=\int\int\frac{\psi^*_{v'}(\mathbf{x}_1)\;\;\psi^*_c(\mathbf{x}_2)\;\;\psi_v(\mathbf{x}_1)\;\;\psi_{c'}(\mathbf{x}_2)}{\overline{\epsilon}(\mathbf{r}_1,\mathbf{r}_2)\;\;|\mathbf{r}_1-\mathbf{r}_2|}\times d\mathbf{x}_1\,d\mathbf{x}_2\,, \tag{3}$$

$$K_{vc,v'c'}=\int\int\frac{\psi^*_{v'}(\mathbf{x}_1)\;\;\psi^*_c(\mathbf{x}_2)\;\;\psi_{c'}(\mathbf{x}_1)\;\;\psi_v(\mathbf{x}_2)}{\overline{\epsilon}(\mathbf{r}_1,\mathbf{r}_2)\;\;|\mathbf{r}_1-\mathbf{r}_2|}\times d\mathbf{x}_1\,d\mathbf{x}_2\,. \tag{4}$$

Note that J and K have both diagonal ($v=v',c=c'$) and off-diagonal components. The screening of the e-h interaction, caused by the polarization of the medium, is described phenomenologically by the *microscopic*, position-dependent dielectric constant $\overline{\epsilon}$, and will be discussed later. A diagonalization of the Hamiltonian matrix (2) yields the low-energy excited states of the quantum dot.

The single-particle wave functions $\psi_i(\mathbf{r},\sigma)$ and energies ϵ_i entering Eqs. (2)–(4) are obtained here using an atomistic pseudopotential approach that avoids effective-mass approximations. The total, microscopic pseudopotential V_{ps} of the system consisting of the quantum dot and the surrounding barrier is written as superposition of atomic potentials, which are derived[8,17] from measured bulk transition energies, effective masses, and deformation potentials, and from *ab initio* bulk wave functions calculated in the framework of density-functional theory. The single-particle states are the solutions of the Schrödinger equation

$$[-(1/2)\,\nabla^2+V_{ps}(\mathbf{r})+\hat{V}_{so}]\psi_i(\mathbf{r},\sigma)=\epsilon_i\,\psi_i(\mathbf{r},\sigma)\,, \tag{5}$$

where $\hat{V}_{so}$ is the spin-orbit operator.[17,18] Since the single-particle levels of a quantum dot are widely spaced in energy compared to the characteristic exchange energies, only a few single-particle states near the band edges are expected to contribute to the exchange splitting of the lowest exciton states. Thus, we can selectively solve Eq. (5) for the band-edge states using the folded spectrum method.[19]

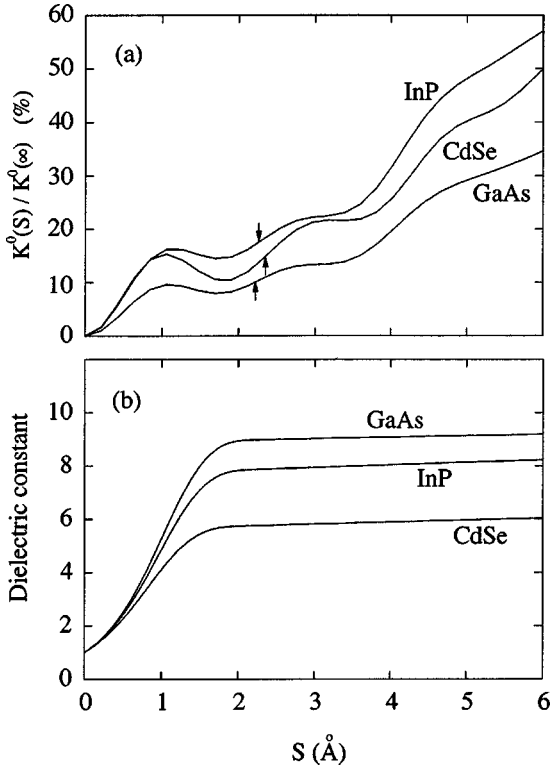

FIG. 1. (a) The unscreened exchange integral $K^0_{vc,vc}(S)$ (normalized by its value at $S\to\infty$) as a function of the cutoff radius S for GaAs ($R=22.5$ Å), InP ($R=17.4$ Å), and CdSe ($R=19.2$ Å) spherical quantum dots. The asymptotic values of $K^0_{vc,vc}(\infty)$ are 18.1, 21.3, and 18.2 meV, respectively. The arrows denote the Wigner-Seitz radii of the three materials. (b) shows, for the same quantum dots, the distance-dependent dielectric constant $\overline{\epsilon}(S)$ used in Eqs. (3) and (4) to screen the e-h interaction.

We consider spherical nanocrystals made of zinc-blende GaAs and InP and wurtzite CdSe, with effective radii ranging from $\sim$6 Å to $\sim$23 Å. The effective radius is defined in terms of the number of atoms in the dot (N_{dot}) as $R=a_0(\gamma N_{dot})^{1/3}$, where a_0 is the bulk lattice constant, $\gamma=3/32\pi$ for zinc-blende dots, and $\gamma=3\sqrt{3}c_0/32\pi a_0$ for wurtzite dots. The surface dangling bonds are passivated using hydrogenlike potentials. Crystal-field effects, which were previously treated perturbatively,[2–4] are naturally described here by specifying the atomic positions.

The exchange integrals $K_{vc,v'c'}$ of Eq. (4) include both the SR part and the LR part of the e-h exchange interaction. The effective range of the SR interaction in bulk periodic solids is comparable with the Wigner-Seitz radius R_{ws}.[9] To establish the effective range of the exchange interaction in quantum dots, we replace the Coulomb potential $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ in Eq. (4) with a cutoff potential $\theta(S-|\mathbf{r}_1-\mathbf{r}_2|)\cdot|\mathbf{r}_1-\mathbf{r}_2|^{-1}$; the e-h interaction is thus set to zero if $|\mathbf{r}_1-\mathbf{r}_2|>S$. The unscreened ($\overline{\epsilon}=1$) exchange integral $K^0_{vc,vc}$ between the valence-band maximum and the conduction-band minimum in the spin-up configuration is shown in Fig. 1(a) as a function of the e-h separation S. We see that the integral $K^0_{vc,vc}(S)$ keeps increasing far beyond $S\sim R_{ws}$, unequivocally indicating the existence of LR exchange interactions in quantum dots.

TABLE I. Multipole components (Ref. 20) (M=monopole, D=dipole) of the LR contribution to the unscreened exchange integral $K^0_{vc,vc}=E_{SR}+E_{LR}$. The numbers in parentheses denote the components of the indirect (X-derived) GaAs exciton exchange energy. All energies are in meV.

	R (Å)	$E_{LR}^{M\text{-}M}$	$E_{LR}^{M\text{-}D}$	$E_{LR}^{D\text{-}D}$	E_{LR}	E_{SR}
CdSe	19.2	12.7	1.3	0.1	15.4	2.8
InP	17.4	11.7	2.2	0.3	16.9	4.4
GaAs	22.5	14.6	0.5	0.0	15.6	2.6
		(−0.1)	(0.0)	(0.0)	(0.1)	(1.3)

To understand the physical origin of the LR exchange interaction, we analyze the unscreened exchange integral $K^0_{vc,vc}$ in terms of the standard multipole-expansion method.[9] By partitioning the system into N eight-atom unit cells $\{\Omega_n, n=1,\ldots N\}$, the LR contribution to $K^0_{vc,vc}$ can be written as

$$E_{LR}=\sum_{m\neq n}^{N}\int\int\frac{\chi_m^*(\mathbf{r}_1)\ \chi_n(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1\,d\mathbf{r}_2\,, \tag{6}$$

where $\chi_n(\mathbf{r})=\Sigma_\sigma\,\psi_v(\mathbf{r},\sigma)\,\psi_c^*(\mathbf{r},\sigma)$ if $\mathbf{r}\in\Omega_n$ and 0 otherwise.[20] E_{LR} is further decomposed into multipole contributions; in particular, the monopole-monopole (M-M) term is given by

$$E_{LR}^{M\text{-}M}=\sum_{m\neq n}^{N}\frac{q_m^*\,q_n}{|\mathbf{R}_m-\mathbf{R}_n|}, \tag{7}$$

where $q_n=\int\chi_n(\mathbf{r})\,d\mathbf{r}$ is the monopole moment of the transition density $\chi_n(\mathbf{r})$ and $\mathbf{R}_n$ denotes the position of the unit cell Ω_n. The leading terms in the multipole expansion of E_{LR} are shown in Table I for GaAs, InP, and CdSe nanocrystals. In the case of direct (Γ-derived) excitons, E_{LR} is dominated by the monopole-monopole contribution, while the dipole-dipole contribution is small due to the spherical symmetry of the nanocrystals.[21] The situation is thus qualitatively different from the case of bulk excitons, where the monopole-monopole interaction vanishes ($q_n=0$) because of the local orthogonality (within each bulk unit cell) of ψ_v and ψ_c. We also find that the monopole-monopole term scales approximately as $1/R$ with the dot size, whereas the SR part (as well as the dipole-dipole contribution to the LR part) scales as $\sim 1/R^3$. Our results contradict the predictions of $\mathbf{k}\cdot\mathbf{p}$ models[22] that the monopole term vanishes in direct-gap II-VI quantum dots.

Having established the importance of LR exchange interactions in quantum dots, we consider next the effects of dielectric screening. The degeneracy between the longitudinal exciton mode and the upper polariton branch at $\mathbf{k}=0$ in bulk semiconductors[13] suggests that the LR exchange interaction should be screened by the dielectric constant as is the polariton splitting. We will thus use a phenomenological distance-dependent dielectric constant to screen the exchange interaction in quantum dots according to the e-h separation. The screened Coulomb potential of Eqs. (3) and (4) can be rewritten[23] as $\int\epsilon^{-1}(\mathbf{r}_1,\mathbf{r})\ |\mathbf{r}-\mathbf{r}_2|^{-1}\,d\mathbf{r}$. Assuming that $\epsilon^{-1}(\mathbf{r}_1,\mathbf{r})\approx\epsilon^{-1}(\mathbf{r}_1-\mathbf{r})$, the screened Coulomb potential can be calculated in reciprocal space as $4\pi\epsilon^{-1}(\mathbf{k})/k^2$, where

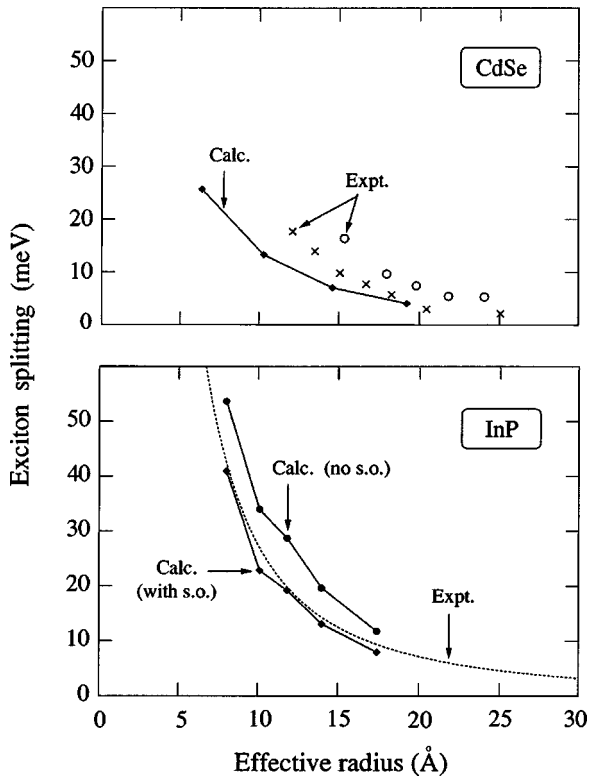

FIG. 2. Exciton splitting Δ of InP and CdSe spherical quantum dots, as a function of the dot radius R. The experimental data for CdSe were taken from Ref. 3 (crosses) and Ref. 5 (circles). The dotted line in the InP plot is a fit to the experimental results of Ref. 6. Calculated results are shown both with and without spin-orbit coupling.

$\epsilon^{-1}(\mathbf{k})$ is the Fourier transform of $\epsilon^{-1}(\mathbf{r}_1-\mathbf{r})$. The inverse dielectric constant ϵ^{-1} consists of an electronic (high-frequency) contribution ϵ_{el}^{-1} and an ionic (low-frequency) contribution $\Delta\epsilon_{ion}^{-1}$, which are approximated here by the Thomas-Fermi model of Resta[23] and by the polaronic model of Haken:[24]

$$\epsilon_{el}^{-1}(k)=\frac{k^2+q^2\sin(kR_\infty)\,/\,(\epsilon_\infty^{dot}\,kR_\infty)}{k^2+q^2} \tag{8a}$$

$$\Delta\epsilon_{ion}^{-1}(k)=\left(\frac{1}{\epsilon_0^{dot}}-\frac{1}{\epsilon_\infty^{dot}}\right)\left(\frac{1/2}{1+\rho_h^2k^2}+\frac{1/2}{1+\rho_e^2k^2}\right). \tag{8b}$$

Here $q=2\,\pi^{-1/2}(3\pi^2n_0)^{1/3}$ (where n_0=electron density) is the Thomas-Fermi wave vector, and R_∞ is the solution of the equation $\sinh(qR_\infty)/(qR_\infty)=\epsilon_\infty^{dot}$. Also, $\rho_{h,e}=(\hbar/2m_{h,e}\omega_{LO})^{1/2}$, where $m_h\,(m_e)$ is the hole (electron) effective mass and ω_{LO} is the frequency of the bulk LO phonon mode. ϵ_∞^{dot} and ϵ_0^{dot} are the quantum-dot *macroscopic* high-frequency and low-frequency dielectric constants, which are obtained here from a modified Penn model where the effective-mass gap is replaced by the pseudopotential-calculated gap. The dielectric constant $\bar{\epsilon}$ obtained with the present model is plotted in Fig. 1(b) as a function of the e-h separation S. Note that $\bar{\epsilon}\to 1$ when $S\to 0$. Thus, the SR ex-

change interaction is unscreened, whereas the LR exchange interaction is significantly screened.

The exciton splitting Δ, defined as the energy difference between the lowest spin-allowed and the lowest spin-forbidden exciton states, is calculated by direct diagonalization of the Hamiltonian matrix (2). We find that the basis set generated from the four single-particle states at the top of the valence band and the two single-particle states at the bottom of the conduction band is sufficient to obtain the exciton splitting with an accuracy of about 10% relative to a larger configuration-interaction expansion. The exciton splitting of InP and CdSe nanocrystals is shown in Fig. 2 as a function of size. For InP dots we compare the singlet-triplet splitting obtained by solving Eq. (5) with vanishing spin-orbit coupling to the exciton splitting obtained in the presence of spin-orbit coupling; we see that the inclusion of spin-orbit interaction lowers Δ by $\sim$30%. We also find the following.

(i) Our calculated exciton splitting is in reasonably good agreement with available experimental results,[3,5,6] even though no empirical adjustments are used.

(ii) The screened LR component of the exchange interaction is comparable in magnitude with the unscreened SR component, and in a parameter-free calculation cannot be ignored. Interestingly, the phenomenological model of Eq. (1), which neglects LR exchange interactions, agrees with our calculations for CdSe nanocrystals, but not for InP nanocrystals. Recent *ab initio* calculations for bulk CdSe (Ref. 25) have shown that the exchange parameter ΔE_x used in Ref. 3 is roughly twice as large as the calculated short-range parameter.

(iii) For zinc-blende InP dots, both the calculated exciton splitting[8] and the experimentally measured redshift[6] scale as $\sim 1/R^2$ with the dot radius R. This is in contrast with the $1/R^3$ scaling law predicted by Eq. (1).

In conclusion, we have shown that the e-h exchange interaction in quantum dots is characterized by a previously unexpected LR contribution originating from the local non-orthogonality between valence and conduction states of the quantum dot within each unit cell. This LR interaction is specific to quantum-confined systems, and cannot be derived from the bulk exchange splitting by simple scaling arguments. Our method permits reliable predictions of the exciton splitting in quantum dots even in the absence of experimental information on the magnitude of the bulk exchange splitting and exciton radius.

This work was supported by the U.S. DOE, OER-BES, Division of Materials Science, under Grant No. DE-AC36-83CH10093.

[1] P.D.J. Calcott *et al.*, J. Phys.: Condens. Matter **5**, L91 (1993).
[2] M. Nirmal *et al.*, Phys. Rev. Lett. **75**, 3728 (1995).
[3] Al. L. Efros *et al.*, Phys. Rev. B **54**, 4843 (1996).
[4] D.J. Norris *et al.*, Phys. Rev. B **53**, 16 347 (1996).
[5] M. Chamarro *et al.*, Phys. Rev. B **53**, 1336 (1996).
[6] O.I. Micic *et al.*, J. Phys. Chem. **101**, 4904 (1997).
[7] U. Banin *et al.*, Superlattices Microstruct. **22**, 559 (1997).
[8] H. Fu and A. Zunger, Phys. Rev. B **56**, 1496 (1997). The dielectric constant used in this paper differs from the one used here in the way ionic screening is included.
[9] R.S. Knox, Solid State Phys., Suppl. **5**, 1 (1963).
[10] W.R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).
[11] T. Takagahara, Phys. Rev. B **47**, 4569 (1993).
[12] Y. Abe, Y. Osaka, and A. Morita, J. Phys. Soc. Jpn. **17**, 1576 (1962); L.J. Sham and T.M. Rice, Phys. Rev. **144**, 708 (1966).
[13] L.C. Andreani, F. Bassani, and A. Quattropani, Lett. Nuovo Cimento **10**, 1473 (1988); K. Cho, Solid State Commun. **33**, 911 (1980).
[14] V.A. Kiselev and A.G. Zhilich, Sov. Phys. Solid State **14**, 1233 (1972;); **15**, 1351 (1972).
[15] A. Franceschetti and A. Zunger, Phys. Rev. Lett. **78**, 915 (1997).
[16] S.V. Goupalov and E.L. Ivchenko, J. Cryst. Growth **184/185**, 393 (1998).
[17] L.W. Wang and A. Zunger, Phys. Rev. B **51**, 17 398 (1995).
[18] The present calculations for GaAs quantum dots do not include spin-orbit coupling.
[19] L.W. Wang and A. Zunger, J. Chem. Phys. **100**, 2394 (1994); J. Phys. Chem. **98**, 2158 (1994).
[20] The exact value of $E_{LR,}$ and its decomposition shown in Table I, depend slightly on the definition of the domains $\{\Omega_n\}$, but the resulting qualitative conclusions are unchanged.
[21] In the case of indirect (X-derived) excitons the LR part is negligible, and only the SR part contributes to the exchange integral.
[22] I. Kang and F. Wise, J. Opt. Soc. Am. B **14**, 1632 (1997).
[23] R. Resta, Phys. Rev. B **16**, 2717 (1977).
[24] H. Haken, Nuovo Cimento **10**, 1230 (1956).
[25] H. Fu, L.W. Wang, and A. Zunger (unpublished).