

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

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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. ©163-1829-98!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

$$H_{exch}^{EMA} \approx 2j a_x^3 DE_x d\mathbf{r}_h \cdot \mathbf{r}_e \mathbf{s} \cdot \mathbf{J}, \quad \sim!$$

where j is a structure-dependent parameter ($j \approx p/4$ for cubic lattice structure and $j \approx p/3$ for hexagonal lattice structure), \mathbf{s} and \mathbf{J} are the electron and hole spin operators, a_x is the bulk exciton radius, and DE_x is the bulk exchange splitting. This model relies heavily on the knowledge of a_x and DE_x @; 0.1 meV,² 0.001 meV ~Ref. 7!#, which are often subject to large experimental uncertainties. The solutions of the model Hamiltonian ~! fit well the observed redshift in CdSe nanocrystals,²⁻⁴ but in the case of spherical zincblende quantum dots Eq. ~! 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 ; $R^{2.2}$ dependence is seen. While the prefactor of Eq. ~! 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.

~! 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.

~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 $\$F_{vc}\%$ obtained from the ground state F_0 by exciting an electron from the occupied single-particle state

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

$$E_{LR} \approx \sum_{m \neq n}^N \iint \frac{x_m^* x_n}{|\mathbf{r}_m - \mathbf{r}_n|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (6)$$

where $x_n(\mathbf{r}) \approx \sum_{\mathbf{s}} c_v(\mathbf{r}, \mathbf{s}) c_c^*(\mathbf{r}, \mathbf{s})$ if $\mathbf{r} \in V_n$ and 0 otherwise.²⁰ E_{LR} is further decomposed into multipole contributions; in particular, the monopole-monopole (M - M) term is given by

$$E_{LR}^{M-M} \approx \sum_{m \neq n}^N \frac{q_m^* q_n}{|\mathbf{R}_m - \mathbf{R}_n|}, \quad (7)$$

where $q_n \approx \int x_n(\mathbf{r}) d\mathbf{r}$ is the monopole moment of the transition density $x_n(\mathbf{r})$ and \mathbf{R}_n denotes the position of the unit cell V_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 (G -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 ($q_n \approx 0$) because of the local orthogonality (within each bulk unit cell) of c_v and c_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 $1/R^3$. Our results contradict the predictions of $\mathbf{k} \cdot \mathbf{p}$ models²² 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 $\mathbf{k} \approx 0$ in bulk semiconductors¹³ suggests that the LR exchange interaction

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

The exciton splitting D , 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 D 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 DE_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 splitting⁸ and the experimentally measured redshift⁶ 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 experi-