Direct Pseudopotential Calculation of Exciton Coulomb and Exchange Energies in Semiconductor Quantum Dots

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The effects of electron-hole interaction on the exciton energy of semiconductor quantum dots are calculated using pseudopotential wave functions. A comparison with the widely used, but never tested, effective-mass approximation (EMA) shows that the electron-hole Coulomb energy is significantly (~40%) overestimated by the EMA, and that the scaling with the dot size R is sublinear in $1/R$. The exchange splitting is much smaller than the Coulomb energy, and in the case of CdSe quantum dots shows significant deviations from the $1/R^3$ scaling predicted by the EMA. [S0031-9007(96)02243-0]

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Perhaps the single most important quantity that determines the optical properties of semiconductor quantum dots is the exciton energy [1]. As the size of the quantum dot decreases from the bulk limit to the nanometer range, quantum confinement effects significantly increase both the single-particle energy gap and the electron-hole Coulomb and exchange interaction, leading to a strong dependence of the exciton energy on the quantum dot size. In the strong confinement limit, where the size of the quantum dot is much smaller then the bulk exciton radius, correlation effects become negligible [2–4], and the electron-hole Coulomb and exchange integrals have the form

$$E_{\mathrm{Coul}} = \frac{e^2}{\epsilon} \sum_{\sigma_h,\sigma_e} \int \frac{|\psi_h(\mathbf{r}_h,\sigma_h)|^2 |\psi_e(\mathbf{r}_e,\sigma_e)|^2}{|\mathbf{r}_h - \mathbf{r}_e|} d^3r_h d^3r_e\,, \tag{1}$$

$$E_{\mathrm{exch}} = e^2 \sum_{\sigma_h,\sigma_e} \mathrm{Re} \int \frac{\psi_h^*(\mathbf{r}_h,\sigma_h)\psi_e^*(\mathbf{r}_e,\sigma_e)\psi_h(\mathbf{r}_e,\sigma_e)\psi_e(\mathbf{r}_h,\sigma_h)}{|\mathbf{r}_h - \mathbf{r}_e|} d^3r_h d^3r_e\,, \tag{2}$$

where ψ_e and ψ_h are the microscopic electron (e) and (h) hole *single-particle* wave functions of spin σ, and ϵ is the dielectric constant of the quantum dot, which is, in general, different from the bulk dielectric constant. Simple particle-in-a-box models [2,3,5] suggest that the single-particle energy-gap shift $\Delta\epsilon_g = \epsilon_g - \epsilon_g^{\mathrm{bulk}}$ scales as $1/R^2$ with the size of the quantum dot, while the Coulomb energy E_{Coul} scales only as $1/R$, so that $E_{\mathrm{Coul}} \ll \Delta\epsilon_g$ in the limit $R \rightarrow 0$. Recent calculations [6–10] have shown, however, that (i) the scaling of the energy gap is slower than $1/R^2$, mainly because of band nonparabolicity effects [6–8], and (ii) the dielectric constant ϵ decreases when the size is reduced [9,10], leading to a less efficient exciton screening. These results point to the conclusion that the electron-hole Coulomb energy can be as important as the single-particle energy gap in predicting the exciton energy of small semiconductor quantum dots. Furthermore, each excitonic energy level can be split by the electron-hole *exchange* interaction [11,12]. While the singlet-triplet splitting ΔE_{exch} is exceedingly small (~0.1 meV) in bulk materials, it can be greatly enhanced by quantum confinement, and has been recently invoked to explain the resonant Stokes shift between absorption and emission in Si [13,14] and CdSe [15] nanocrystals.

Despite the quantitative importance of the electron-hole Coulomb and exchange energies in small quantum dots, the highly simplified one-band effective-mass approximation (EMA) has been almost universally used to estimate these quantities, even when the calculation of the single-particle energy gap requires more sophisticated and reliable methods (such as multiband $\mathbf{k} \cdot \mathbf{p}$ [16], tight-binding [6], or pseudopotentials [7,8]). In fact, the EMA provides simple, analytical expressions for E_{Coul} and ΔE_{exch}: Assuming an infinite potential barrier at the boundaries of the quantum dot, and using the envelope functions of a noninteracting electron-hole pair, one obtains the well-known equations [5,12]

$$E_{\mathrm{Coul}}^{\mathrm{EMA}} = C_{\mathrm{Coul}} \frac{e^2}{\epsilon R}\,, \tag{3}$$

$$\Delta E_{\mathrm{exch}}^{\mathrm{EMA}} = C_{\mathrm{exch}} \left(\frac{a_x}{R}\right)^3 E_x\,, \tag{4}$$

where R is the dimension of the quantum dot, E_x and a_x are the bulk exciton exchange splitting and exciton radius, respectively, and C_{Coul}, C_{exch} are dimensionless constants that depend only on the shape of the quantum dot [17]. For example, in the case of a spherical dot of radius R, the electron and hole ground-state envelope functions $f_e(r) = f_h(r) = (2\pi R)^{-1/2} \sin(\pi r/R) r^{-1}$ yield in Eqs. (1) and (2) $C_{\mathrm{Coul}} = 1.786$ and $C_{\mathrm{exch}} = 2.111$.

Despite the great popularity of the simple EMA expressions (3) and (4), there are now reasons to believe that the use of EMA wave functions to calculate $E_{\rm Coul}$ and $\Delta E_{\rm exch}$ is inadequate. Recent advances in computational physics [8], enabling the direct solution of the Schrödinger equation for large quantum dots without resorting to the EMA, have revealed that the microscopic wave functions are quite different from the EMA wave functions. Figure 1 contrasts the valence-band maximum and conduction-band minimum wave functions of a 6000-atom GaAs quantum dot as obtained by a plane-wave pseudopotential calculation (see below) with the EMA envelope functions used in Eqs. (3) and (4) to evaluate $E_{\rm Coul}$ and $\Delta E_{\rm exch}$. We see that the pseudopotential wave functions are more extended than the EMA wave functions and do not exhibit the simple sinelike envelope function predicted by the EMA. We have calculated the electron-hole Coulomb and exchange energies of semiconductor nanocrystals using such accurate, local-density approximation (LDA)—derived pseudopotential wave functions. We have considered quantum dots of IV, III-V, and II-VI materials: Si (indirect gap at all sizes), GaAs (direct gap at large sizes and indirect gap at small sizes [18]), and CdSe (direct gap at all sizes). We find that (i) the EMA significantly *overestimates* the Coulomb energy $E_{\rm Coul}$ by as much as 40% in small quantum dots, (ii) the quantity $\epsilon E_{\rm Coul}$ has a *sublinear* dependent on $1/R$, and (iii) the exchange splitting $\Delta E_{\rm exch}$ is significantly smaller than $E_{\rm Coul}$, and in the case of CdSe quantum dots does not follow the $1/R^3$ scaling law predicted by the EMA. These conclusions have an immediate implication on the manner in which the results of electronic structure calculations are being currently compared with measured excitonic energies [2,3,5–8,16].

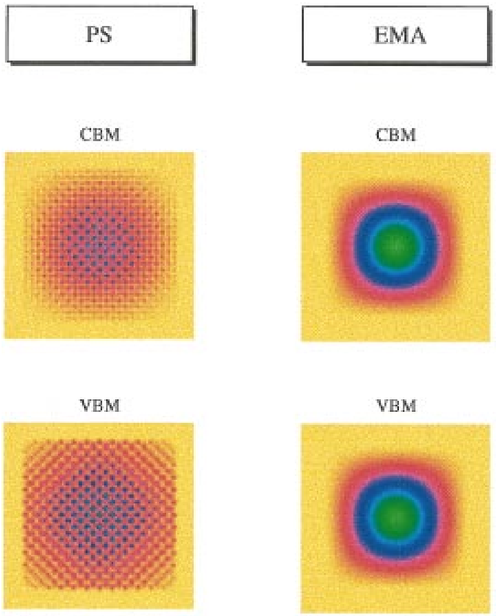

FIG. 1(color). The valence-band maximum (VBM) and conduction-band minimum (CBM) wave functions of a 6000-atom (110) × (1$\bar{1}$0) × (001) GaAs quantum dot, as obtained from a plane-wave pseudopotential calculation (left-hand side), are compared with the EMA envelope functions used in the calculation of the Coulomb and exchange energies (right-hand side). The wave function amplitude, averaged along the [001] direction, is plotted in the (001) plane.

In the self-consistent field (SCF) approach the electron and hole single-particle wave functions are obtained by minimizing the exciton energy under the assumption of uncorrelated exciton wave function. In the pseudopotential framework this leads to the coupled Hartree-like equations

$$\left[-\frac{\hbar^2}{2m_0}\nabla_e^2 + V_{\rm ps}(\mathbf{r}_e) - \frac{e^2}{\epsilon}\int \frac{|\psi_h(\mathbf{r}_h)|^2}{|\mathbf{r}_e - \mathbf{r}_h|} d^3 r_h\right]\psi_e(\mathbf{r}_e) = E_e\psi_e(\mathbf{r}_e), \quad (5a)$$

$$\left[-\frac{\hbar^2}{2m_0}\nabla_h^2 + V_{\rm ps}(\mathbf{r}_h) + \frac{e^2}{\epsilon}\int \frac{|\psi_e(\mathbf{r}_e)|^2}{|\mathbf{r}_h - \mathbf{r}_e|} d^3 r_e\right]\psi_h(\mathbf{r}_h) = E_h\psi_h(\mathbf{r}_h), \quad (5b)$$

where m_0 is the *bare* electron mass and $V_{\rm ps}(\mathbf{r})$, is the total *microscopic* pseudopotential of the quantum dot, is given here by a superposition of atomic screened potentials:

$$V_{\rm ps}(\mathbf{r}) = \sum_\alpha v_\alpha(\mathbf{r} - \mathbf{R}_\alpha). \quad (6)$$

We use the atomic potentials of Ref. [8] for Si, Ref. [19] for GaAs, and Ref. [20] for CdSe. These potentials were fitted to measured bulk transition energies, deformation potentials, and effective masses, and to surface work functions. Very significantly, these potentials were also constrained to reproduce LDA-calculated bulk wave functions (see procedure in Ref. [20]). The surface dangling bonds are passivated using hydrogenlike potentials in order to remove the surface states from the band gap and to decouple the band-edge states from surfacelike states. Equations (5a) and (5b) are solved self-consistently in a plane-wave representation using the folded-spectrum method [8] to single out the band-edge electron and hole wave functions from the remaining eigenstates, with a computational cost that scales only linearly with the size of the system. The Coulomb energy is then obtained from Eq. (1) as $E_{\rm Coul} = (1/\epsilon)\int \rho_h(\mathbf{r})V_e(\mathbf{r})d^3r$, where $\rho_h(\mathbf{r}) = e|\psi_h(\mathbf{r})|^2$ is the hole charge density and $V_e(\mathbf{r})$, the electrostatic Coulomb potential due to the electron, satisfies the Poisson equation $\nabla^2 V_e(\mathbf{r}) = -4\pi\rho_e(\mathbf{r})$ with $\rho_e(\mathbf{r}) = e|\psi_e(\mathbf{r})|^2$. The Poisson equation is solved inside a computational domain including the hydrogen-passivated quantum dot and a surrounding region of vacuum; the boundary conditions are obtained by a multipole expansion of the electron Coulomb potential. The Laplacian operator is discretized on a real-space grid, and the resulting linear system is solved using a conjugate-gradients algorithm.

A simpler approximation is to calculate perturbatively $E_{\rm Coul}$ from the *unperturbed* electron and hole wave functions ψ_e^0 and ψ_h^0, which are solutions of the single-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2 + V_{\rm ps}(\mathbf{r})\right]\psi_i^0(\mathbf{r}) = \epsilon_i^0\psi_i^0(\mathbf{r}). \qquad (7)$$

The results of self-consistent and perturbative calculations for the exciton ground-state Coulomb energy [21,22] of GaAs quantum dots are compared in Table I. As we can see, the perturbative approach mimics the self-consistent results within 10%, so it is a reasonably good approximation in the size range considered here. The validity of perturbation theory can be understood as follows. In small quantum dots, where the Coulomb integral is larger, the unperturbed single-particle energy levels are widely spaced, and perturbation theory can be applied to estimate electron-hole interaction. In larger quantum dots the energy levels are more closely spaced, but the Coulomb integral is smaller, and perturbation theory is still valid. The three highest occupied energy levels of GaAs quantum dots are very close in energy (two of them are actually degenerate). This degeneracy is split by the electron-hole interaction in the SCF calculation, but the splitting is very small (less than 2 meV in all the cases considered here).

Using unperturbed electron-hole wave functions, we have calculated the exciton Coulomb energy of Si, GaAs, and CdSe quantum dots of different sizes and shapes. To avoid clouding the results by the uncertainties in the size-dependent quantum dot dielectric constant [9,10], we write $E_{\rm Coul} = A_{\rm Coul}/\epsilon$, and calculate the coefficient $A_{\rm Coul}$. The effective size R is obtained from the number of atoms N as $R = a_0(\gamma N)^{1/3}$, where a_0 is the bulk lattice constant and $\gamma = 3/32\pi$ for spherical Si dots of radius R, $\gamma = 1/8\sqrt{2}$ for rectangular GaAs dots of size $R \times R \times \sqrt{2}R$, and $\gamma = \sqrt{3}\,c_0/8a_0$ for cubical wurtzite CdSe dots of size $R \times R \times R$. The Coulomb energy of the exciton ground state [21] is compared in Table II with the EMA Coulomb energy obtained from Eq. (3). As we can see, the EMA consistently overestimates $A_{\rm Coul}$ by as much as 40% in small quantum dots. We have also calculated the pseudopotential Coulomb energy of several pairs of states close to the band edges, finding that $A_{\rm Coul}$ is at most 40 meV larger than the ground-state Coulomb energy.

TABLE I. Electron-hole Coulomb energy $E_{\rm Coul}$ of GaAs rectangular quantum boxes, obtained using the self-consistent field approximation (SCF) and first-order perturbation theory (FOPT). A modified Penn model [22] is used to evaluate the size-dependent dielectric constant.

Effective size (Å)	$E^{\rm SCF}_{\rm Coul}$ (meV)	$E^{\rm FOPT}_{\rm Coul}$ (meV)
9.8	389	374
13.8	258	251
17.7	195	187
21.7	158	149
25.7	127	123
29.7	110	106
33.7	97	93
37.7	81	79

There are several reasons for the overestimation of the Coulomb energy by the EMA. First, the EMA envelope functions are required unrealistically to vanish exactly at the boundary of the quantum dot, while the pseudopotential wave functions are allowed to decay variationally and spill out into the vacuum region, as illustrated in Fig. 1. While the inclusion of a finite potential barrier in the EMA calculations leads to a reduction of the Coulomb energy [23], the concept of a band discontinuity used by the EMA is ambiguous when the quantum dot is embedded in glass, organic solvents, or vacuum, and the applicability of the EMA itself becomes uncertain in these cases. Second, the contribution to the Coulomb energy resulting from the *microscopic* oscillations of the wave function (Fig. 1) are completely neglected in the EMA. Finally, even when the microscopic oscillations are integrated out, the pseudopotential *macroscopic* envelope function can still

TABLE II. Electron-hole Coulomb and exchange energies of spherical Si quantum dots, rectangular GaAs quantum dots, and wurtzite CdSe quantum boxes, as obtained from first-order perturbation theory. The columns labeled $A^{\rm PS}_{\rm Coul}$ and $A^{\rm EMA}_{\rm Coul}$ show the unscreened Coulomb energy of the ground-state electron-hole pair, calculated using pseudopotential wave funcitons (PS), and effective-mass envelope functions (EMA). The screened Coulomb energy $E^{\rm PS}_{\rm Coul} = A^{\rm PS}_{\rm Coul}/\epsilon$ is obtained using a modified Penn model [22] for the dot dielectric constant; $\Delta E^{\rm PS}_{\rm exch}$ is the exciton exchange splitting.

Effective size (Å)	$A^{\rm PS}_{\rm Coul}$ (eV)	$A^{\rm EMA}_{\rm Coul}$ (eV)	$A^{\rm EMA}_{\rm Coul}/A^{\rm PS}_{\rm Coul}$	$E^{\rm PS}_{\rm Coul}$ (meV)	$\Delta E^{\rm PS}_{\rm exch}$ (meV)
Si spherical quantum dots					
7.5	2.671	3.446	1.29	340	62
8.9	2.251	2.893	1.28	270	35
10.4	1.954	2.474	1.27	223	21
13.5	1.670	1.907	1.14	176	13
GaAs rectangular quantum dots					
9.8	2.845	3.947	1.39	374	93
13.8	2.120	2.813	1.33	251	29
17.7	1.700	2.182	1.28	187	14
21.7	1.423	1.782	1.25	149	8
25.7	1.221	1.506	1.23	123	6
29.7	1.076	1.303	1.21	106	4
33.7	0.962	1.149	1.19	93	
37.7	0.837	1.027	1.23	79	
41.7	0.765	0.929	1.21	71	
45.7	0.705	0.847	1.20	64	
49.7	0.654	0.779	1.19	59	
53.7	0.610	0.721	1.18	54	
CdSe cubical quantum dots					
9.0	3.502	4.875	1.39	669	173
16.6	2.077	2.639	1.27	294	97
24.3	1.495	1.808	1.21	184	57

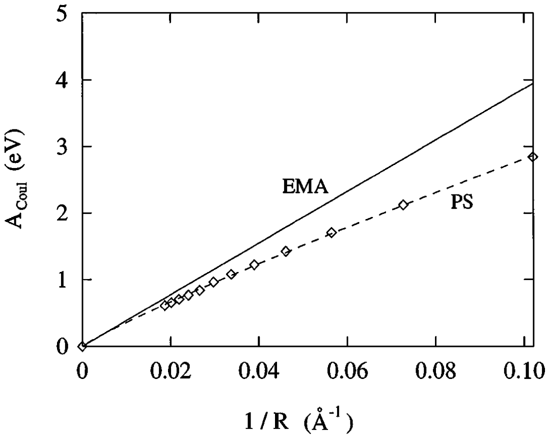

FIG. 2. Unscreened Coulomb energy A_{Coul} of GaAs quantum dots calculated using unperturbed pseudopotential wave functions (PS) and effective-mass envelope functions (EMA).

differ from the corresponding EMA envelope function (Fig. 1). The electron-hole Coulomb energy of GaAs quantum dots is plotted in Fig. 2 as a function of the inverse size $1/R$. The pseudopotential Coulomb energy can be fitted by the power law $E_{\text{Coul}} \sim 1/R^{\alpha}$, where $\alpha =$ 0.82, 0.90, and 0.86 for Si, GaAs, and CdSe quantum dots, respectively; this should be contrasted with the universal $1/R$ scaling law predicted by the EMA.

We have also calculated the electron-hole exchange splitting of Si, GaAs, and CdSe quantum dots using unperturbed electron-hole wave functions. We do not restrict the exchange to its short-range term alone [15,17]. The results are summarized in the last column of Table II. Even for the smallest dots considered here the exchange splitting is almost 1 order of magnitude smaller than the Coulomb energy. While in Si and GaAs quantum dots the exchange splitting scales approximately as $1/R^3$, as predicted by the EMA, the scaling follows a much lower power law in the case of CdSe quantum dots.

In conclusion, we have used microscopic, LDA-quality wave functions to calculate the exciton Coulomb and exchange energies of semiconductor nanocrystals. We find that in the strong confinement regime the Coulomb energy is well reproduced by a simple perturbative approach, but the results differ from the widely accepted EMA calculations by as much as 40%; furthermore, the Coulomb energy has a sublinear scaling with the inverse size. We also find that the exchange energy is significantly smaller than the Coulomb energy, and that in the case of CdSe quantum dots the exchange splitting deviates from the $1/R^3$ scaling law predicted by the EMA.

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