

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

Alberto Franceschetti and Alex Zunger

*National Renewable Energy Laboratory, Golden, Colorado 80401*

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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 than the bulk exciton radius, correlation effects become negligible [2–4], and the electron-hole Coulomb and exchange integrals have the form

$$E_{\text{Coul}} = \frac{e^2}{\epsilon} \sum_{s_h, s_e} \int \frac{j_{C_h}(\mathbf{r}_h, \mathbf{s}_h) j_{C_e}(\mathbf{r}_e, \mathbf{s}_e)}{|\mathbf{r}_h - \mathbf{r}_e|} d\mathbf{r}$$

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  $E_{\text{Coul}}$  and  $DE_{\text{exch}}$  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  $E_{\text{Coul}}$  and  $DE_{\text{exch}}$ . 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  $E_{\text{Coul}}$  by as much as 40% in small quantum dots, (ii) the quantity  $eE_{\text{Coul}}$  has a *sublinear* dependent on  $1/R$ , and (iii) the

exchange splitting  $DE_{\text{exch}}$  is significantly smaller than  $E_{\text{Coul}}$ , 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].

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

$$\left[ 2 \frac{\hbar^2}{2m_0} \right]$$

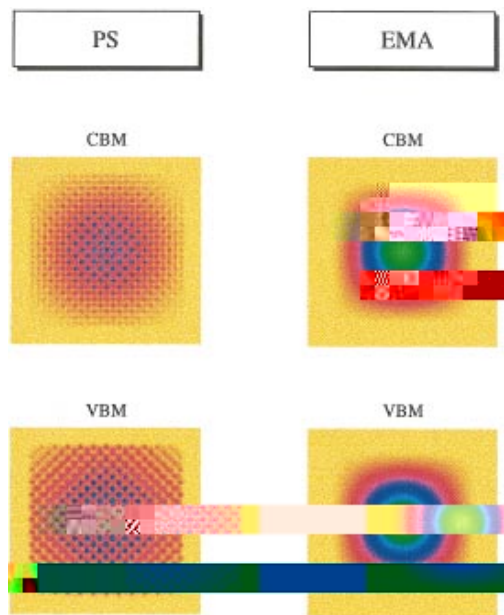


FIG. 1(color). The valence-band maximum (VBM) and conduction-band minimum (CBM) wave functions of a 6000-atom  $s110d \ 3 \ s110d \ 3 \ s001d$  GaAs quantum dot, as obtained from a plane-wave pseudopotential calculation (left-hand side), are compared with the EMA envelope functions used in the calculation of the Coulomb and exchange energies (right-hand side). The wave function amplitude, averaged along the [001] direction, is plotted in the (001) plane.

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

$$\left[ \frac{\hbar^2 \nabla^2}{2m_0} + V_{\text{ps}}(\mathbf{r}) \right] c_i^0(\mathbf{r}) = \epsilon_i^0 c_i^0(\mathbf{r}). \quad (7)$$

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

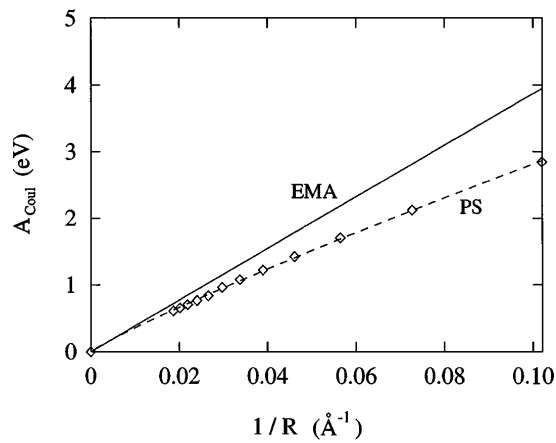


FIG. 2. Unscreened Coulomb energy  $A_{\text{Coul}}$  of GaAs quantum dots calculated using unperturbed pseudopotential wave functions (PS) and effective-mass envelope functions (EMA).

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  $E_{\text{Coul}} \propto 1/R^a$ , where  $a = 0.82, 0.90$ , 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.