Optical transitions in charged CdSe quantum dots

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Using a many-body approach based on single-particle pseudopotential wave functions, we calculate the dependence of the optical transitions in CdSe nanocrystals on the presence of ''spectator'' electrons or holes. We find that (i) as a result of the different localization of the electron and hole wave functions, the *absorption* lines shift by as much as 22 meV/unit charge when electrons or holes are loaded into the quantum dot. (ii) The lowest *emission* line is significantly red shifted with respect to the lowest allowed absorption line. (iii) Trapping of a ''spectator'' hole in a surface state is predicted to lead to dramatic changes in the absorption spectrum, including the appearance of new transitions.

Semiconductor quantum dots can be charged by deliberate injection of carriers (via electrical contacts,[1] or via a scanning-tunneling-microscopy tip,[2]) by photoionization processes removing one or more carriers from the quantum dot,[3] or by capture of external charges.[4] The effects of charging on the optical properties of *self-assembled* InAs/GaAs quantum dots have been recently measured both in absorption[5] and emission.[6] It was found that when electrons are progressively loaded into the quantum dots, the absorption and emission energies are redshifted relative to the neutral dots. Furthermore, low-energy lines disappear from the absorption spectrum,[5] while new high-energy lines appear in the photoluminescence spectrum.[6] In *colloidal* quantum dots, charging of surface states is believed to be at the origin of a variety of unusual phenomena, including the occurrence of a permanent dipole moment even in zincblende dots,[7] intermittency (blinking) of photoluminescence,[3] spectral diffusion and Stark shift,[8] upconversion of photoluminescence,[9] and possibly even the occurrence of long spin lifetimes.[10] However, there are still no reports on the absorption or emission spectra of charged colloidal dots.

The effects of charging on the interband optical transitions can be examined using a screened Hartree-Fock model, where the initial and final states are expressed as Slater determinants. The energy $\Delta E_{h,e}(N_{e_s})$ required to optically excite an electron from the valence-band state h to the conduction-band state e in the presence of N_{e_s} ''spectator electrons'' (e_s) is:

$$\Delta E_{h,e}(N_{e_s}) = (\varepsilon_e - \varepsilon_h - J_{h,e}) + \sum_{e_s=1}^{N_{e_s}} (J_{e,e_s} - J_{h,e_s})$$
$$+ \Delta E_{\text{exch}}(N_{e_s}), \qquad (1)$$

where ε_e and ε_h are the single-particle energies of the optically excited electron and hole, $J_{h,e}$ is their mutual Coulomb attraction, J_{e,e_s} is the Coulomb repulsion between the optically excited electron and the spectator electrons, J_{h,e_s} is the Coulomb attraction between the optically excited hole and the spectator electrons, and ΔE_{exch} is the exchange energy between the electron-hole pair and the spectator electrons. Similarly, for N_{h_s} ''spectator holes'' (h_s):

$$\Delta E_{h,e}(N_{h_s}) = (\varepsilon_e - \varepsilon_h - J_{h,e}) + \sum_{h_s=1}^{N_{h_s}} (J_{h,h_s} - J_{e,h_s})$$
$$+ \Delta E_{\text{exch}}(N_{h_s}). \qquad (2)$$

These expressions illustrate the effects of charging on the electron-hole excitation energies: (i) Since the wave functions of the electron e and the hole h are generally different, it follows that $J_{e,e_s} \neq J_{h,e_s}$ and $J_{e,h_s} \neq J_{h,h_s}$. As a result, the Coulomb interaction between the photoexcited electron-hole pair and the spectator particles [second term in Eqs. (1) and (2)] can shift the excitation energies $\Delta E_{h,e}$. This Coulomb shift is missed by simple effective-mass models assuming identical wave functions for the electron and the hole. (ii) The exchange energy ΔE_{exch} [last term in Eqs. (1) and (2)] depends on the relative spin orientation of the spectator particles and the photoexcited electron and hole. Therefore, in the presence of spectator electrons or holes the excitonic transitions can split into spin-multiplet lines. (iii) The excitation energies $\Delta E_{h,e}$ can depend on whether the spectator particles are delocalized over the quantum dot or localized at the surface of the dot. (iv) By occupying previously empty conduction levels, the spectator particles can block optical transitions that would be otherwise allowed in a neutral dot (Pauli blocking). These physical effects and the practical ability to inject carriers in colloidal and self-assembled quantum dots[1,2] open the way to novel engineering of the optical properties of nanostructures via controlled loading of ''spectator carriers'' into them. In this paper we use a many-body approach based on atomistic pseudopotential wave functions to predict the interband absorption and emission spectra of a CdSe nanocrystal (~ 40 Å diameter) as a function of the net charge present in the dot. We discuss how the presence of

TABLE I. Near band-edge single-particle energy levels (in eV) of a 38.5 Å-diameter CdSe nanocrystal, calculated using the pseudopotential approach.

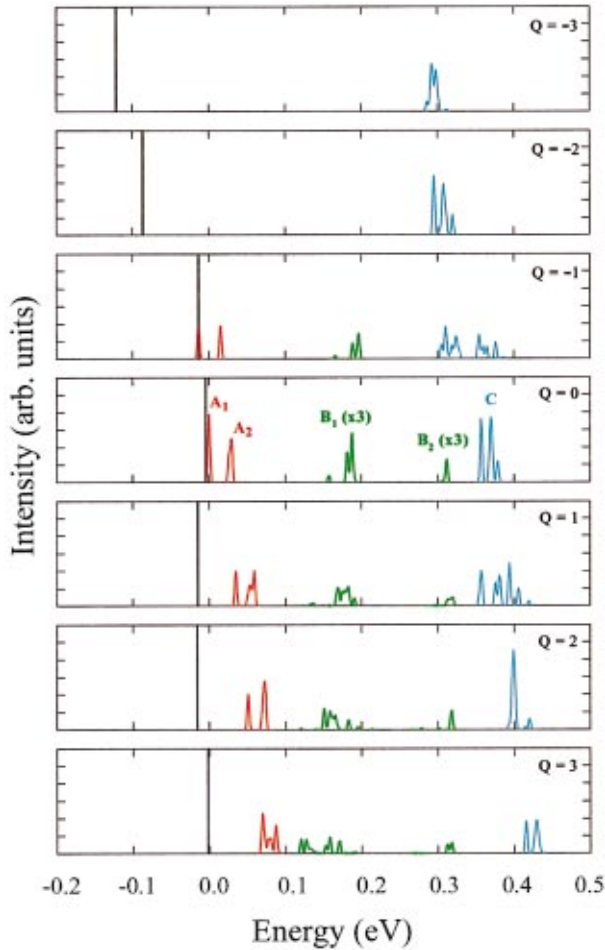| Holes states		Electron states	
h_1	0.000	e_1	2.350
h_2	-0.029	e_2	2.649
h_3	-0.039	e_3	2.657
h_4	-0.041	e_4	2.660

FIG. 1. (Color) Absorption spectrum of a $38.5-$Å-diameter CdSe nanocrystal as a function of the charge Q present in the dot. The labels A, B, and C refer to different transitions, as discussed in the text. The vertical black lines indicate the position of the lowest emission energies. The zero of the energy scale coincides with the lowest absorption line (A_1) of the neutral dot ($Q=0$).

spectator electrons or holes can alter the optical transitions in quantum dots, leading to Coulomb shifts, exchange splittings, and Pauli blocking.

The single-particle energies ε_i and wave functions $\psi_i(\mathbf{r},\sigma)$ of the quantum dot are obtained by solving the pseudopotential Schrödinger equation (atomic units are used in the following)

$$[-\nabla^2/2 + V_{ps}(\mathbf{r}) + \hat{V}_{nl}]\psi_i(\mathbf{r},\sigma) = \varepsilon_i \psi_i(\mathbf{r},\sigma), \quad (3)$$

where $V_{ps}(\mathbf{r})$ is the total pseudopotential of the quantum dot and $\hat{V}_{nl}$ is a short-range operator that accounts for the non-local part of the potential as well as spin-orbit coupling. The total pseudopotential $V_{ps}(\mathbf{r})$ is calculated from the superposition of screened atomic pseudopotentials, which are fitted[11] to reproduce the measured bulk transition energies, deformation potentials, and effective masses, as well as the bulk single-particle wave functions calculated using density-functional theory in the local-density approximation.

The excited states of the quantum dot are expanded in terms of Slater determinants obtained by creating holes in the valence band and adding electrons to the conduction band. Since correlation effects due to charging are small[12] on the

scale of the Coulomb and exchange energies of Eqs. (1) and (2), we retain in the many-body expansion only Slater determinants having the same single-particle energy. This allows us to accurately treat the electron-electron, electron-hole, and hole-hole Coulomb and exchange interactions. In this approximation we neglect (i) the response of the single-particle wave functions to the electrostatic field set up by the net charge (i.e., self-consistent effects), and (ii) the coupling between orbital configurations with different energies (i.e., configuration-interaction effects). These assumptions are sufficiently accurate in three-dimensional quantum structures in the strong-confinement regime.[12–15] In Ref. 13 we compared the electron-hole Coulomb energies of neutral ($Q=0$) quantum dots calculated using unperturbed single-particle wave functions with the results of a self-consistent Hartree calculation. We found that the Coulomb energies change by less than 5% when self-consistent effects are taken into account. In Ref. 14 we showed that the main effect of the configuration interaction on the excitonic energy levels of quantum dots is a nearly uniform down shift of 2–5 meV.

The many-body Hamiltonian is then diagonalized in the basis of the Slater determinants. The Coulomb and exchange matrix elements are calculated using the atomistic wave functions obtained from Eq. (3), and are screened by a phenomenological dielectric constant:

$$V(ij,kl) = \int \int \frac{\psi_i^*(x)\,\psi_j^*(x')\psi_k(x)\,\psi_l(x')}{\epsilon(\mathbf{r},\mathbf{r}',R)|\mathbf{r}-\mathbf{r}'|}\,dx\,dx' \quad (4)$$

where $x=(\mathbf{r}\sigma)$. The screening function $\epsilon(\mathbf{r},\mathbf{r}',R)$ depends[14] on the interparticle separation $|\mathbf{r}-\mathbf{r}'|$ and on the nanocrystal radius R. Since $\epsilon(\mathbf{r},\mathbf{r}',R)$ tends to 1 when $\mathbf{r}\to\mathbf{r}'$, the short-range exchange and Coulomb interactions are *unscreened*.[14] The Coulomb energies of Eqs. (1) and (2) are given by $J_{i,j} = V(ij,ij)$. In calculating the Coulomb and exchange integrals of Eq. (4) one should include the effects of the surface polarization charge generated by the dielectric mismatch between the quantum dot and the surrounding material.[16] Since optical transitions do not modify the net charge of the quantum dot, however, the polarization contribution is almost identical in the initial and final state, and can be neglected.[16] The diagonal matrix elements of the Hamiltonian contain the single-particle energies ε_i obtained from Eq. (3), which describe the single-particle excitations of the neutral dot. The single-particle energies are modified by the electrostatic potential generated by the presence of spectator particles. In the many-body Hamiltonian, however, the *bare* single-particle energies must be used in order to avoid double counting of the interaction.

We consider here a nearly spherical CdSe nanocrystal of diameter $D=38.5$ Å having the wurtzite lattice structure. The size and shape of this dot is fairly typical of nanocrystals grown by the colloidal chemistry method. The surface dangling bonds are passivated using a ligandlike potential. Table I gives the pseudopotential-calculated near band-edge electron and hole single-particle energy levels of this quantum dot. The level at the bottom of the conduction band (e_1) has an s-like envelope function, while the next three levels (e_2, e_3, and e_4) have a p-like envelope function. The two levels at the top of the valence band (h_1 and h_2) have an s-like envelope function, and are split by crystal-field effects. The

next two levels (h_3 and h_4) have a p-like envelope function. We find that this sequence of energy levels is typical of a wide range of nanocrystal sizes.

Figure 1 shows the calculated absorption spectrum (color lines) and the lowest emission energies (black vertical lines) as a function of the net charge Q present in the quantum dot. We assume that the system relaxes to the electronic ground state before an electron-hole pair recombines (in emission) or is created (in absorption). We can identify three groups of peaks (denoted A, B, and C in Fig. 1) in the absorption spectrum. Group A originates from the $h_1 \rightarrow e_1$ transition (A_1) and the $h_2 \rightarrow e_1$ transition (A_2). The splitting between the A_1 and A_2 peaks corresponds to the crystal-field splitting (finite in wurtzite-structure quantum dots) between the single-particle levels h_1 and h_2 (see Table I). Peaks B_1 and B_2 originate from the $h_9 \rightarrow e_1$ and the $h_{23} \rightarrow e_1$ transitions, respectively. The hole states h_9 and h_{23} have a small s-like component, so they are optically coupled to the s-like electron state e_1. Group C originates from the $(h_3, h_4) \rightarrow (e_2, e_3, e_4)$ transitions, and shows a fine structure consisting of multiple optically allowed lines. This structure arises from the fact that the h_3 and h_4 hole states (as well as the e_2, e_3, and e_4 electron states) are nondegenerate (see Table I). Further splitting is induced by electron-hole, electron-electron, and hole-hole exchange interactions between the optically excited electron-hole pair and the spectator particles, as shown by Eqs. (1) and (2). In the following we discuss the main features of the absorption and emission spectra in the presence of spectator charges.

Pauli blocking of the $h_n \rightarrow e_1$ transitions. Figure 1 shows that the low-energy absorption peaks A_1, A_2, B_1, and B_2 disappear when two or more electrons are loaded in the dot ($Q = -2$ or $Q = -3$). The reason is that when the e_1 level is occupied by two electrons, interband transitions into the e_1 level ($h_n \rightarrow e_1$ transitions) are blocked. Interestingly, we do not see Pauli blocking of the A_1 transition in the case of holes (at least up to $Q = 3$) as one would expect if the h_1 level were doubly occupied. In fact, the lowest-energy configuration of the system with Q holes does not follow the Aufbau principle, which states that the electron (hole) levels are occupied in order of increasing (decreasing) single-particle energies. For example, for $Q = 2$ the initial configuration has one hole in the h_1 level and one hole in the h_3 level, since this configuration minimizes the hole-hole Coulomb repulsion. This arrangement leaves room for the $h_1 \rightarrow e_1$ transition (A_1 line) to occur even when $Q = 2$.

Dependence of the optical absorption on the charge Q. Figure 1 shows that peaks A and C are redshifted as electrons are progressively loaded into the quantum dot, while peak B_1 is blueshifted. The derivative dE_i/dQ of the absorption energies with respect to the charge Q is approximately 22 meV/e for the A_1, A_2, and C peaks, and -10 meV/e for the B_1 peak. Wojs and Hawrylak[17] calculated the shift of the emission energy in charged self-assembled quantum dots using the effective-mass approximation, and found that the lowest-energy transition (''peak A'') is red shifted when electrons are loaded into the quantum dot. Since in their model the electron and hole effective-mass orbitals were almost identical,[17] the direct Coulomb shift of the emission

line [second term in Eqs. (1) and (2)] was small, and the redshift was attributed to electron-electron exchange interactions [third term in Eqs. (1) and (2)]. In contrast, we find that in CdSe nanocrystals the shift is primarily due to direct Coulomb interactions between the optically excited electron-hole pair and the spectator particles. For example, since the hole state h_1 is more localized than the electron state e_1, it follows that $J_{h_1,e_1} > J_{e_1,e_1}$. As a result, the transition energy $\Delta E_{h_1,e_1}$ (peak A_1) is redshifted when a spectator electron is loaded into the quantum dot. Figure 2 shows the shift of peaks A–C with charge, both in the single-configuration approximation and in a simpler model retaining only the diagonal Coulomb energies $J_{i,j}$ between the optically excited electron-hole pair and the spectator particles [second term in Eqs. (1) and (2)]. We see that the diagonal Coulomb approximation reproduces closely the evolution of the peaks, confirming that the shifts are due to the direct Coulomb interactions. The dominance of the direct Coulomb term over the exchange term shows that it is possible to have a *blue* shift upon electron charging, if the hole state is *less* localized than the electron state. This is what we observe, for example, in the case of the B_1 transition.

Stokes shift of the emission line relative to absorption. The lowest-energy emission line is redshifted with respect to the lowest-energy absorption line. Few cases can be distinguished: (i) In the case of a neutral dot ($Q = 0$) the Stokes shift is small (a few meV), and is due to the electron-hole exchange interaction.[14] The $h_1 \rightarrow e_1$ transition is split by the exchange interaction into two doublets [see Fig. 3(a)]: The higher-energy doublet is optically allowed, while the lower energy doublet is optically forbidden. (ii) When one spectator electron is present in the dot ($Q = -1$) there is no Stokes shift: Since the final configuration has two electrons in the e_1 level, the electron-hole exchange interaction does not split the excitonic transition. As a result, the lowest emission energy coincides with the lowest absorption energy. (iii) In the cases $Q = -2$ (two spectator electrons) and $Q = -3$ (three spectator electrons) the Stokes shift is large (~ 400 meV). This is so because the lowest emission line originates from the $e_1 \rightarrow h_1$ recombination, while the lowest (allowed) absorption line originates from the $h_3 \rightarrow e_2$ transition. The $h_1 \rightarrow e_1$ transition (A_1 line) is blocked, because the e_1 state is already occupied by two electrons. (iv) In the case $Q = 1, 2, 3$ holes the Stokes shift is relatively large (about $50 - 70$ meV). This is due to the fact that the lowest-energy transition is optically forbidden, as it corresponds to a transition from a p-like hole state (h_3 for $Q = 1$ and $Q = 3$, h_4 for $Q = 2$) to the s-like e_1 electron state.

Effects of surface trapping. It is now becoming clear[18,19] that surface states play an important role in the optical properties of free-standing nanocrystals. In order to examine the generic effects of charges trapped in a surface state on the optical absorption, we have removed the passivating atom from a threefold-coordinated Se atom, thus creating a single dangling bond. The solution of the Schrödinger equation (3) yields a surface state s_1 whose energy is ~ 50 meV above the valence-band maximum. This states extends into the core of the quantum dot. Figure 3 compares the absorption spec-
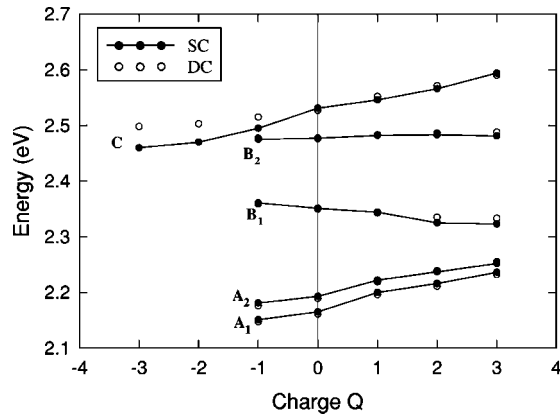
FIG. 2. Dependence of the absorption energies, calculated using the single-configuration (SC) approximation, on the charge Q (solid lines and circles). The empty circles show the absorption energies in the diagonal Coulomb approximation (DC), which corresponds to Eqs. (1) and (2) where only the Coulomb energies are retained.
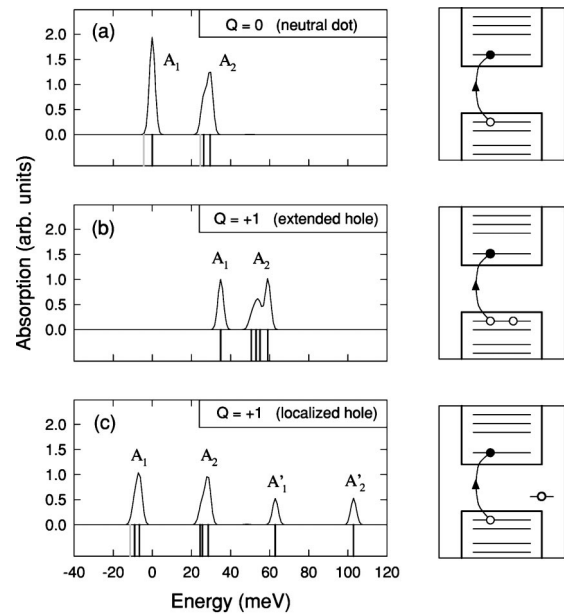

FIG. 3. The low-energy absorption spectrum of a neutral dot (a) is compared with the absorption spectrum of a charged dot ($Q=1$) where the spectator hole is delocalized over the quantum dot (b) or trapped in a surface state (c). The peaks are labeled as in Fig. 1. Also shown are the energies of the forbidden (gray vertical lines) and allowed (black vertical lines) transitions. The panels on the right-hand side of the figure show in the three cases the interband transitions responsible for the A_1 absorption line.

trum in the presence of a spectator hole in the h_1 level with the absorption spectrum when the additional hole is trapped in the surface state s_1. Also shown is the absorption spectrum of the neutral dot ($Q=0$). We see that in the presence of a hole localized in the surface state the peaks A_1 and A_2 shift to the red by ~ 40 meV, compared to the case where the hole is delocalized. In addition, two new peaks, denoted A_1' and A_2' in Fig. 3, appear in the absorption spectrum. The reason for this behavior is twofold: (i) The Coulomb electron-hole attraction and hole-hole repulsion are modified by the trapping of the hole at the surface of the nanocrystal. Since the spectator hole is spatially separated from the active electron-hole pair, the Coulomb interaction is reduced. Compared to the neutral dot ($Q=0$), we find that the Coulomb interactions blue shift the A_1 transition by $J_{h_1,h_1}-J_{e_1,h_1} =35$ meV when the spectator hole is delocalized over the quantum dot, and by $J_{s_1,h_1}-J_{e_1,s_1}=27$ meV when the spectator hole is localized in the state s_1. (ii) The exchange interaction between the photoexcited hole in the quantum dot and the spectator hole localized in the surface state causes an exchange splitting of the A_1 and A_2 transitions, which results

in the appearance of the A_1' and A_2' lines. Interestingly, the exchange splitting is quite large despite the h_1 and s_1 states having different spatial localization. The reason is that the s_1 wave function penetrates the interior of the quantum dot, and has a significant overlap with the h_1 wave function.

In conclusion, we have shown that the presence of spectator carriers in a quantum dot significantly alters the interband optical transitions. Experimental measurements of absorption and emission spectra in charged CdSe dots are called for.

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