Absorption Blue Shift in Laser-Excited Semiconductor Microspheres

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The energy of an electron-hole pair in laser-excited semiconductor microcrystallites is computed with plasma screening and dielectric polarization taken into account. A strong excitation-induced blue shift of the absorption is predicted which causes a large optical nonlinearity for crystallite sizes exceeding the bulk-exciton Bohr radius.

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Quantum confinement effects in semiconductor systems with reduced dimensions have attracted considerable attention within the last few years. Besides the well-known multiple-quantum-well structures which provide confinement in one dimension, quite recently also semiconductor microcrystallites were investigated which confine the laser-excited electron-hole pairs in all three space dimensions.[1-5] Such systems are readily available in the form of colloids[4] or semiconductor microcrystallite-doped glasses. The nonlinear optical properties of the glasses are presently being studied extensively[2,3,6-11] and experimental results on four-wave mixing, phase conjugation, luminescence, and femtosecond carrier dynamics have been reported.

It is now well established that the finite size of the microcrystallites causes an increase in the kinetic energy of the confined quasiparticles. Efros and Efros have shown[1] that quantitatively different confinement effects occur depending on the ratio of the crystallite radius R and the Bohr radius of the electron-hole pairs, of the holes and of the electrons, respectively. For the different regimes of crystallite sizes one has either quantization of the center of mass motion of the electron-hole pair, of the hole motion, or of the electron motion. Besides these kinetic energy effects, quite recently Brus[4] has also calculated the important modification of the electrostatic energy of an electron-hole pair due to dielectric polarization at the boundary of the crystallites.

In the present Letter, we predict strong excitation-dependent quantum-size effects for the regime in which the crystallite radius is larger than the Bohr radius a_0^0 of the exciton in the corresponding bulk material. Under these conditions, without laser excitation one has only a relatively small blue shift of the exciton ground-state energy in comparison to the bulk material. The exciting light, however, leads to the creation of additional electron-hole pairs, which screen the Coulomb potential causing an increase of the exciton Bohr radius a_0 and therefore an excitation-dependent ratio R/a_0. For larger Bohr radii confinement effects become increasingly important, leading to a pronounced *excitation-induced* blue shift of the exciton absorption and, hence, to strong optical nonlinearities in the spectral regime of the semiconductor band gap.

In detail, we consider a system of semiconductor microspheres with $R > a_0^0$ embedded in a host material with dielectric constant ε_2. For semiconductors such as CdS, CdSe, or GaAs, this implies crystallite sizes around 100 Å up to several hundred angstroms, respectively, for which it is justified to assume the bulk semiconductor band structure and to apply the effective-mass approximation. In fact, it has been shown[12] that the effective-mass approximation holds even for very small crystallites, containing as little as 95 atoms. In our computations, finite-size effects enter in two ways: (i) The electrostatic energy of an electron-hole pair is modified because of polarization effects and (ii) the quantum-mechanical motion of the quasiparticles is influenced through the condition that the wave functions vanish at the crystallite boundaries.

As usual, we compute the electrostatic energy as $W = \frac{1}{2}\int d^3r\, V(\mathbf{r})\rho(\mathbf{r})$, where ρ is the charge density, which vanishes for $r > R$, and the potential V obeys Poisson's equation. The charge density inside the sphere is composed of the external charge ρ^{ext} (two point charges $+e$ at $\mathbf{r}_1$ and $-e$ at $\mathbf{r}_2$, respectively) and of the induced plasma charge ρ^{ind}, which is related to V through $\rho^{\text{ind}} = -(\varepsilon_1/4\pi)\kappa^2 V$, where the inverse screening length is given by $\kappa = [(4\pi e^2/\varepsilon_1)(\partial n/\partial\mu)]^{1/2}$. The quantity ε_1 is the background dielectric constant of the crystalline, n is the average free-carrier concentration, and μ is the quasi chemical potential. The Poisson equation for V has to be solved by use of appropriate boundary conditions for a sphere.

Since the electrostatic energy diverges for pointlike external charges (self-interaction), we compute only the variation $\delta W = W(R) - W(\infty)$. The properly subtracted bulk electrostatic energy is the screened Coulomb potential

$$-(e^2/|\mathbf{r}_1-\mathbf{r}_2|)\exp(-\kappa|\mathbf{r}_1-\mathbf{r}_2|).$$

Because of linear superposition, one may solve the problem by calculating the potential U for a single point charge,

$$V(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) = U(\mathbf{r};\mathbf{r}_1) - U(\mathbf{r};\mathbf{r}_2).$$

Expanding U in terms of Legendre polynomials, applying the conditions of total internal charge neutrality, of finiteness in the origin and vanishing at infinity, one obtains an explicit expression for U, and hence δW, in terms of Bessel functions.[13] For vanishing κ our result reduces to that of Ref. 4 (although it is not explicitly given there).

As a second step, we have to solve the quantum-mechanical two-body problem with the Hamiltonian

$$H = -\frac{(\hbar\nabla_1)^2}{2m_1} - \frac{(\hbar\nabla_2)^2}{2m_2} - \frac{e^2 e^{-\kappa|\mathbf{r}_1-\mathbf{r}_2|}}{\varepsilon_1|\mathbf{r}_1-\mathbf{r}_2|} + \delta W(\kappa r_1,\kappa r_2,\mathbf{r}_1\cdot\mathbf{r}_2/r_1 r_2,\kappa R,\varepsilon_1/\varepsilon_2)$$

taking into account the boundary conditions for the wave functions at the surface of the sphere. In bulk semiconductors $(R\rightarrow\infty)$, one can separate the center of mass and the relative motions of the electron and hole in the presence of a screened Coulomb potential. Although the Schrödinger equation cannot be solved exactly even in this relatively simple case, one has a very good approximation if one replaces the screened Coulomb potential by the Hulthén potential,[14,15] for which the s wave functions Ψ and the energy eigenvalues E are explicitly known. Details of the calculation for bulk semiconductors are given in Ref. 15. Here, we only mention that within the discussed approximations, the electron-hole ground-state energy is $E = -E_R(1-1/g)^2$, where E_R is the Rydberg energy. The exciton Bohr radius in the presence of screening is $a_0 = a_0^b g/(g-1)$ with $g = 12/(\pi^2 a_0^b \kappa)$. Without screening, $g=\infty$, and one obtains the known Coulomb results, while for $g=1$ no bound states exist.

If the radius R of the semiconductor microspheres considerably exceeds a_0^b, one expects only small size-dependent energy corrections. However, through the screening effects caused by the laser-generated electron-hole plasma of density n, the exciton radius a_0 increases and approaches R. For the situation $a_0 \simeq R$, one can approximate the pair wave function Ψ as a product of the electron and hole wave functions in a spherical potential well representing the crystallite and compute the lowest energy level of the electron-hole pair as $E_x = E_g + \langle\Psi|H|\Psi\rangle$. Here, E_g is the bulk band-gap energy in the presence of the electron-hole plasma.[15] In the regime $R \simeq a_0$, one obtains the total shift $\delta E_x = E_x(\kappa,R) - E_x(0,\infty)$ of the bound-state energy due to finite-size effects as

$$\frac{\delta E_x}{E_R} = \left(1-\frac{1}{g}\right)^2 + \left(\frac{\pi a_0^b}{R}\right)^2 + \frac{2a_0^b}{R}\bar{V}\left(\kappa R;\frac{\varepsilon_1}{\varepsilon_2}\right).$$

The first term on the right-hand side of this equation describes the reduction of the exciton binding energy in a bulk semiconductor due to screening,[15] the second term is the kinetic energy contribution due to quantum confinement,[1,4] and the third term represents the average electrostatic energy of the electron-hole pair inside the microcrystallite in the presence of plasma screening. The function $\bar{V}$ has been computed numerically and is plotted in Fig. 1 for two ratios of $\varepsilon_1/\varepsilon_2$. For $\varepsilon_1=\varepsilon_2$ no dielectric polarization occurs at the interface between microcrystallite and bulk material and only the screening effects are present. For large κR the function $\bar{V}$ becomes independent of $\varepsilon_1/\varepsilon_2$ since for strong screening the Coulomb potential essentially decreases to zero within

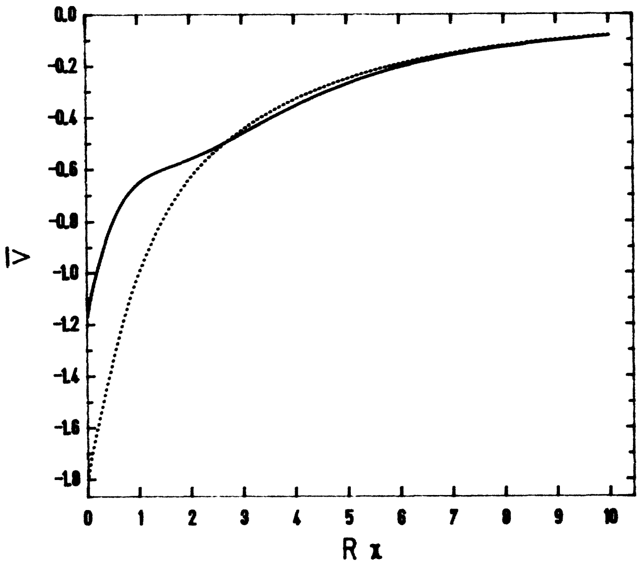

FIG. 1. Comparison of the average electrostatic energy $\bar{V}$ of an electron-hole pair in a microcrystallite (in units of $2E_R a_0^b/R$) for two ratios of the background dielectric constants of the crystallite, ε_1, and of the host material, ε_2. Solid line, $\varepsilon_1/\varepsilon_2=10$; dotted line, $\varepsilon_1/\varepsilon_2=1$. R is the radius of the microcrystallites, κ is the inverse screening length, E_R is the bulk-exciton Rydberg, and a_0^b is the bulk-exciton Bohr radius (see text).

TABLE I. Shift of the bound-state energy for different crystallite sizes. $g=12/(\pi^2 a_0^b \kappa)$, where κ is the inverse screening length and a_0^b is the exciton Bohr radius in the unexcited bulk semiconductor.

R/a_0^b	g	$\delta E_x/E_R$
3	1.5	0.86
5	1.25	0.323
10	1.1111	0.0967

TABLE II. Shift of the bound-state energy for different crystallite sizes $R > a_0$ without screening.

R/a_0^*	$\delta E_x/E_R$
3	0.158
5	0.055
10	0.0131

the sphere, eliminating surface polarization effects. In Table I we give some typical results for different ratios of R/a_0^* and screenings such that the excitation-dependent exciton Bohr radius a_0 equals the radius R of the semiconductor microsphere. For stronger screenings $\bar{V}$ approaches zero (see Fig. 1) and δE_x becomes practically excitation independent. To determine the excitation-dependent part of the energy shifts which give rise to nonlinear optical properties, we give in Table II the corresponding energy variations without screening ($g = \infty$, weak excitation), which have to be computed for the regime $R > a_0$ and which can already be obtained from Ref. 1 taking into account the dielectric corrections.[4] The results are presented in Table II for the example of CdS. The comparison shows that the screening induces a strong *additional* blue shift of the exciton energy, which reaches $\simeq 70\%$ of the exciton binding energy for $R = 3a_0^*$. For CdS, this large shift should therefore be observable for materials with microcrystallites of the order of $R \simeq 84$ Å, a value which is easily obtainable by use of semiconductor-doped glasses or colloids. A very promising method for the manufacture of appropriate microcrystallites also for materials such as GaAs seems to be anisotropic reactive-ion etching procedure[16] applied to multiple-quantum-well structures having the desired layer thickness.

In conclusion, we have presented a simple calculation which predicts a strong excitation-induced blue shift of the exciton resonance in semiconductor microcrystallites. The physical origin of this shift is the plasma screening which causes an increasing exciton Bohr radius and hence a plasma density-dependent increase of the confinement energy. The static equivalent of this energy shift is well established[1-4] and is obtained by a decrease of the microcrystallite radius for fixed exciton Bohr radius. Based on the same physical picture of increasing confinement effects for increasing ratio of exciton Bohr radius and crystallite radius, we predict an excitation-induced absorption blue shift which is of the order of the exciton binding energy and which leads to a decreasing absorption in the spectral region below the semiconductor band gap. This shift therefore causes an excitation-dependent absorption in these semiconductor microcrystallites and hence a significant optical nonlinearity. The magnitude of the predicted absorptive changes are equivalent to those obtained by almost complete ionization of the exciton in the case without quantum confinement. The electron-hole density required to observe the size-induced shift is only about 60% of the Mott density in the corresponding bulk material. These properties make the semiconductor microcrystallites an extremely interesting system in which to study nonlinear optical effects, such as optical bistability, nonlinear wave interaction, wave mixing, to name only a few examples, as well as for device applications, such as optical logic gates.

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