Exciton-phonon interaction in CdSe and CuCl polar semiconductor nanospheres

J. C. Marini and B. Stebe
Université de Metz, Institut de Physique-Electronique et Chimie, Laboratoire d'Optoélectronique et de Microélectronique, 1 Boulevard Arago, 57078 Metz Cedex 3, France

E. Kartheuser
Université de Liège, Institut de Physique, B4000 Sart-Tilman, Liège 1, Belgium
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We present a theoretical study of the effect of longitudinal-optical phonons and surface-optical phonons on the electronic states of conduction electrons and donorlike excitons in a spherical semiconductor quantum dot. The effect of the quantum confinement is described by an infinitely deep potential well in the framework of the envelope-function approximation associated with two nondegenerate bands. The charge-carrier–phonon coupling is treated within the adiabatic approximation. A variational calculation of the ground-state energy of the donorlike exciton is performed using a one-parameter trial envelope function, which includes electron-hole correlation effects. The results show that in the case of a donorlike exciton located at the center of the microsphere, the effect of the lattice polarization gives rise to a lowering of the absolute value of the energy for all values of the microsphere radius R. The Huang-Rhys factor S, which is a measure of the charge-carrier–phonon interaction and the extent of the charge-carrier density, has been determined as a function of R. For the donorlike exciton, S reaches a minimum value, respectively, equal to $S_0=0.2$ for $R_0=12.7$ nm and $S_0=3.1$ for $R_0=2.3$ nm in the case of CdSe and CuCl.

I. INTRODUCTION

Recent[1] remarkable progress in crystal growth technique has made it possible to fabricate semiconductor structures with characteristic dimensions of the order of the de Broglie wavelength. In these "nanostructures" the quantum confinement effects become predominant and give rise to many interesting electronic and optical properties. In particular, the electron energy becomes quantized and depends on the medium size, the light-matter interaction is reinforced in comparison with what happens in bulk materials, and the exciton states remain stable till room temperature. This explains the increasing interest in these nanostructures in the fields of optoelectronics and microelectronics. In fact, there exist different kinds of nanostructures: the two-dimensional (2D) quantum wells and superlattices, the one-dimensional (1D) quantum wires, and the zero-dimensional (0D) quantum dots and microcrytals, depending on whether the quantum confinement concerns only one, two, or all three dimensions.

The present paper deals with spherical quantum dots which are intensively studied because of their prominent optical properties associated with the excitonic lines.[2–22] We study the effect of the exciton-phonon interaction in polar spherical quantum dots with special emphasis on CdSe and CuCl microspheres embedded in a glass matrix.

In these structures the dielectric constants of the sphere and the glass matrix differ from each other and surface optical (SO) modes[23] have to be included in order to describe the electron optical-phonon interaction.[24–28] Recently, a great amount of theoretical and experimental work has been devoted to the study of the coupling between exciton states and LO and SO phonons in spherical quantum dots.[27–36] However, the corresponding results are in contradiction with each other and it has not yet been clearly established whether this coupling depends on the crystal size or not. In a previous preliminary study, we showed that the exciton-phonon interaction depends strongly on the microsphere radius.[37]

In the present work we describe the exciton in a donorlike model assuming the hole to be located at the center of the sphere. A variational calculation of the exciton ground-state energy is performed in the framework of the envelope-function approximation associated with two nondegenerate bands. The one-parameter trial function used in the variational procedure takes into account electron-hole correlation and the effect of charge-carrier–phonon interaction is treated within the adiabatic approximation.

The paper is organized as follows. In Sec. II we present the effective Hamiltonian of an electron in a microsphere of radius R, interacting with longitudinal optical phonons and surface optical phonons. In order to clarify our theoretical model of a donorlike exciton we first calculate the ground-state energy of the confined electron within the adiabatic approximation. The results obtained improve the work of Pan and Pan[26] especially in the limit of a large-size spherical medium. Section III deals with the variational determination of the donorlike exciton ground-state energy including electron-hole correlation. We notice that the charge-carrier–LO-phonon interaction is strongly affected by the electron-hole correlation especially for small-size microspheres. Section IV is devoted to discussion of the numerical results and comparison with experiment in the case of

CdSe. The numerical results obtained in Sec. III show that the combined effect of electron- and hole–LO-phonon interactions leads to an R-dependent lowering of the donorlike exciton ground-state energy and a Huang-Rhys factor[38] in reasonable agreement with experiment.

II. ELECTRON-PHONON STATES

In this section, we present the Fröhlich continuum model used in order to describe the electron–LO- and SO-phonon interactions in a semiconductor nanosphere. We discuss the canonical transformations leading to the total wave function of the confined electron-phonon system which takes the form of a product of an electronic part and a phonon part. Making use of this *Produktansatz* we determine the ground-state energy of the confined electron in the framework of Ritz's variational method.

A. The effective electron-phonon Hamiltonian

The effective Hamiltonian of an electron with band mass m confined in a spherical quantum dot is given by

$$H = H_0 + H_{ep} \ . \tag{1}$$

Here the electronic part is

$$H_0 = \frac{p^2}{2m} + V_w \tag{2}$$

where the quantum confinement is described by an infinitely deep potential well

$$V_w = \begin{cases} 0, & r < R \quad (3a) \\ \infty, & r \geq R \ , \quad (3b) \end{cases}$$

which is reasonably well adapted to the case of a semiconductor spherical quantum dot. Since the original quantum-mechanical treatment of the electron–SO-phonon interaction,[39] a great amount of theoretical work has been devoted to electron–optical-phonon interaction in confined systems and particularly in spherical microcrystals.[26,27] We describe the electron–optical-phonon contribution H_{ep} in (1) by the well-known Fröhlich continuum model[40] adapted to the physical situation of an electron in a spherical environment embedded in a glass matrix. Within this model, the microsphere of radius R is specified by the static dielectric constant ϵ_0 and that measured at high frequency ϵ_∞, whereas the glass matrix is characterized by a dielectric constant ϵ_{out}.

From general considerations, the details of which may be found in the work of Pan and Pan[26] and Klein *et al.*,[27] the electron-phonon contribution can be written as

$$H_{ep} = H_{\text{LO}} + H_{\text{SO}} + H_I \ , \tag{4}$$

where

$$H_{\text{LO}} = \sum_{klm} \hbar\omega_{\text{LO}} a^\dagger_{lm}(q) a_{lm}(q) \tag{5a}$$

and

$$H_{\text{SO}} = \sum_{lm} \hbar\omega_l b^\dagger_{lm} b_{lm} \tag{5b}$$

are, respectively, the kinetic energy related to the LO and SO phonons. The operators $a^\dagger_{lm}(q)(b^\dagger_{lm})$ and $a_{lm}(q)$ (b_{lm}) are, respectively, creation and annihilation operators of a (LO) (SO) phonon of wave number q and frequency ω_{LO} (ω_l). Here we assume that the LO-phonon frequency is independent of q and given by the well-known Lyddane-Sachs-Teller relation as a function of the transverse optical TO phonon frequency ω_{TO} whereas the eigenfrequencies of the SO modes depend on the quantum number l, as [23,24]

$$\omega_l^2 = \frac{\epsilon_{\text{out}} + (\epsilon_{\text{out}} + \epsilon_0) l}{\epsilon_{\text{out}} + (\epsilon_{out} + \epsilon_\infty) l} \omega_{\text{TO}}^2 \ . \tag{6}$$

In order to facilitate the discussion of the limiting case of a large-size microsphere, i.e., the bulk situation, we write the electron-phonon interaction Hamiltonian H_I as follows:

$$H_I = \sum_{qlm} [V_l(q) j_l(qr) Y_{lm}(\theta,\phi) a_{lm}(q) + \text{H.c.}] + \sum_{lm} [S_l (r/R)^l Y_{lm}(\theta,\phi) b_{lm} + \text{H.c.}] \ , \tag{7a}$$

where H.c. stands for Hermitian conjugate. The first term in expression (7a) describes the interaction between the confined electron and the longitudinal optical vibration modes while the second term in (7a) accounts for the electron–SO-phonon interaction.

This leads to the following electron-phonon coupling coefficients:

$$V_l(q) = -\left[4\pi\hbar\omega_{\text{LO}} \frac{e^2}{j^2_{l+1}(qR) R^3 q^2} \right]^{1/2} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right]^{1/2} \tag{7b}$$

for LO phonons, and

$$S_l = -\frac{\sqrt{l}\,\epsilon_\infty}{l\epsilon_\infty + (l+1)\epsilon_{\text{out}}} \omega_{LO} \left[\frac{2\pi\hbar e^2}{\omega_l R} \right]^{1/2} \times \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right]^{1/2} \tag{7c}$$

for SO modes. The values of q are the roots of the spherical Bessel function[41] $j_l(qR)$ of order l. The functions $Y_{lm}(\theta,\phi)$ correspond to the spherical harmonics. In the case of LO volume modes, $l = 0,1,2,\ldots$, although for the SO modes, $l = 1,2,\ldots$. In all cases $m = -l,\ldots,l$.

B. Adiabatic approximation

Let us now suppose that the motion of the electron is much faster than that of the heavier ions. This arises in the two following physical situations.

(1) In the case of a microsphere with a small radius R, the quantum confinement produces an orbital shrinking which increases the electron speed.

(2) In the case of strong electron-phonon coupling, such as for CuCl, electron self-localization occurs, i.e., fast electron oscillations.

This implies that, in these physical situations, the pho-

non field experiences a static distribution of electronic charge and there is no correlation between the instantaneous position of the electron and the induced polarization field, which is usually called the adiabatic approximation. As a consequence, in the framework of the adiabatic approximation we can write the total wave function of the electron-phonon system as a product of an electronic wave function $\psi(\mathbf{r})$ and a phonon part $|\chi\rangle$. Notice that when the sphere radius is large, the adiabatic approximation is only valid for strong electron-phonon coupling. Here we shall restrict ourselves to the study of the ground-state energy of the confined electron. As a result, the well-known[42] electronic ground-state wave function is given by the product of a spherical harmonic with $l=0, m=0$ and the zeroth-order spherical Bessel function, i.e, a radial function. Therefore the SO-phonon field does not interact with the electron in its ground state and this contribution can be disregarded in the present work. Within the adiabatic approximation, the only effect of the electron–LO-phonon coupling is to displace the equilibrium positions of the ions. This displacement is performed by means of the canonical transformation

$$H'=S_0^{-1}HS_0 \tag{8a}$$

with

$$S_0=\exp\left[\sum_{qlm}V_l(q)\frac{\rho_0(q,l,m)}{|e|\hbar\omega_{\mathrm{LO}}}a_{lm}(q) - V_l^*(q)\frac{\rho_0^*(q,l,m)}{|e|\hbar\omega_{\mathrm{LO}}}a_{lm}^{\dagger}(q)\right], \tag{8b}$$

which is a generalization of the well-known Landau-Pekar adiabatic approach[43] adapted to the motion of an electron in a sphere. The unitary operator S_0 in (8b) is expressed in terms of the Fourier transform

$$\rho_0(q,l,m)=|e|\int_{\text{sphere}}d\mathbf{r}\,j_l(qr)Y_{lm}(\theta,\phi)|\psi_0(r)|^2 \tag{8c}$$

of the ground-state electronic charge distribution.

The adiabatic transformation being carried out, the total wave function of the electron–LO-phonon system is given by the *Produktansatz*

$$\Psi_0=\psi_0(\mathbf{r})S_0^{-1}|0\rangle\ , \tag{9}$$

where $|0\rangle$ is the vacuum state. This leads to the total energy

$$E_0=\langle\psi_0(\mathbf{r})|H_e|\psi_0(\mathbf{r})\rangle+\sum_{qlm}|V_l(q)|^2\frac{|\rho_0(q,l,m)|^2}{e^2\hbar\omega_{\mathrm{LO}}}\ . \tag{10a}$$

Here the first contribution is the expectation value of the effective Hamiltonian

$$H_e=\frac{P^2}{2m}-\sum_{qlm}\frac{|V_l(q)|^2}{|e|\hbar\omega_{\mathrm{LO}}}[\rho_0^*(q,l,m)j_l(qr)Y_{lm}(\theta,\phi)+\text{H.c.}] \tag{10b}$$

and the second contribution on the right-hand side of (10a) describes the lattice distortion energy.

C. Determination of the electron ground-state energy

Following the variational method we use for the electronic wave function $\psi_0(\mathbf{r})$ the one-parameter trial function given by

$$\psi_\alpha(\mathbf{r})=N\frac{\sin\pi r/R}{r}\exp(-\alpha^2r^2)\ , \tag{11}$$

which satisfies the boundary conditions of the confined electron and leads to the Gaussian-type behavior proposed by Pekar[43] in the asymptotic limit ($R\to\infty$). We obtain for the Fourier transform

$$\rho_\alpha(q,l,m)=\delta_{l,0}e|N^2(4\pi)^{1/2}\times\int_0^R dr\sin^2(\pi r/R)\frac{\sin(qr)}{qr}\times\exp(-2\alpha^2r^2)\ . \tag{12a}$$

In the asymptotic limit we recover the result

$$\rho_\alpha^a(q,l,m)=\delta_{l,0}|e|(4\pi)^{1/2}q\exp[-q^2/(8\alpha)] \tag{12b}$$

of previous theoretical work[44] and for $\alpha=0$ we get

$$\rho_0(q,l,m)=\delta_{l,0}|e|(4\pi)^{-1/2}\frac{1}{qR}\times\{\mathrm{Si}(qR)-\tfrac{1}{2}[\mathrm{Si}(qR+2\pi)+\mathrm{Si}(qR-2\pi)]\} \tag{12c}$$

where Si represent the sine integral function.[41]

The variational determination of the ground-state energy requires the minimization of the total energy

$$E_0(\alpha,R)=T(\alpha,R)+V_{ep}(\alpha,R) \tag{13a}$$

with respect to the variational parameter α. Here

$$T(\alpha,R)=\frac{\hbar^2}{m}\left\{\frac{1}{2}\frac{\pi^2}{R^2}+\alpha^2\left[1+\frac{F_{121}(\alpha,R)}{F_{012}(\alpha,R)}-2\alpha^2\frac{R^2}{\pi^2}\frac{F_{212}(\alpha,R)}{F_{012}(\alpha,R)}\right]\right\} \tag{13b}$$

is the contribution corresponding to the kinetic energy of the confined electron, where

$$F_{hij}(\alpha,R)=\int_0^i dx\,x^h[\sin(ix)]^j\exp(-2[\alpha Rx/\pi]^2)\ . \tag{13c}$$

The second term in (13a) represents the electron–LO-phonon interaction energy given by

$$V_{ep}(\alpha,R)=-\frac{e^2}{R}\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right][F_{012}(\alpha,R)]^{-2}\times\sum_{n=1}^{\infty}\frac{1}{n^2}J_n^2(\alpha,R) \tag{13d}$$

with

$$J_n(\alpha,R)=\int_0^{\pi}\sin^2(x)\frac{\sin(nx)}{x}\exp[-2(\alpha Rx/\pi)^2]\ . \tag{13e}$$

Notice that for $\alpha=0$ we recover the result for $E_0(0,R)$ obtained by Pan and Pan.[26] Figure 1 shows the variations of the electron–LO-phonon interaction energy V_{ep} as a function of the microsphere radius R. The results are given for CdSe using the material parameters[45] $\epsilon_0=9.56$, $\epsilon_\infty=6.23$, $\hbar\omega_{LO}=26.46$ meV, $m/m_0=0.13$, and $\epsilon_{ext}=1$, and for CuCl with material data[45] $\epsilon_0=7.9$, $\epsilon_\infty=3.61$, $\hbar\omega_{LO}=25.64$ meV, $m/m_0=0.5$, and $\epsilon_{ext}=1$. The results are displayed in atomic units (a.u.) of length $\epsilon_\infty\hbar^2/(me^2)$ and energy $me^4/(\epsilon_\infty^2\hbar^2)$, i.e., respectively 2.53 nm, 0.09 eV for CdSe and 0.38 nm, 1.05 eV for CuCl. We clearly see that the present variational calculations converge to the results of Pan and Pan[26] for very small values of R for which the electron quantum confinement predominates. Indeed, Pan and Pan have estimated the electron ground-state energy in the adiabatic limit using the charge distribution $\rho_0(q,l,m)$ given by (12c). For increasing R, the present results reach an extremum, respectively, for $R_0=76$ nm and $R_0=7.3$ nm in the case of CdSe and CuCl. This behavior is due to the combined action of the R-dependent quantum confinement and the electron–LO-phonon interaction.

In the limit $R\to\infty$ the saturation value of $V_{ep}(\alpha,R)$ is given by the corresponding value in the bulk material.[44] Since the charge distribution $\rho_0(q,l,m)$ used by Pan and Pan[26] does not properly account for the electron–LO-phonon interaction in the asymptotic limit, their saturation value is given by $V_{ep}=0$ for $R\to\infty$.

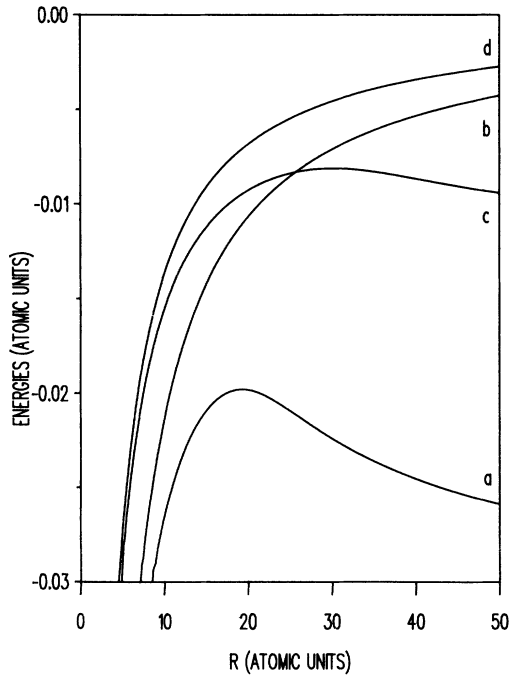

FIG. 1. Size dependence of the electron–LO-phonon interaction energies V_{ep} in the case of a CuCl microsphere (curves *a* and *b*) and a CdSe microsphere (curves *c* and *d*): curves *a* and *c*, present results; curves *b* and *d*, results of Pan and Pan (Ref. 21).

III. EXCITON–LO-PHONON COUPLING

In polar semiconductors the hole masses are usually much larger than the electron mass. Moreover, it has been shown[11] that an exciton modeled by a hole localized at the center of the sphere interacting with an electron at a distance r leads to the most stable situation. This simple model is called the donorlike exciton.

In this section we study the effect of the electron–LO-phonon interaction on the ground-state energy of the donorlike exciton. Using the notations introduced in Sec. II, the effective Hamiltonian of a donorlike exciton in interaction with LO phonons is given by

$$H_x=H-\frac{e^2}{\epsilon_\infty r}-\sum_{qlm}[V_l(q)j_l(0)Y_{00}a_{lm}(q)+\text{H.c.}]\ , \tag{14}$$

where the effective Hamiltonian H corresponds to the motion of a confined electron as defined in (1). The second term in the right-hand side of (14) represents the Coulomb interaction between the hole localized at $r=0$ and the electron at a distance r from the center of the sphere. Clearly, since the electron-hole Coulomb interaction enhances the localization of the electron around the hole, in addition to the electron quantum confinement, the validity of the adiabatic approximation is even strengthened. The last term in expression (14) describes the interaction between the localized hole and the LO phonons. This contribution can be eliminated by means of a first canonical transformation[46] whose effect is to displace the equilibrium position of the ions. Apart from a nonphysical divergent term,[47] the effect of this displacement on the lattice polarization leads to the following electron-hole exchange interaction:

$$V_{exch}=\sum_{qlm}\frac{|V_l(q)|^2}{\hbar\omega_{LO}}j_l(0)Y_{00}[j_l(qr)Y_{lm}(\theta,\phi)+\text{H.c.}]\ . \tag{15a}$$

After straightforward summation we obtain

$$V_{exch}=\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\frac{e^2}{r}\left[1-\frac{r}{R}\right]\ , \tag{15b}$$

which cancels for $r=R$ and partially compensates the electron-hole Coulomb energy. Proceeding in the same manner as in Sec. II, we finally operate a second canonical transformation related to the adiabatic approximation.

In order to describe the ground state of the donorlike exciton by means of the variational technique, we now use for the electronic part of the *Produktansatz* the following trial wave function:

$$\psi_\alpha(\mathbf{r})=N(\alpha)\frac{\sin\pi r/R}{r}\exp(-\alpha r) \tag{16a}$$

with

$$N(\alpha)=\left[\frac{\alpha}{\pi^3}\frac{R^2\alpha^2+\pi^2}{1-\exp(-2\alpha R)}\right]^{1/2}\ . \tag{16b}$$

The variational parameter α is a measure of the electron-

hole correlation. We obtain for the expectation value of the total energy

$$E_x=\frac{\hbar^2}{2m}\left[\frac{\pi^2}{R^2}+\alpha^2\right]+V_c(\alpha,R)+V_{\text{exch}}(\alpha,R)+V_{ep}(\alpha,R)\ , \tag{17a}$$

where the first term specifies the kinetic energy and the last three contributions are respectively the Coulomb energy, the electron-hole exchange energy, and the electron–LO-phonon interaction energy given by

$$V_c(\alpha,R)=-\frac{e^2}{\epsilon_\infty}4\pi N^2(\alpha)I(\alpha,R)\ , \tag{17b}$$

$$V_{\text{exch}}(\alpha,R)=e^2\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\left[4\pi N^2(\alpha)I(\alpha,R)-\frac{1}{R}\right]\ , \tag{17c}$$

with

$$I(\alpha,R)=\int_0^\pi dx\frac{\sin^2(x)}{x}\exp(-2\alpha Rx/\pi)\ , \tag{17d}$$

and

$$V_{ep}(\alpha,R)=-S(\alpha,R)\hbar\omega_{\text{LO}}\ , \tag{17e}$$

with

$$S(\alpha,R)=\frac{e^2}{R}\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\frac{[4RN^2(\alpha)]^2}{\hbar\omega_{\text{LO}}}\sum_{n=1}^{\infty}\frac{1}{n^2}J_n^2(\alpha,R)\ , \tag{17f}$$

$$J_n(\alpha,R)=\int_0^\pi dx\,\sin(nx)\frac{\sin^2(x)}{x}\exp(-2\alpha Rx/\pi)\ . \tag{17g}$$

The quantity $S(\alpha,R)$ is the Huang-Rhys factor[38] associated with the donorlike exciton. It is a measure of the electron–LO-phonon coupling strength and the extent of the exciton charge distribution. This physical parameter can be directly obtained from experiments involving optical transitions. The expectation value is now minimized with respect to the variational parameter α.

IV. RESULTS AND DISCUSSION

The present section is devoted to a discussion of the numerical results obtained in the case of CdSe and CuCl microspheres using the materials parameters given in Sec. II. Figure 2 shows the variation of the exciton energy including electron–LO-phonon interaction, E_x, and without electron–LO-phonon interaction, E_x^0, as a function of the microsphere radius. We recall that the results are displayed in atomic units (a.u.) of length $\epsilon_\infty\hbar^2/(me^2)$ and energy $me^4/(\epsilon_\infty^2\hbar^2)$, i.e., respectively, 2.53 nm, 0.09 eV for CdSe and 0.38 nm, 1.05 eV for CuCl. For very small values of R, the kinetic energy predominates due to the quantum confinement, whereas for intermediate values of R, both the Coulomb energy and the

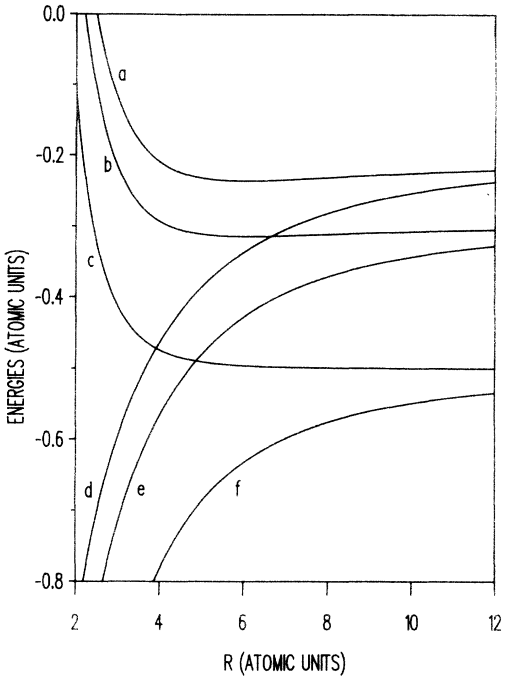

FIG. 2. Exciton energy with electron–LO-phonon coupling, E_x (curve *a*, CuCl, curve *b*, CdSe), and without electron–LO-phonon coupling, E_x^0 (curve *c*), as functions of the sphere radius; correlation energy with, W (curve *d*, CuCl, curve *e*, CdSe), and without electron–LO-phonon coupling, W_0 (curve *f*).

electron–LO-phonon interaction contribute to the binding energy of the exciton. In the limit $R\to\infty$, the numerical results converge to the bulk values $-\frac{1}{2}[11\epsilon_\infty/(16\epsilon_0)+\frac{5}{16}]^2$ and $-\frac{1}{2}$. In order to analyze the effect of electron-hole correlation on the donorlike exciton we have also plotted the quantity

$$W=E_x-E_0 \tag{18a}$$

including electron-phonon coupling and without electron-phonon coupling, denoted W_0. Here E_0 is the energy corresponding to the free-electron case described in Sec. II but calculated with the trial function given by expression (16). Figure 2 clearly shows that, for small radii of the microspheres, the quantum confinement strongly affects the correlation energy and lowers the influence of the lattice polarization on the electron-hole correlation.

In the asymptotic limit ($R\to\infty$), W_0 reaches the value $E_x^0=-\frac{1}{2}$ because the free-electron energy cancels, while in the presence of electron–LO-phonon coupling we obtain the saturation value

$$W^{3D}=-\frac{1}{2}\left[\frac{11}{16}\frac{\epsilon_\infty}{\epsilon_0}+\frac{5}{16}\right]^2+\frac{1}{2}\left[\frac{5}{16}\left[1-\frac{\epsilon_\infty}{\epsilon_0}\right]\right]^2\ . \tag{18b}$$

In Fig. 3 the charge-carrier–lattice polarization energy defined as

$$V_p(R)=V_{\text{exch}}(R)+V_{ep}(R) \tag{19}$$

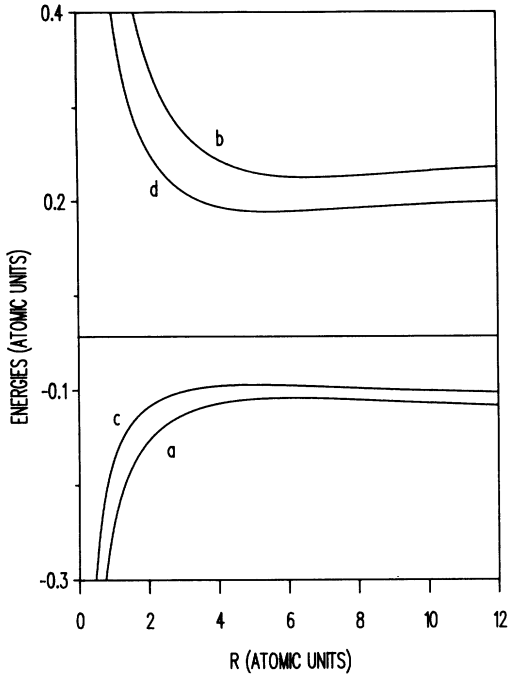

FIG. 3. Lattice polarization energy V_p and electron phonon energy V_{ep} as functions of the microsphere radius R and for CuCl (curves a and b) and CdSe (curves c and d).

and the electron–LO-phonon interaction energy are plotted as functions of the sphere radius. We notice that both quantities V_p and V_{ep} are strongly size dependent and exhibit an extremum, respectively, for $R_0 \simeq 13$ nm and $R_0 \simeq 2$ nm in the case of CdSe and CuCl. This extremum is due to the combined action of the quantum

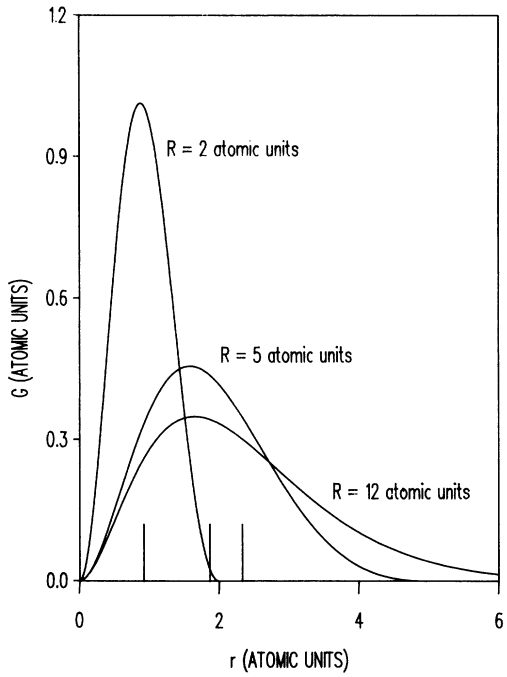

FIG. 4. Radial distribution function G of the donorlike exciton in the case of a CuCl microsphere with three different radii as a function of the electron position. The vertical lines specify the average electron-hole distance.

TABLE I. Electron-hole correlation parameter α and Huang-Rhys factor S of a donorlike exciton.

Material	CuCl				CdSe			
R (nm)	1	2.3	3.5	4.5	1.6	2.3	4.5	12.7
α (nm^{-1})	0.9	1.2	1.4	1.5	0.14	0.14	0.15	0.22
S[a]	4.3	3.1	3.3	3.5	0.8	0.6	0.3	0.2
S_{exp}[b]					1.4	0.5		

[a]Reference 49.
[b]References 29 and 30.

confinement and the Coulomb interaction on the exciton charge distribution: for small radii $R < R_0$, the quantum confinement effect prevails and drastically enhances the absolute values of V_p and V_{ep} whole for $R > R_0$ the electron-hole Coulomb interaction predominates and leads to the corresponding bulk values[48] V_p^{3D} and V_{ep}^{3D} in the limit $R \to \infty$. For the weak polar material CdSe $V_p^{3D} = 16.5$ meV and $V_{ep}^{3D} = -7.5$ meV whereas for the ionic material CuCl $V_p^{3D} = 246$ meV and $V_{ep}^{3D} = -111$ meV. Figure 4 shows the radial distribution function of the donorlike exciton given by

$$G(r) = 4\pi |N(\alpha)|^2 r^2 \left[\frac{\sin(\pi r/R)}{r} \right]^2 \exp(-2\alpha r) . \quad (20)$$

The results are plotted as a function of r for $R = 0.8$, 1.9, and 45 nm, which correspond to typical size values obtained in the case of CuCl microspheres. We also show the average electron-hole distance $\langle r \rangle$ for the different values of the microsphere radius. Finally, the values of the electron-hole correlation parameter α and the Huang-Rhys factor S are given in Table I for typical radii in the cases of CdSe and CuCl. The available experimental values S_{exp} are those for CdSe, CdS, and $CdS_{1-x}Se_x$ obtained from absorption, luminescence, hole burning, and resonant Raman scattering.[29–33] The increase of S with decreasing sphere radius R obtained in the present work has been observed by Uhrig *et al.*[32] in $CdS_{1-x}Se_x$ quantum dots.

In conclusion, we have shown that the exciton binding energy and its microsphere size dependence are strongly affected by the lattice polarization. The simple theoretical model of a donorlike exciton developed in the framework of the adiabatic approximation including electron-hole correlation is in reasonable agreement with experiment.

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