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Optical properties of confined polaronic excitons in spherical ionic quantum dots

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We report the results of a variational calculation of the energy and the oscillator strength of the exciton ground state in a spherical ionic quantum dot as a function of radius, assuming infinite potential barriers. The strong interaction of the exciton with optical phonons is taken into account by using an effective potential between the electron and the hole as derived by Pollmann and Büttner. The values of the exciton ground-state energies calculated using this effective potential are compared with the results of a recent calculation that treats the exciton interaction with confined and interface phonons independently, and excellent agreement is found. Comparisons with two simpler models of excitons reveal that the high degree of confinement in small quantum dots suppresses polaronic corrections in exciton properties. The reduction of the electron-hole correlation in small quantum dots is observed in the behavior of oscillator strength, which becomes less dependent on the form of the effective interaction as the dot size is reduced. A proper definition of exciton transition energy in ionic materials is pointed out, where self-energy renormalization effects are important. The results of our calculation are presented for quantum dots of some ionic materials such as CdSe, GaN, ZnO, and CuCl.

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I. INTRODUCTION

The past 30 years have witnessed enormous activity in studying the growth and structural, electrical, and optical properties of low-dimensional semiconductor structures such as quantum wells, quantum wires, and quantum dots. The ability to grow these structures with well-controlled dimensions and compositions has been made possible by rapid advances in modern fabrication techniques such as molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), and their several variants such as chemical beam epitaxy, atomic layer epitaxy, migration enhanced epitaxy, etc. The effect of confinement on the electronic and optical properties increases as one goes from quantum wells to quantum dots. The prospects of emergence of novel physical phenomena and their potential use in designing new and more efficient microelectronic devices constitute the most important motivations of the strong ongoing interest in these low-dimensional systems. The electronic and optical properties of quantum well structures have been investigated extensively during the last three decades. Significant interest in studying these properties in quantum-dot structures, however, is relatively recent. It is now possible to fabricate high-quality quantum dots in a number of semiconducting systems with fairly controlled compositions and dimensions using a variety of techniques. This has allowed extensive investigations of their physical properties, which are reviewed in several books and review articles.[1–4] The beneficial effects of strong confinement on the performance of electronic devices have been pointed out. For instance, it was suggested as early as in 1982 that lasers based on quantum-dot structures should exhibit superior performance than those based on quantum wires and quantum wells due to a noticeable modification of the density of states.[5] It was predicted that these lasers would have high differential gain, high-frequency modulation, ultralow threshold current density, and high-temperature stability of the threshold current density, simultaneously. These advantages have been realized, to a large extent, in a number of quantum-dot-based laser structures.[6,7]

In recent years there has been a great surge of interest in studying the electronic and optical properties of low-dimensional structures based on wide-band-gap, highly ionic semiconductors for their applications in optoelectronic devices in the blue and ultraviolet regions of the spectrum. Quantum-dot structures based on GaN (Refs. 8–10), ZnSe (Ref. 11), ZnO (Ref. 12), MgO (Ref. 13), CuCl (Ref. 14), CdS (Ref. 15), and CdSe (Refs. 16 and 17) have been fabricated and their optical properties as modified by strong confinement effects have been studied. The exciton binding energies in these systems are rather large, and the lasing action is expected to be excitonic in character and therefore should lead to lower values of the threshold current densities and larger values of the differential gain. Recently an all-optical single-electron read-out device based on GaN quantum dots[18] has also been proposed, which can potentially play an important role in quantum computing. In order to fully realize these potentialities a proper understanding of the exciton-related phenomena in these highly ionic confined structures is essential.

It has been recognized for a long time that in ionic materials such as those mentioned above, the exciton–optical-phonon interaction has a significant effect on their optical properties. For instance, the exciton binding energies, their oscillator strengths and radiative lifetimes are modified considerably by the exciton–optical-phonon interaction. This interaction is also expected to play an important role in determining the optical properties of quantum dots based on ionic materials. Several groups have studied the dependence of the exciton–LO-phonon interaction in quantum-dot systems and have arrived at conclusions that are often at variance and even contradictory. It has been claimed, for instance, that the Fröhlich-type exciton–LO-phonon interaction should vanish in small nanocrystals.[19] However, it has been suggested in another study, using a donorlike exciton model and adiabatic approximation, that the strength of exciton–LO-phonon interaction is independent of the dot size.[20] This conclusion has, however, been contradicted by another group,[21] which claims that the exciton–LO-phonon interaction should increase with decreasing dot size. For further discussion on these results the reader is referred to a recent work by Oshiro, Akai, and Matsuura.[22]

In view of the importance of the effects of the exciton–optical-phonon interaction on the excitonic properties in ionic quantum dots, a proper and accurate description of this interaction is required to describe the observed data. An oversimplified picture in which only the electron and the hole masses are renormalized to their respective polaron masses is in fact quite inaccurate. In polar semiconductors the interaction between the electrons and holes depends on their mutual distance in such a way that when this distance is much larger than their respective polaron radii, the electrons and holes interact like two polarons through the Coulomb potential screened by static dielectric constant. In the opposite limit, however, when the distance between them becomes comparable to or less than the sum of the two polaron radii, the two oppositely polarized virtual phonon clouds overlap and partially cancel out their renormalization effects, so that the electron-hole interaction approaches the dynamically screened Coulomb interaction when their mutual distance is reduced further. Such a description of the effective electron and hole interaction in bulk semiconductors, encompassing the above-mentioned limiting cases has already been given through some effective potentials.[23–27]

In this paper, we present the results of a variational calculation of the exciton energy and oscillator strength of the ground state in quantum dots composed of ionic materials. We assume that the quantum dots are spherical in shape with infinite potential barriers. Furthermore, the barrier material is assumed to be nonpolar and the effects of image charges are also ignored. We consider parabolic conduction and valence bands with isotropic electron and hole masses. The effects of valence band mixing are not included in our calculations. We describe the exciton–LO-phonon interaction by means of the effective potential between the electron and the hole as derived by Pollmann and Büttner[24,25] (PB) in the case of bulk ionic materials using a variational approach. We show that the quantum-dot-type confinement has a very significant effect on the values of both the ground-state energy and the oscillator strength of the exciton. The description of an excitonic state with the statically screened Coulomb interaction potential is shown to have limited validity, leading to reasonable quantitative results only for weakly polar materials such as GaAs.

Recently, Oshiro, Akai, and Matsuura[22] have calculated the variation of the total energy of the exciton ground state as a function of size in spherical ionic quantum dots using infinite potential barriers. In their calculation they use an interaction Hamiltonian in which electrons and holes interact with the confined optical phonons and interface phonons. We find that the variation of the total ground-state energy as a function of size, which we calculate using the PB potential, agrees very well with that calculated by these authors. This excellent agreement along with our results in a few selected ionic materials will be discussed.

II. THEORY

The Hamiltonian of an interacting electron-hole pair, perfectly confined in an ionic quantum dot of radius R and coupled to the bulk longitudinal optical (LO) phonons, is expressed as

$$H=\sum_{i=e,h}\left(\frac{p_i^2}{2m_i}+V_{\mathrm{conf}}(r_i)\right)-\frac{e^2}{\varepsilon_\infty|\vec{r}_e-\vec{r}_h|}+\hbar\omega_{LO}\sum_{\vec{q}} a_{\vec{q}}^{\dagger}a_{\vec{q}} + \sum_{\vec{q}}\,[V_{\vec{q}}a_{\vec{q}}(e^{i\vec{q}\cdot\vec{r}_e}-e^{i\vec{q}\cdot\vec{r}_h})+\mathrm{H.c.}], \tag{1}$$

where the subscript $i=e$ and $i=h$ denotes an electron and a hole, respectively, m_i are the isotropic effective band masses, $\vec{r}_i$ are the position, and $\vec{p}_i$ are the momentum operators. The spherically symmetric confinement potential is assumed to provide perfect confinement and is written as

$$V_{\mathrm{conf}}(r)=\begin{cases}0 & (r<R)\\ \infty & (r\geqslant R).\end{cases} \tag{2}$$

In the Hamiltonian, $a_{\vec{q}}^{\dagger}$ and $a_{\vec{q}}$ are the creation and annihilation operators of the phonons of wave vector $\vec{q}$, and $\hbar\omega_{LO}$ is the dispersionless optical phonon energy. The last term defines the Fröhlich-type charge-phonon interaction with the interaction amplitude given by $V_{\vec{q}}=-i(2\pi e^2\hbar\omega_{LO}/V\varepsilon^*)^{1/2}/q$, where V is the normalization volume and $\varepsilon^*=(1/\varepsilon_\infty-1/\varepsilon_0)^{-1}$, ε_0 and ε_∞ being the static and the high-frequency dielectric constants, respectively.

Starting with the same Hamiltonian, but without the confinement potential, Pollmann and Büttner[24,25] were able to obtain simple expressions of the effective Hamiltonians to describe the excitons in bulk ionic media and successfully explain the measured values of the exciton transition energies. Their procedure consists of transforming the model Hamiltonian twice by using two well-known unitary transformations and then performing a variational calculation to determine the displacement amplitudes of the system using bound state wave functions of hydrogenic type. In its final form, it is possible to express the detailed effective interaction potential and the self-energy of the electron-hole pair in terms of an effective exciton radius and the relative coordinate $\vec{r}=\vec{r}_e-\vec{r}_h$. We choose to proceed with such an effective Hamiltonian having the following form:

$$H_{\mathrm{eff}}=\sum_{i=e,h}\left(\frac{p_i^2}{2m_i}+V_{\mathrm{conf}}(r_i)\right)+V_{\mathrm{eff}}(r)+E_{\mathrm{self}}. \tag{3}$$

The effective potential $V_{\mathrm{eff}}(r)$ and the self-energy term are written as

$$V_{\mathrm{eff}}(r)=-\frac{e^2}{\varepsilon_0 r}-\frac{e^2}{\varepsilon^* r}\left[\frac{C^4}{B^4}-\frac{m_e h_e}{\Delta m}e^{-rA_e/R_e} + \frac{m_h h_h}{\Delta m}e^{-rA_h/R_h}-\left(h_\mu+\frac{C^3 r}{2B^3 a_{ex}}\right)e^{-rB/R_\mu}\right], \tag{4}$$

$$E_{\mathrm{self}}=-(\alpha_e g_e+\alpha_h g_h-\alpha_\mu g_\mu)\hbar\omega_{LO}, \tag{5}$$

where $\Delta m=m_h-m_e$ is the mass difference. Defining $M=m_e+m_h$ as the total mass and $m_\mu=m_e m_h/M$ as the exciton reduced mass,

$$\alpha_i=\frac{e^2}{2\varepsilon^* R_i\hbar\omega_{LO}}, \quad R_i=\sqrt{\frac{\hbar}{2m_i\omega_{LO}}} \quad (i=e,h,\mu) \tag{6}$$

are the dimensionless phonon-coupling constants, and the characteristic polaron radii for the electron, the hole, and the reduced mass m_μ, respectively. The remaining coefficients have the following explicit forms:

$$\begin{gathered}
A_i^2=1+R_i^2/a_{ex}^2 \quad (i=e,h);\\
B^2=1+C^2, \quad C^2=R_\mu^2/a_{ex}^2;\\
h_i=1+(m_jR_i/m_ia_{ex})^2 \quad (j\neq i=e,h);\\
h_\mu=-(m_e/m_h+m_h/m_e)C^2+C^4/B^4; \qquad (7)\\
g_i=A_i\left(1-\frac{1}{2}R_i^2/a_{ex}^2\right)^2 \quad (i=e,h);\\
g_\mu=C^2\left(4+\frac{1}{2}C^2+C^2/B^2-2A_ed_e-2A_hd_h\right)/B;\\
d_i=\frac{1+A_iB\sqrt{m_j/M}}{A_i+B\sqrt{m_j/M}} \quad (j\neq i=e,h).
\end{gathered}$$

The effective interaction Hamiltonian defined above has an explicit and crucial dependence on a quantity called the exciton radius, a_{ex}. It is a measure of the size of the exciton and its value is determined variationally. Originally the Pollmann-Büttner effective potential between the electron and the hole was derived for a bulk semiconductor using a one-parameter hydrogenic trial wave function, $\Psi_0(r)=N\exp(-\lambda r/a_0)$, where $a_0=\hbar^2\varepsilon_0/m_\mu e^2$ is the exciton Bohr radius. Consequently, the value of the exciton radius used in the effective Hamiltonian has a bulk limit given by $a_{ex}=\langle\Psi_0|1/r|\Psi_0\rangle^{-1}=a_0/\lambda$. In the present case, however, the variational trial wave function we use also contains one-particle electron and hole envelope functions, which are compatible with the nature of the spherical-dot potential geometry:

$$\Psi(r_e,r_h,r)=Nj_0(\pi r_e/R)j_0(\pi r_h/R)\exp(-\lambda r/a_0). \tag{8}$$

In the above, N is the normalization constant, j_0 is the zeroth-order spherical Bessel function of first kind, and λ is a variational parameter. To account for the confinement effects we simply generalize the definition of exciton radius using the new wave function: $a_{ex}=\langle\Psi|1/r|\Psi\rangle^{-1}$. As expected, such a form will have the correct bulk limit and will lead to a smaller exciton size when the dot size is reduced.

We should also note that in this treatment of the effective electron-hole interaction, the renormalization of the electron and hole masses is not needed as shown by Pollmann and Büttner in their work.[25] We assume that the above form of the effective potential, which is derived for bulk, is not significantly modified in the presence of the external confinement. Such an approximation has been used successfully to describe the measured diamagnetic shifts in the case of a polaronic exciton in a magnetic field,[28] where the magnetic field provides the means of confinement. The direct influence of the confinement potential on the strength of the electron-hole interaction potential and on the polaronic self-energy of the exciton as well is through the quantity exciton radius (a_{ex}) as defined above. Due to the confinement, the value of exciton size attains a strong dependence on the size of the quantum dot, and thereby modifies the values of those quantities as a function of dot radius. Although preserving the formal expressions of the effective potential and the self-energy terms as derived for bulk, and assuming that these forms are not significantly modified even in the case of quantum-dot confinement is an approximation, as will be discussed in the next section, the formulation is seen to yield quite accurate results by only an appropriate redefinition of a_{ex}. In fact such an approach is in accordance with the bulk-phonon approximation that is applied in this study, where the confinement effects are taken to affect the wave functions of the electron and the hole only, but not the nature of phonon field.

To calculate the ground-state energy of the system we minimize the expectation value of the effective Hamiltonian, Eq. (3),

$$E_0=\min_\lambda\langle\Psi|H_{\mathrm{eff}}(\lambda)|\Psi\rangle. \tag{9}$$

The energy of the exciton ground state contains contributions from the confinement subband energies of the electron and the hole, the screened Coulomb correlation energy, and the detailed renormalization effects of the exciton-phonon coupling. The subband energies, having a strong ($\sim 1/R^2$) dependence on the dot size, dominate the total energy in small quantum dots. The PB effective potential, on the other hand, describes the collective form of the potential energy due to the Coulomb interaction and the polarization fields of the oppositely charged electron and hole.

Even without the confinement effects, the PB description of the exciton-phonon interaction in an ionic medium brings about significant improvements over some simplified approaches. Let us briefly review the details of how the PB potential provides a successful description of the exciton-phonon interaction, first in the bulk limit. The first term in Eq. (4) corresponds to a statically screened Coulomb interaction. As compared to the original form of the Hamiltonian (1), the elimination of phonon coordinates to obtain an effective electron-hole interaction transforms the Coulomb interaction from a dynamically screened to a statically screened one, in the leading order. However, the remaining terms in Eq. (4) as well as the self-energy expression, Eq. (5), are essential to describe the detailed and nontrivial interaction of the two charges with opposite polarization fields around them. The crucial parameter that determines the form of the effective interaction is the ratio of the exciton radius a_{ex} to the polaron radii R_i. It is instructive to check the limiting

TABLE I. Values of the various physical parameters used in our calculation. The electron and the hole masses are expressed in units of the free electron mass. The LO-phonon energies are given in meV. The polaron radii (R_e, R_h), and the Bohr radius (a_0) are given in Å units. $E_{\rm Ry}$ is the Rydberg energy in units of meV. All other symbols are defined in the text.

Material	m_e	m_h	ε_0	ε_∞	$\hbar\omega_{LO}$	α_e	α_h	R_e	R_h	a_0	$E_{\rm Ry}$
CdSe [a]	0.10	0.40	9.3	6.1	26.5	0.40	0.81	37.9	19.0	61.5	12.59
GaN [b]	0.20	0.80	9.8	5.4	92.0	0.45	0.90	14.4	7.20	32.4	22.67
ZnO [c]	0.24	0.78	8.1	4.0	72.0	0.85	1.54	14.8	8.24	23.4	38.06
CuCl [d]	0.44	3.60	7.4	3.7	27.2	2.01	5.73	17.8	6.24	9.99	97.42

[a] Reference 22.

[b] References 48 and 49.

[c] References 27 and 32.

[d] References 27 and 50.

cases of this ratio in an ionic material. In the limits of strong and weak binding it is easy to show that

$$\lim_{a_{ex}/R_i\to 0} E_{\rm self}=0, \qquad \lim_{a_{ex}/R_i\to\infty} E_{\rm self}=-(\alpha_e+\alpha_h)\hbar\omega_{LO}. \tag{10}$$

For large exciton radii the total self-energy approaches the sum of the two individual self-energies of the free polarons. For very small exciton radii the total self-energy of the exciton vanishes because the polarization clouds of the electron and the hole cancel each other. In general, and under the influence of the confinement potential, the partial cancellation of the polarization fields is well described by Eq. (5). Similarly, in these extreme limits the effective potential gets the following asymptotic forms:

$$\lim_{\frac{a_{ex}}{R_i}\to 0} V_{\rm eff}(r)=-\frac{e^2}{\varepsilon_\infty r},$$

$$\lim_{\frac{a_{ex}}{R_i}\to\infty} V_{\rm eff}(r)=-\frac{e^2}{\varepsilon_0 r}-\frac{e^2}{\varepsilon^* r}\,\frac{(m_h e^{-r/R_h}-m_e e^{-r/R_e})}{(m_h-m_e)}. \tag{11}$$

With these reasonable limits, the PB Hamiltonian gives a successful description of the polaronic excitons.[25] In the present study the main effect of the confining potential is to shrink the charge densities of both the electron and the hole, decreasing the relative distance between them, which in turn makes the effective electron-hole interaction potential to be less screened through the PB term. Thus by leading to smaller values of a_{ex}, the high degree of confinement is expected to diminish the polaronic effects in the exciton state.

Apart from the ground-state energy of the exciton, an important quantity of interest is the oscillator strength, which is sensitively dependent on the confinement of the electron and hole wave functions and the overlap between them. Using the envelope-function approximation, the oscillator strength for the exciton ground state is given by[29–31]

$$f_{ex}=\frac{2P^2}{m_0\Delta E}\left|\int \Psi(\vec{x}=\vec{r}_e=\vec{r}_h)d^3x\right|^2, \tag{12}$$

where P describes the intracell matrix elements, m_0 is the bare electron mass, $\Delta E=E_{ex}-E_0$, and E_{ex} and E_0 are the energies of the states with and without the exciton, respectively. Since we are interested in comparing the effect of using the PB potential on the oscillator strength with that of using the statically screened Coulomb potential, we calculate the ratio of the two oscillator strengths, $f_{ex}/f_{ex}^{(s)}$, which can be expressed in terms of these energies and the simple integrals over the exciton wave functions.

We now consider two simpler models of the exciton for comparison of their results with those of the present effective potential approach. One of the models is the so-called "shallow-exciton model" where the Coulomb interaction is statically screened and the exciton self-energy is assumed to be the sum of the individual self-energy shifts of the electron and the hole polarons. The validity of this model is limited to excitons of larger size in weakly polar materials, and in weak confinement case, because the overlapping of the polarization fields of the particles is neglected entirely. We will denote the quantities as obtained within this model by the superscript (s), like in the case of the ground-state energy: $E_0^{(s)}$. The other model is the so-called "bare-exciton model" where the coupling to the phonons is completely ignored, and the Coulomb interaction of the electron-hole pair is considered with dynamical screening ε_∞. The PB effective potential formulation is formally expected to reproduce the results of the bare-exciton model in the high-confinement limit. In the following the superscript (b) will denote the quantities relevant to this model.

III. RESULTS AND DISCUSSION

We have calculated the variation of the ground-state exciton energy as a function of the dot radius in four representative ionic materials, i.e., CdSe, GaN, ZnO, and CuCl. The values of the various physical parameters used in our calculations are given in Table I. We display the results for CdSe dots in Fig. 1. The ground-state energy of the system as calculated using all three models under consideration is presented. We first note that the model with the effective PB

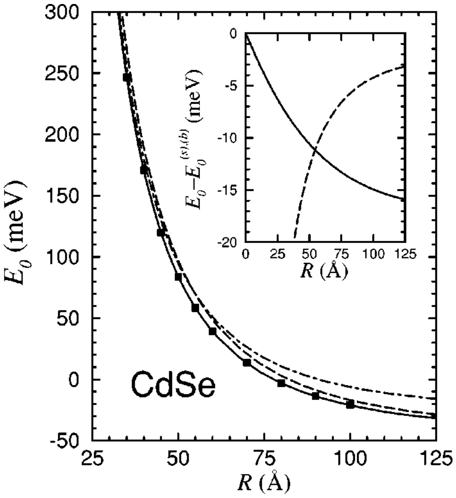

FIG. 1. Size dependence of the total ground-state energy (E_0) of the exciton-phonon system in a CdSe quantum dot. The solid curve is obtained using Pollmann-Büttner effective potential. The results of Oshiro *et al.* (Ref. 22) which are represented by solid squares, are included for comparison. The dashed and dot-dashed curves correspond to shallow-exciton ($E_0^{(s)}$) and bare-exciton ($E_0^{(b)}$) models, respectively. In the inset, the energy differences $E_0-E_0^{(s)}$ (dashed curve) and $E_0-E_0^{(b)}$ (solid curve) are drawn.

potential provides the lowest upper bounds to the ground-state energy throughout the displayed domain of dot size. The inset shows the deviations of E_0 from the results of the simpler models $E_0^{(s)}$ and $E_0^{(b)}$. A clear immediate feature arising from the content of the inset is that at high degrees of confinement the difference $E_0-E_0^{(b)}$ tends to vanish, showing that the PB potential effectively transforms to a dynamically screened Coulomb potential, and the polaronic self-energy corrections of the exciton vanish almost entirely. For large sizes of the quantum dot the bare-exciton model provides larger ground-state energies than the shallow-exciton model, because the latter includes self-energy terms. The solid squares in Fig. 1 are the results of a recent calculation of the ground-state energy[22] in which the exciton is taken to interact separately with the confined and interface phonon modes of the dot. In our calculation, however, the so-called "bulk-phonon" approximation is adopted. The qualitative and the quantitative agreement between the results of the two calculations is excellent. Similar agreement was also found in the case of quantum wells.[32] Several groups[33–37] have shown that in quantum wells the interaction of an exciton with all three phonon modes (confined, interface, and half-space) can effectively be reduced, with a high degree of accuracy, to a bulk-LO-phonon–exciton interaction. The same seems to be true in the case of quantum dots as well as indicated by our calculation.

As mentioned above, Oshiro, Akai, and Matsuura[22] have considered the effect of excitons interacting with confined LO phonons and interface phonons on the exciton energy, exciton-phonon interaction energy, and the virtual phonon number. They find that the polaronic effects on these quantities decrease as the dot size is reduced, a result also obtained by us using the PB potential. In addition, the polaronic contribution of the bulk-type confined LO phonons to the above-mentioned quantities is much larger than that of the interface phonons, especially in larger ($R \gtrsim a_0$) quantum dots. The excellent agreement between the energy of the exciton ground state that we calculate and that calculated by Oshiro, Akai, and Matsuura[22] in CdSe quantum dots is clear evidence of this feature.

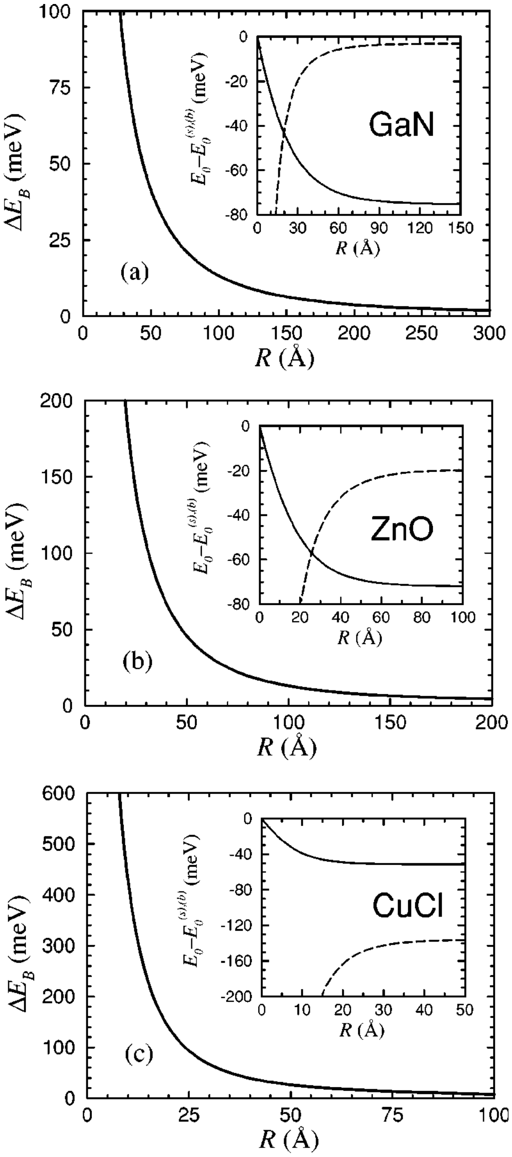

FIG. 2. Variation of change in exciton binding energy, ΔE_B, as a function of dot size, for (a) GaN, (b) ZnO, and (c) CuCl. The insets show the deviations between the results of different models: the solid curves are $E_0-E_0^{(b)}$, and the dashed curves are $E_0-E_0^{(s)}$.

In Fig. 2 we present results in quantum dots made of materials more ionic than CdSe, such as GaN, ZnO, and CuCl. In order to eliminate the dominating contribution of the subband energies in small-sized dots we define a quantity "change in exciton binding energy," ΔE_B, which has a vanishing bulk value,

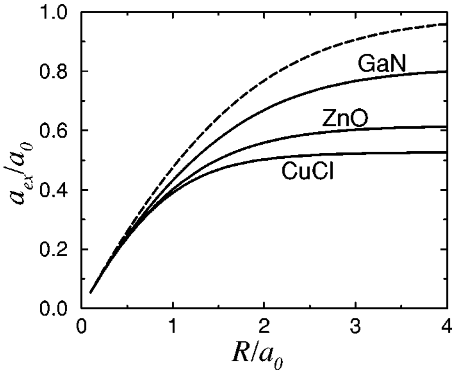

FIG. 3. Variation of exciton radius a_{ex} as a function of confinement in CuCl, ZnO, and GaN quantum dots. The dashed curve is the same for all materials, and corresponds to $a_{ex}=\langle\Psi|1/r|\Psi\rangle^{-1}$ when the Coulomb interaction is taken as statically screened. Both the exciton radius and the dot size are scaled by the corresponding Bohr radius.

$$\Delta E_B(R)=\frac{\hbar^2\pi^2}{2m_\mu R^2}-E_0(R)+E_0^{\text{bulk}}, \tag{13}$$

where E_0^{bulk} is the exciton ground-state energy calculated using the PB potential in bulk medium. As shown in Fig. 2, the general form of the size dependence of ΔE_B is qualitatively the same for all materials. The actual value of the onset of the confinement effects is, however, proportional to the exciton Bohr radius. Due to confinement in all spatial directions the increase in the value of ΔE_B is quite pronounced.

A series of insets in Fig. 2 compares the values of the ground-state energy obtained using the PB potential to those obtained using other simplified models mentioned above. The general trend is that as the material becomes more ionic the results of the static screening model get poorer. Moreover, the discrepancy becomes larger in smaller dots. On the other hand, the bare-exciton model has an opposite behavior; although it does not give satisfactory results in the bulk limit, the confinement effects increase its validity, making this model a formal asymptote of the PB model in the limit of extremely small dots.

In the PB model, the effect of confinement on the exciton ground-state energy is reflected by the parameter, the exciton radius a_{ex}. Figure 3 shows the variation of this parameter as a function of dot size. In the bulk limit the exciton size is determined by the relative strength of the interaction between the electron and the hole. The polaronic corrections are seen to favor more bound excitons with smaller sizes.[24] When the dimension of the dot is reduced, the size of the exciton is determined mainly by the boundaries of the confinement potential. This is depicted in Fig. 3 by the linear asymptotic behavior of a_{ex} independent of the type of the material.

We now discuss the modifications obtained in the values of the oscillator strength of the exciton ground state when the exciton model is considered with the PB potential. As mentioned above, the actual size of the exciton is smaller than that calculated with the simple "shallow-exciton model." The difference in the two models is reflected more dramatically in the results of the calculation of the oscillator strength. In Fig. 4 we display the variation of the ratio of the two oscillator strengths as calculated with those models as a function of the dot size. The enhancements are seen to be larger in more polar quantum dots. In the bulk limit, for instance, with the PB potential, we see that the oscillator strength is actually about 7.3 times (4.4 times) larger than the value obtained with the Coulomb potential for CuCl (ZnO). Although both f_{ex} and $f_{ex}^{(s)}$ increase with the decreasing dot size, their ratio starts to get smaller and approaches unity in the high-confinement limit. This is because in very small dots, the confinement effect takes over and strongly suppresses the correlation between the electron and the hole, thereby drastically reducing the significance of the form of the interaction.

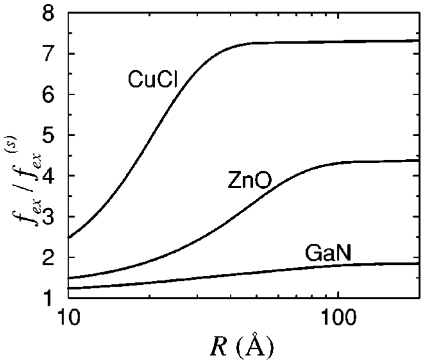

FIG. 4. Variation of the ratio of oscillator strengths as a function of confinement in quantum dots of GaN, ZnO, and CuCl. f_{ex} and $f_{ex}^{(s)}$ are the oscillator strengths as calculated using Pollmann-Büttner and statically screened Coulomb potentials, respectively.

We shall now comment briefly on the approximations we have made in our calculations. We have used effective mass approximation and have assumed parabolic conduction and valence bands with isotropic effective masses, thus completely ignoring the nonparabolicity of the conduction band and complex nature of the valence band structure. The application of both the effective mass approximation and the Fröhlich continuum Hamiltonian is valid in quantum dots where the values of R are considerably larger than those of lattice constants. The validity of these approximations is somewhat limited in the case of CuCl, where the characteristic sizes of the exciton and the polarons become comparable to the lattice constant. Therefore the results for CuCl quantum dots are intended to provide only an estimate of the excitonic properties. We have assumed infinite values for the conduction and valence band offsets and have not considered the effect of the image charges due to dielectric mismatch on the exciton ground-state energy. It is well known that the dielectric mismatch between the confined material and the barrier material has a significant effect on the energy levels of quantum wells[38,39] and quantum wires.[40] Similar effects are also expected in quantum dots. Recently Fonoberov, Pokatilov, and Balandin[41] have calculated the effect of dielectric mismatch on the lowest-energy levels in spherical quantum dots assuming infinite potential barriers. They find that the inclusion of the dielectric mismatch effect in their calculation leads to the addition of three terms to the exciton Hamiltonian, namely, the electron self-energy, the hole self-energy (both positive), and a negative contribution to the interaction potential. The value of the exciton binding energy is therefore enhanced but the exciton transition energy is relatively insensitive to the dielectric mismatch. The weak dependence of the optical gap on the surrounding medium in quantum dots is also concluded by pseudopotential calculations.[42]

The surface and interface effects are also completely ignored. It should be noted that the effects of the exciton-phonon interaction and the image potential on the exciton energy in ionic quantum structures have been treated independently. However, it has been pointed out by Sak[43] and by Evans and Mills[44] that these two effects are not independent of each other, thus leading to a very complex resultant interaction, the effect of which on the exciton binding energy is very difficult to calculate.

The use of the effective mass approximation leads to larger values of the confinement energies[45] than those obtained by other band structure calculations such as tight-binding[46] and pseudopotential approaches.[47] We note that proper incorporation of exciton–optical-phonon interactions in the band structure calculations is a formidable task. It should be emphasized that our primary objective in this work is twofold: (i) to investigate the effect of the exciton–optical-phonon interaction on the exciton ground state as calculated using the PB formulation of this interaction, and (ii) to compare our results with those obtained by considering the exciton interacting with the phonon modes of the quantum dot, namely, confined and interface phonons.[22] As mentioned earlier our results of the total ground-state energy of the exciton agree remarkably well with those obtained using the latter model. Our approach is considerably simpler than that followed by Oshiro, Akai, and Matsuura[22] and thus can easily be generalized to study the effects of external perturbations such as electric and magnetic fields on the properties of the exciton ground state in ionic quantum dots. We believe that the effect of the exciton–optical-phonon interaction on the ground-state energy of an exciton in ionic quantum dots as calculated using effective mass theory should not be significantly different from that determined by including the complexities of the band structure even if such a determination was feasible.

In order to compare directly the results of our calculations with experimental data we need to determine the transition energy of the excitonic ground state. This is obtained by adding E_0 to the appropriate band-gap energy. The proper value of the band-gap energy to use is the one that has not been renormalized by the self-energies of the free electron and hole polarons. The experimentally measured values of the energy band gaps (E_g), however, are always renormalized by these self-energies. Thus the transition energy of the ground-state exciton can be defined as

$$E_T(R)=[E_g+(\alpha_e+\alpha_h)\hbar\omega_{LO}]+E_0(R). \tag{14}$$

Obviously, E_0 contains the self-energy terms of the confined electron and the hole in the exciton ground state, which have different values than those of a free electron and a free hole. The value of the transition energy of the excitonic ground state thus calculated should be compared with its experimental value in ionic quantum dots.

As mentioned earlier, quantum-dot structures based on a variety of ionic materials have been fabricated using epitaxial crystal-growth techniques, such as MOCVD and MBE, and chemical approaches. Their structural and optical properties have been studied in considerable detail. The observed excitonic transitions are generally quite broad, reflecting the size distribution of the ensemble. Data on single quantum dots of these materials are still very limited. In general, the transitions are shifted to the higher-energy side, reflecting the effects of spatial confinement except in the case of GaN quantum dots where the piezoelectric and spontaneous polarization electric fields shift the transition to lower energies. It is clearly not very meaningful to compare the values of the excitonic transition energies we calculate with the experimental data in ionic quantum dots as we have not included the effects of the finite potential barrier, complex band structure, dielectric mismatch, and surface and interface polarization in our calculations. The contribution of these effects and that of the exciton-phonon interaction to the exciton transition energy, as we have calculated, should be considered for a proper comparison with experimental data.

In summary, we have calculated the variation of the energy and the oscillator strength of the ground state of an exciton in a spherical ionic quantum dot as a function of radius, assuming infinite values of the electron and hole band offsets. The effective potential between the electron and the hole as derived by Pollmann and Büttner is used to describe the strong interaction of the exciton with optical phonons. We follow a variational approach and find that the effect of the exciton-phonon interaction on the energy and the oscillator strength of the exciton ground state is reduced with decreasing size of the quantum dot. We compare our results with those obtained using two simpler models in which the interaction between the electron and the hole is screened by static and dynamic dielectric constants, respectively, and discuss regions of their validity. The values of the exciton ground-state energies calculated using Pollmann-Büttner potential are also compared with the results of a recent calculation that treats exciton interaction with the confined and interface phonons independently, and excellent agreement is found. We observe a reduction in the importance of electron-hole correlation in small quantum dots in the behavior of oscillator strength, which becomes less dependent on the form of the effective potential as the dot size is reduced. We also provide a definition of the excitonic transition energy in ionic quantum dots that properly takes into account the self-energy terms. And finally we present the results of our calculations in quantum dots of ionic materials such as CdSe, GaN, ZnO, and CuCl.

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