

# Electron-phonon interaction in a spherical quantum dot with finite potential barriers: The Fröhlich Hamiltonian

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A Fröhlich Hamiltonian describing the electron-phonon interaction in a spherical quantum dot embedded in another polar material is derived, taking into account interactions with both bulk longitudinal optical and surface optical phonons. The Hamiltonian is appropriate to the general case of a finite confining potential originating from a bandgap mismatch between the materials of the dot and the surrounding matrix. This Hamiltonian is then used to treat the electron-phonon interaction in the adiabatic approximation for CdSe/ZnSe and CuCl/NaCl quantum dot systems. It is found that, as the radius of the dot decreases, the magnitude of the electron-phonon interaction energy first increases, passes through a maximum, and then gradually decreases to the value appropriate to the situation where the electron is weakly localized inside the dot. As the height of the interface barrier decreases, the absolute value of the electron-phonon interaction energy also decreases. These results indicate that the dependence of the electron-phonon interaction on the radius of the dot is much smaller than predicted from the simplified model with infinite value of the bandgap mismatch.

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## I. INTRODUCTION

Remarkable progress in semiconductor nanotechnology has made it possible to fabricate a wide array of semiconductor heterostructures. In these structures electronic states are subject to a strong dimensional confinement effect arising from the mismatch in the bandgaps of the constituent materials. Among various kinds of nanostructures (quantum wells and superlattices with electronic confinement in one dimension, quantum wires with two-dimensional confinement potentials and quantum dots with the quantum confinement present in all three dimensions), the quantum dot (QD) systems have attracted the most attention because of their potential applications to electronic and optoelectronic devices<sup>1,2</sup> and the interesting quantum-mechanical phenomena associated with them.

The electron-phonon coupling in nanostructures also has different features from that in the bulk. Namely, there is a strong increase of its strength with the reduction of dimensionality (from 3D in the bulk to 0D in the quantum dot), and there exist surface optical (SO) modes<sup>3</sup> due to the difference in the dielectric constants of the materials inside and outside the structure. To discuss phonon effects on electrons in nanostructures in a proper way, these phonon features (polaron effects) have to be taken into account.

Since the QD is one of the simplest examples of quantum confined structures, the polaron effects on an electron have been studied extensively both theoretically and experimentally. Polaron effects have been studied theoretically in QD's of various forms: cylindrical QD's,<sup>4</sup> rectangular quantum boxes,<sup>5</sup> and QD's with a parabolic confinement potential.<sup>6-8</sup> In the spherical quantum dots polaron effects have been extensively investigated within the dielectric continuum model.<sup>9-11</sup> These effects were first studied for the case of a free polaron in a spherical QD (an electron confined in the QD interacts with phonons) implementing an adiabatic approximation,<sup>9-11</sup> in which surface optical phonon modes

do not contribute to the polaron energy shift. Second-order perturbation theory<sup>12</sup> was also used to calculate the polaron shift; it was found that the bulk-type phonons play the dominant role in the polaron energy shift. The all-coupling variational technique<sup>13</sup> valid for a wide range of material parameters was also developed and systematic calculations of the polaron energy shift were performed. The major results of these considerations are that (1) the bulk LO phonons play the most important role in the polaron effects and the contribution from the SO phonons is either negligible or nonexistent and (2) with the increase of the dot's radius the magnitude of the polaron energy shift decreases rapidly from a large value and then gradually approaches its bulk value.

However, almost all models utilized in the above papers suffer from one important drawback: they all assume that the discontinuity at the interface of the QD has an infinite value. The effect of the finite value of the discontinuity was considered in Refs. 11,12; however, the electron-phonon Hamiltonian was not given there in explicit form. The assumption of an infinite surface barrier gives rise to the fact that the electron is always confined perfectly inside the dot. When the bandgap mismatch has a finite value, the electron can penetrate into the barrier material. Since the real semiconductor quantum dots are usually embedded in another polar material, e.g., a GaAs QD in a AlGaAs matrix, this may result in a significant change of the total electron-phonon interaction energy since an electron in the barrier will also interact with LO phonons pertinent to that medium. Thus the full electron-phonon interaction Hamiltonian should comprise all these effects: the interaction of an electron with the internal LO phonons of the QD material together with the interaction with phonons in the outer medium and the electron-SO-phonon interaction due to the presence of the interface (surface of the dot) should all be considered together.

In the present work we derive a Fröhlich Hamiltonian describing the electron-phonon interaction in a spherical quantum dot embedded in another polar material, taking into

account interactions with both internal and external LO and SO phonons. This Hamiltonian is valid for quantum dot systems with finite values of the bandgap mismatch on the surface of the dot (finite values of the confinement potential). In order to derive this Hamiltonian, various phonon modes responsible for polarization of the medium were first considered and then the interaction of a charged particle (electron or hole) with them was calculated. The electron-phonon interaction in confined systems was first studied by Fuchs and Kliewer,<sup>14</sup> Licari and Evrard,<sup>15</sup> and Lucas *et al.*<sup>16</sup> Later Wendler<sup>17</sup> extended their method for the calculation of the phonon modes in layered semiconductor heterostructures. Klein *et al.*<sup>9</sup> obtained the Hamiltonian describing the electron-phonon interaction in spherical QD's embedded in a nonpolar material assuming perfect confinement of an electron in the dot. This Hamiltonian was used in the works cited above and was also adapted for the cases of the bound polaron<sup>10,18</sup> and exciton<sup>10,19</sup> confined in the QD. Recently the approach of Licari and Evrard and Wendler was also used to derive the electron-phonon interaction Hamiltonian for quantum wire systems,<sup>20</sup> again assuming perfect confinement of an electron in the system. The electron-phonon interaction was also studied in quantum well structures within the second-order perturbation theory<sup>21</sup> assuming finite value of the interface barrier.

This paper is organized in the following way. In the next section the derivation of the electron-phonon Hamiltonian is presented; first the interaction with SO modes is considered and then the electron-LO-phonon interaction is calculated. In the following section this new Hamiltonian is applied to the problem of the single polaron confined in spherical quantum dot. To simplify the consideration, the electron-phonon interaction is treated in the adiabatic approximation in Zn<sub>1-x</sub>Cd<sub>x</sub>Se/ZnSe (Ref. 22) and CuCl/NaCl QD systems. Finally, the last section gives some concluding remarks and outlines possible future directions of research.

## II. THE ELECTRON-PHONON INTERACTION HAMILTONIAN

We consider a sphere of radius  $R$  made of a polar material with dielectric constant  $\varepsilon_1(\omega)$  (material 1) embedded in an infinite polar medium of dielectric constant  $\varepsilon_2(\omega)$  (material 2). We need to derive the Fröhlich Hamiltonian describing the interaction of an electron with longitudinal optical (LO) phonons. In this situation the only relevant modes are the internal and external LO (bulk) and the surface (SO) modes. Since we have two different polar media there should exist two different types of LO phonons associated with them, which we call bulk LO phonons, and one type of SO phonons.

Proceeding from the standard electrostatic Maxwell equations written for the dielectric continuum model

$$\nabla \cdot \mathbf{D} = 0, \quad (1)$$

$$\mathbf{D} = \varepsilon \mathbf{E} = \mathbf{E} + 4\pi \mathbf{p}, \quad (2)$$

$$\mathbf{E} = -\nabla \varphi, \quad (3)$$

where  $\mathbf{D}$ ,  $\mathbf{E}$ ,  $\mathbf{p}$ ,  $\varphi$  are the dielectric displacement vector, electric field, the polarization density, and the polarization potential, respectively, we easily get the Poisson equation for the potential  $\varphi(\mathbf{r})$  in this system

$$\varepsilon_i(\omega) \Delta \varphi = 0, \quad i = 1, 2. \quad (4)$$

From this equation we have two possibilities.

(1)  $\varepsilon_i(\omega) = 0$ , which, since the dielectric constant is given by

$$\varepsilon_i(\omega) = \varepsilon_{i\infty} \frac{\omega^2 - \omega_{iLO}^2}{\omega^2 - \omega_{iTO}^2}, \quad i = 1, 2, \quad (5)$$

corresponds to the polarization due to the bulk LO modes of eigenfrequency  $\omega_{iLO}$ . Here  $\varepsilon_{i\infty}$  is the high-frequency dielectric constant,  $\omega_{iLO}$  and  $\omega_{iTO}$  are the LO and TO eigenfrequencies related by  $\varepsilon_{i0}/\varepsilon_{i\infty} = (\omega_{iLO}/\omega_{iTO})^2$ ,  $\varepsilon_{i0}$  is the static dielectric constant.

(2)  $\Delta \varphi = 0$ , which will give another type of solution. It was shown in Ref. 15 that the polarization associated with these modes gives rise to a surface charge only, and thus these modes are usually called surface or interface optical (SO) phonon modes. Let us consider these two cases separately and derive the Hamiltonian which describes the interaction of a charged particle (electron or hole) with bulk LO and SO phonons.

### A. Electron-SO-phonon interaction

Assuming that the eigenfrequencies  $\omega_s$  associated with SO phonons are not equal to either  $\omega_{1LO}$  or  $\omega_{2LO}$ , the solution of the Poisson equation

$$\Delta \varphi_i(\mathbf{r}) = 0, \quad i = 1, 2 \quad (6)$$

can be written in the standard form

$$\begin{aligned} \varphi_1(\mathbf{r}) &= \sum_{lm} C_{lm}^{(1)} \left(\frac{r}{R}\right)^l Y_{lm}(\theta, \varphi), \quad r < R, \\ \varphi_2(\mathbf{r}) &= \sum_{lm} C_{lm}^{(2)} \left(\frac{R}{r}\right)^{l+1} Y_{lm}(\theta, \varphi), \quad r > R, \end{aligned} \quad (7)$$

where  $C_{lm}^{(1)}, C_{lm}^{(2)}$  are constants to be determined later, and  $Y_{lm}(\theta, \varphi)$  are the spherical harmonics. Here we have assumed that the outer medium is infinite in extent.

The electrostatic boundary conditions for these potentials can be written as

$$\varphi_1|_{r=R} = \varphi_2|_{r=R}, \quad (8)$$

$$D_{1n} = \varepsilon_1(\omega_s) \frac{\partial \varphi_1}{\partial r} \Big|_{r=R} = D_{2n} = \varepsilon_2(\omega_s) \frac{\partial \varphi_2}{\partial r} \Big|_{r=R}. \quad (9)$$

From the continuity of the potential  $\varphi$  [Eq. (9)], we obtain for the constants  $C_{lm}^{(1)}$  and  $C_{lm}^{(2)}$  that

$$C_{lm}^{(1)} = C_{lm}^{(2)} \equiv C_{lm}, \quad (10)$$

while from the continuity of the normal component of the displacement vector  $\mathbf{D}$  [Eq. (10)], the equation for the SO phonon frequencies follows

$$l\varepsilon_1(\omega_s) + (l+1)\varepsilon_2(\omega_s) = 0. \quad (11)$$

By solving this equation together with Eq. (2), the values of the SO phonon eigenfrequencies  $\omega_s \equiv \omega_l$  can be determined. Note that for  $l=0$  the only solution of this equation is for  $\omega_0 = \omega_{2\text{LO}}$ , which corresponds to the interaction of an electron with bulk LO phonons. Thus the lowest value of the orbital quantum number for SO phonon modes is  $l=1$ .

The polarization densities associated with the potentials defined above [Eq. (4)] can then be cast in the following form

$$\mathbf{p}_1(\mathbf{r}) = - \sum_{lm} \frac{\chi_1(\omega_l)}{4\pi} C_{lm} \nabla \left[ \left( \frac{r}{R} \right)^l Y_{lm}(\theta, \varphi) \right], \quad (12)$$

$$\mathbf{p}_2(\mathbf{r}) = - \sum_{lm} \frac{\chi_2(\omega_l)}{4\pi} C_{lm} \nabla \left[ \left( \frac{R}{r} \right)^{l+1} Y_{lm}(\theta, \varphi) \right], \quad (13)$$

where  $\chi_1(\omega_l)$  and  $\chi_2(\omega_l)$  are susceptibilities of materials 1 and 2, respectively.

In order to determine the constants  $C_{lm}$  and to proceed further with the derivation of the electron-phonon interaction potential, we must calculate the Hamiltonian for a given phonon mode (the free phonon Hamiltonian). We start with the basic equation of motion for the relative displacement of the ions in material  $i$  ( $i=1,2$ ):

$$\mu_i \ddot{\mathbf{u}} = -\mu_i \omega_{i0}^2 \mathbf{u} + e \mathbf{E}_{\text{loc}}, \quad (14)$$

where  $\mu_i$  is the reduced mass for an ionic pair,  $\omega_{i0}$  is the characteristic frequency associated with the short-range interaction, and  $\mathbf{E}_{\text{loc}}$  is the local field at the position of the ionic pair. The oscillating ions produce a polarization field

$$\mathbf{p}(\mathbf{r}) = n e \mathbf{u} + n \alpha \mathbf{E}_{\text{loc}}, \quad (15)$$

where  $n$  is the number density of pairs and  $\alpha$  is the polarizability of a pair.

According to the equation of motion, we may express the Hamilton function  $H_{ph}^{(\text{SO})}$  in the form of the following integral:

$$H_{ph}^{(\text{SO})} = \frac{1}{2} \int d^3 r (n\mu |\dot{\mathbf{u}}|^2 + n\mu \omega_0^2 |\mathbf{u}|^2 - n e \mathbf{u} \mathbf{E}_{\text{loc}}). \quad (16)$$

Using Eq. (12) for the relation between the polarization and the macroscopic electric field  $\mathbf{E}$ , together with the well-known Lorentz relation between the local and macroscopic electric field

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \frac{4\pi}{3} \mathbf{p}, \quad (17)$$

and the equations for LO and TO phonon frequencies  $\omega_{\text{LO}}, \omega_{\text{TO}}$ :

$$\omega_{\text{LO}}^2 = \omega_0^2 + \frac{(8\pi/3)\omega_p^2}{1 + (8\pi/3)n\alpha}, \quad \omega_{\text{TO}}^2 = \omega_0^2 - \frac{(4\pi/3)\omega_p^2}{1 - (4\pi/3)n\alpha}, \quad (18)$$

$$\varepsilon_\infty = \frac{1 + (8\pi/3)n\alpha}{1 - (4\pi/3)n\alpha}, \quad (19)$$

we may rewrite Eq. (16) in the following form:<sup>17</sup>

$$H_{ph}^{(\text{SO})} = \frac{1}{2} \int d^3 r \Theta(\omega_l) (|\dot{\mathbf{p}}|^2 + \omega_l^2 |\mathbf{p}|^2), \quad (20)$$

where

$$\Theta(\omega) = \frac{\omega_p^2}{[\omega_p^2 + 4\pi n \alpha (\omega_0^2 - \omega^2)]^2}, \quad \omega_p^2 = \frac{4\pi n e^2}{\mu}. \quad (21)$$

We now introduce phonon creation  $a_{lm}^\dagger$  and annihilation  $a_{lm}$  operators as follows:

$$\mathbf{p}_1(\mathbf{r}) = - \sum_{lm} \frac{\chi_1(\omega_l)}{4\pi} C_{lm} \nabla \left[ \left( \frac{r}{R} \right)^l Y_{lm}(\theta, \varphi) \right] (a_{lm}^\dagger + a_{lm}), \quad (22)$$

$$\dot{\mathbf{p}}_1(\mathbf{r}) = \sum_{lm} i \omega_l \frac{\chi_1(\omega_l)}{4\pi} C_{lm} \nabla \left[ \left( \frac{r}{R} \right)^l Y_{lm}(\theta, \varphi) \right] (a_{lm}^\dagger - a_{lm}) \quad (23)$$

and analogously for  $\mathbf{p}_2(\mathbf{r})$  and  $\dot{\mathbf{p}}_2(\mathbf{r})$ . These expressions will allow us to obtain the standard free phonon Hamiltonian

$$H_{ph}^{(\text{SO})} = \sum_{lm} \hbar \omega_l \left( a_{lm}^\dagger a_{lm} + \frac{1}{2} \right). \quad (24)$$

Substituting expressions (22) and (23) into Eq. (20) and using the usual commutation relations for the operators  $a_{lm}^\dagger$  and  $a_{lm}$

$$[a_{lm}^\dagger, a_{l'm'}] = \delta_{ll'} \delta_{mm'}, \quad [a_{lm}^\dagger, a_{l'm'}^\dagger] = [a_{lm}, a_{l'm'}] = 0, \quad (25)$$

and the first Green's identity

$$\int d^3 r \nabla \phi \cdot \nabla \psi = - \int d^3 r \phi \Delta \psi + \int ds \phi \frac{\partial \psi}{\partial r} \quad (26)$$

to perform the integration, we obtain constants  $C_{lm}$  in the form

$$C_{lm}^2 = \frac{2\pi\hbar}{\omega_l R} \frac{1}{\chi_1^2(\omega_l) \Theta_1(\omega_l) l + \chi_2^2(\omega_l) \Theta_2(\omega_l) (l+1)}. \quad (27)$$

The electron-phonon interaction Hamiltonian describing the interaction of the point charge (electron or hole) at position  $\mathbf{r}_e$  with the polarization  $\mathbf{p}(\mathbf{r})$  is given by

$$H_{ep}^{(\text{SO})} = -e \int d^3 r \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}_e|} \cdot \mathbf{p}(\mathbf{r}). \quad (28)$$

Substituting in this equation the polarizations  $\mathbf{p}_1(\mathbf{r})$  and  $\mathbf{p}_2(\mathbf{r})$  together with constants  $C_{lm}$  determined above, we will obtain for the electron-SO-phonon interaction the following expression:

$$H_{ep}^{(SO)} = -\frac{e}{4\pi} \sum_{lm} C_{lm} \{ [\chi_1(\omega_l) I_{lm} + \chi_2(\omega_l) J_{lm}] a_{lm} + \text{H.c.} \}, \quad (29)$$

$$I_{lm} = \int_{r < R} d^3r \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}_e|} \cdot \nabla \left[ \left( \frac{r}{R} \right)^l Y_{lm}(\theta, \varphi) \right],$$

$$J_{lm} = \int_{R > r} d^3r \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}_e|} \cdot \nabla \left[ \left( \frac{R}{r} \right)^{l+1} Y_{lm}(\theta, \varphi) \right].$$

In order to evaluate the integrals, we again apply the first Green's identity which transforms the integrals over the volume into the integrals over the surface of the sphere with radius  $R$ :

$$\begin{aligned} \chi_1(\omega_l) I_{lm} + \chi_2(\omega_l) J_{lm} &= [\chi_1(\omega_l) l + \chi_2(\omega_l) (l+1)] \\ &\times \frac{1}{R} \int_{r=R} ds \frac{1}{|\mathbf{r} - \mathbf{r}_e|} Y_{lm}(\theta, \varphi). \end{aligned} \quad (30)$$

This last integral can be easily evaluated by making use of the well-known expansion

$$\begin{aligned} \frac{1}{|\mathbf{r} - \mathbf{r}_e|} \Big|_{r=R} &= \frac{4\pi}{2l+1} \\ &\times \begin{cases} \sum_{lm} \frac{1}{R} \left( \frac{r_e}{R} \right)^l Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta_e, \varphi_e), & r_e < R, \\ \sum_{lm} \frac{1}{r_e} \left( \frac{R}{r_e} \right)^l Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta_e, \varphi_e), & r_e > R. \end{cases} \end{aligned} \quad (31)$$

Realizing also that  $\chi_i(\omega) = \varepsilon_i(\omega) - 1$ , the factor  $\chi_1(\omega_l) l + \chi_2(\omega_l) (l+1)$  becomes equal to  $-(2l+1)$  so that the final expression for the electron-SO-phonon interaction can be given as follows:

$$H_{ep}^{(SO)} = -\sum_{lm} \alpha_l [V_{lm}(\mathbf{r}) a_{lm} + \text{H.c.}], \quad (32)$$

with<sup>11</sup>

$$\alpha_l = \left( \frac{2\pi\hbar}{\omega_l R} \frac{1}{\chi_1^2(\omega_l) \Theta_1(\omega_l) l + \chi_2^2(\omega_l) \Theta_2(\omega_l) (l+1)} \right)^{1/2}, \quad (33)$$

$$\chi_i^2(\omega) \Theta_i(\omega) = \varepsilon_{i\infty} \frac{\omega_{iLO}^2 - \omega_{iTO}^2}{(\omega^2 - \omega_{iTO}^2)^2}, \quad i=1,2, \quad (34)$$

$$V_{lm}(\mathbf{r}) = \begin{cases} (r/R)^l Y_{lm}(\theta, \varphi), & r < R, \\ (R/r)^{l+1} Y_{lm}(\theta, \varphi), & r > R. \end{cases} \quad (35)$$

and the frequencies  $\omega_l$  are to be determined from Eq. (11). It should be mentioned here that the quadratic equation (11) has two different solutions due to the presence of two polar materials: one of them is associated with medium 1 and the other with medium 2.

In the limiting case when the outside medium is nonpolarizable, i.e.,  $\varepsilon_2(\omega) \equiv \varepsilon_d = \text{const}$ , there will be only one solution for the eigenfrequencies, and the Hamiltonian can be easily rewritten in the well-known form first obtained by Klein *et al.*<sup>9</sup>

$$H_{ep}^{(SO)} = -\sum_{lm} \alpha_l [V_{lm}(\mathbf{r}) a_{lm} + \text{H.c.}], \quad (36)$$

with the electron-SO-phonon coupling constant

$$\alpha_l = \frac{\varepsilon_{1\infty} \sqrt{l}}{l \varepsilon_{1\infty} + (l+1) \varepsilon_d} \omega_{1LO} \sqrt{\frac{2\pi e^2 \hbar}{\omega_l R} \left( \frac{1}{\varepsilon_{1\infty}} - \frac{1}{\varepsilon_{10}} \right)}, \quad (37)$$

$$\omega_l^2 = \frac{\varepsilon_d + (\varepsilon_d + \varepsilon_{10}) l}{\varepsilon_d + (\varepsilon_d + \varepsilon_{1\infty}) l} \frac{\varepsilon_{1\infty}}{\varepsilon_{10}} \omega_{1LO}^2.$$

Another limiting case is when  $\varepsilon_1(\omega) = \varepsilon_2(\omega)$ , i.e., there is no interface. In this case Eq. (11) will be satisfied only when  $\omega_l = \omega_{LO}$ , and this situation corresponds to the interaction of a charged particle with bulk LO phonons.

## B. Electron-bulk-phonon interaction

In this case we need to consider two separate cases: (1)  $\omega = \omega_{1LO}$  corresponding to the interaction with bulk LO phonons in the material 1 and (2)  $\omega = \omega_{2LO}$  appropriate for the LO modes in the outside medium. We start with the first case.

(1) Here the solution of the Poisson equation

$$\begin{aligned} \varepsilon_1(\omega_{1LO}) \Delta \varphi_1(\mathbf{r}) &= 0, \quad \varepsilon_1(\omega_{1LO}) = 0, \quad r < R, \\ \varepsilon_2(\omega_{1LO}) \Delta \varphi_2(\mathbf{r}) &= 0, \quad \varepsilon_2(\omega_{1LO}) \neq 0, \quad r > R \end{aligned} \quad (38)$$

takes the form

$$\begin{aligned} \varphi_1(\mathbf{r}) &= \sum_{klm} A_{klm} j_l(kr) Y_{lm}(\theta, \varphi), \quad r < R, \\ \varphi_2(\mathbf{r}) &= \sum_{lm} B_{lm} (R/r)^{l+1} Y_{lm}(\theta, \varphi), \quad r > R. \end{aligned} \quad (39)$$

From the continuity of the normal component of the displacement vector on the surface, we obtain that the potential outside the sphere is equal to zero:

$$\varphi_2(\mathbf{r}) = 0, \quad r > R. \quad (40)$$

From the continuity of the electrostatic potential on the interface, we then conclude that

$$j_l(kR) = 0 \quad (41)$$

which specifies the allowed spectrum of  $k \equiv k_{ln} = \mu_{ln}/R$ , where  $\mu_{ln}$  is the  $n$ th root of the  $l$ th order spherical Bessel function  $j_l$ . The unknown constants  $A_{lmn}$  will be determined later from the comparison of the polarization Hamiltonian with the free phonon Hamiltonian written for LO modes in medium 1, similar to the case of the electron-SO-phonon interaction considered above.

(2) In the situation when the frequency  $\omega$  coincides with the eigenfrequency of LO phonons in medium 2,  $\omega_{2LO}$ , the potential outside the dot is given by

$$\varphi_2(\mathbf{r}) = \sum_{klm} \tilde{A}_{klm} f_l(kr) Y_{lm}(\theta, \phi) \quad (42)$$

with

$$f_l(kr) = j_l(kr) + \tilde{B}_{klm} n_l(kr) \quad (43)$$

and  $n_l$  is the spherical Neumann function of the  $l$ th order. Inside the quantum dot the potential is equal to zero, and its continuity on the interface results in the condition

$$f_l(kR) = 0. \quad (44)$$

There is one constant still undetermined ( $\tilde{B}_{klm}$ ). To find it we need to set up boundary conditions on the distant outer interface with radius  $R_2$ :

$$f_l(kR_2) = 0. \quad (45)$$

Together these two last equations determine the allowed spectrum of  $k$  values:  $k \equiv k_{ln} = \nu_{ln}/R$ , and values of  $\tilde{B}_{klm}$ . After the spectrum and constants are found, the value of  $R_2$  can go to infinity so that the final answer is independent of its particular value.

The rest of the calculation is analogous to the derivation of the electron-SO-phonon interaction Hamiltonian. We again set up the polarization vectors associated with phonons: this time there will be two of them, one for each of the LO phonon frequencies. Writing the classical Hamilton function for each polarization separately and equating it to the free phonon Hamiltonian

$$H_{ph}^{(LO)} = \sum_{lmn} \hbar \Omega \left( a_{lmn}^\dagger a_{lmn} + \frac{1}{2} \right) \quad (46)$$

with eigenfrequency  $\Omega = \omega_{1LO}$  or  $\omega_{2LO}$ , respectively, allows us to find the values of the normalization constants  $A_{lmn}$  and  $\tilde{A}_{lmn}$ :

$$A_{lmn} = \frac{4\pi\hbar}{\omega_{1LO} R \mu_{ln}^2 j_{l+1}(\mu_{ln})} \frac{1}{\chi_1^2(\omega_{1LO}) \Theta_1(\omega_{1LO})}, \quad (47)$$

$$\tilde{A}_{lmn} = \frac{2\pi\hbar}{\omega_{2LO} R I_{ln}} \frac{1}{\chi_2^2(\omega_{2LO}) \Theta_2(\omega_{2LO})}, \quad (48)$$

where the normalization integral  $I_{ln}$  is

$$I_{ln} = \nu_{ln}^2 \int_1^R dx x^2 |f_l(\nu_{ln} x)|^2.$$

Then the electron-phonon interaction Hamiltonian can also be easily evaluated.

After some calculations, it turns out that the polarization associated with the frequency  $\omega_{1LO}$  gives rise to a nonzero value of this interaction only when an electron is confined inside the sphere ( $r_e < R$ ). Physically this fact can be understood by noting that in our model phonons are dispersionless and thus the frequency  $\omega_{1LO}$  corresponds to the excitation of phonons only in medium 1. The value of this electron-phonon interaction is equal to (in order to calculate it, the first Green's identity was used together with expansion of  $|\mathbf{r} - \mathbf{r}_e|^{-1}$  in spherical harmonics):

$$H_{ep}^{(1)} = - \sum_{lmn} \beta_{lmn}^{(1)} [V_{lmn}^{(1)}(\mathbf{r}) a_{lmn} + \text{H.c.}], \quad (49)$$

where

$$\beta_{ln}^{(1)} = \left\{ \frac{4\pi e^2}{R} \frac{\hbar \omega_{1LO}}{\mu_{ln}^2 j_{l+1}^2(\mu_{ln})} \left( \frac{1}{\epsilon_{1\infty}} - \frac{1}{\epsilon_{10}} \right) \right\}^{1/2}, \quad (50)$$

$$V_{lmn}^{(1)}(\mathbf{r}) = j_l(k_{ln} r) Y_{lm}(\theta, \varphi). \quad (51)$$

When the electron is outside the sphere ( $r_e > R$ ), it interacts only with the polarization due to phonons in medium 2. The value of this potential is

$$H_{ep}^{(2)} = - \sum_{lmn} \beta_{lmn}^{(2)} [V_{lmn}^{(2)}(\mathbf{r}) a_{lmn} + \text{H.c.}], \quad (52)$$

with

$$\beta_{ln}^{(2)} = \left\{ \frac{2\pi e^2}{R} \frac{\hbar \omega_{2LO}}{I_{ln}} \left( \frac{1}{\epsilon_{2\infty}} - \frac{1}{\epsilon_{20}} \right) \right\}^{1/2}, \quad (53)$$

$$V_{lmn}^{(2)}(\mathbf{r}) = f_l(k_{ln} r) Y_{lm}(\theta, \varphi). \quad (54)$$

Finally, the full electron-phonon Hamiltonian can be written by adding the electron-SO-phonon interaction potential and the free SO phonon Hamiltonian given by Eqs. (36) and (24) to the electron-bulk-phonon potential and the free LO phonon Hamiltonian obtained above:

$$H_{ep} = H_{ep}^{(SO)} + H_{ep}^{(LO)} + H_{ph}^{(SO)} + H_{ph}^{(LO)}, \quad (55)$$

where

$$H_{ep}^{(LO)} = \begin{cases} H_{ep}^{(1)}, & r < R, \\ H_{ep}^{(2)}, & r > R. \end{cases} \quad (56)$$

Note also that if the electron is confined perfectly inside the sphere, then this full Hamiltonian, given now by Eqs. (36),(24),(49),(46), agrees with that of Klein *et al.*<sup>9</sup>

### III. RESULTS OF CALCULATIONS

#### A. Method

In this section we apply the electron-phonon interaction Hamiltonian  $H_{ep}$  obtained above to the problem of a polaron in a spherical QD. We consider an electron which is confined

in a sphere with radius  $R$  and is interacting with LO phonons. In the effective-mass approximation the Hamiltonian of the system is given by sum of the electronic  $H_e$  and the electron-phonon interaction  $H_{ep}$  parts

$$H = H_e + H_{ep}. \quad (57)$$

Here the electronic part is given by

$$H_e = \frac{\mathbf{p}^2}{2m} + V_{\text{QD}}(\mathbf{r}), \quad (58)$$

where  $m$ ,  $\mathbf{p}$ , and  $\mathbf{r}$  are the effective mass, momentum and coordinate of the electron, respectively,  $V_{\text{QD}}(\mathbf{r})$  is the confinement potential of the QD:

$$V_{\text{QD}}(\mathbf{r}) = \begin{cases} 0, & r < R, \\ V_0, & r > R, \end{cases} \quad (59)$$

and  $V_0$  is the value of the conduction band-edge mismatch between the materials of the QD and the surrounding medium (the interface barrier potential experienced by an electron).

Let us assume that the electron moves much faster than the surrounding ions. This situation can be realized (1) when the radius of the QD is sufficiently small so that the quantum confinement gives rises to orbital shrinking of the electronic density and increases the kinetic energy of the electron and (2) when the electron-phonon interaction is so strong that electron self-localization occurs, i.e., fast electron oscillations. This means that the phonon field experiences a static distribution of electronic charge density and there is no correlation between the instantaneous position of the electron and the induced polarization field; this is what is usually called the adiabatic approximation.

Within this approach, the effect of the electron-phonon interaction is to displace the equilibrium positions of the ions. This can be achieved by performing two linear shift canonical transformations corresponding to the interaction with bulk ( $j=1$ ) and surface ( $j=2$ ) phonon modes:

$$U_j = \exp \left\{ \sum_s [f_s^{(j)} a_{js} + (f_s^{(j)})^* a_{js}^\dagger] \right\}, \quad (60)$$

where  $s = \{l, m, n\}$  for  $j=1$ ,  $s = \{l, m\}$  for  $j=2$ , and the parameters  $f_{js}$  are to be determined variationally. With these transformations taken into account, the total wave function of the system is given by the product of the electronic part  $|\psi(\mathbf{r})\rangle$  and the phonon part  $U_1 U_2 |0\rangle$ :

$$|\Psi\rangle = |\psi(\mathbf{r})\rangle U_1 U_2 |0\rangle, \quad (61)$$

where  $|0\rangle$  is the phonon ground state.

The subsequent minimization of the expectation energy value

$$E = \langle \Psi | H | \Psi \rangle \quad (62)$$

with respect to the variational parameters  $f_{js}$ , leads to the following standard expressions for them:

$$f_{lmn}^{(1)} = \begin{cases} -\frac{\langle \psi | V_{lmn}^{(1)}(\mathbf{r}) | \psi \rangle}{\hbar \omega_{1\text{LO}}}, & r < R, \\ -\frac{\langle \psi | V_{lmn}^{(2)}(\mathbf{r}) | \psi \rangle}{\hbar \omega_{2\text{LO}}}, & r > R, \end{cases} \quad (63)$$

$$f_{lm}^{(2)} = -\frac{\langle \psi | V_{lm}(\mathbf{r}) | \psi \rangle}{\hbar \omega_l}. \quad (64)$$

Following the variational method, we choose the electronic wave function in the form<sup>23</sup>

$$\psi(\mathbf{r}) = \psi_0(r) e^{-\gamma r}, \quad (65)$$

where  $\gamma$  is a variational parameter, indicating the degree of the electron-phonon interaction, and  $\psi_0(r)$  is the ground state eigenfunction of the Hamiltonian  $H_e$ :

$$\psi_0(r) = \begin{cases} N \frac{\sin(\zeta r)}{r}, & r < R, \\ N \frac{\sin(\zeta R)}{r} e^{-\eta(r-R)}, & r > R. \end{cases} \quad (66)$$

In this equation  $N$  is the normalization constant given as

$$N^{-2} = 4\pi(A+B) \quad (67)$$

with

$$A = \frac{1 - e^{-2\gamma R}}{4\gamma} - \frac{\gamma + e^{-2\gamma R} [\zeta \sin(2\zeta R) - \gamma \cos(2\zeta R)]}{4(\gamma^2 + \zeta^2)}, \quad (68)$$

$$B = \frac{\sin^2(\zeta R) e^{-2\gamma R}}{2(\zeta + \gamma)}, \quad (69)$$

and  $\zeta = \sqrt{2mE_0/\hbar^2}$ ,  $\eta = \sqrt{2m(V_0 - E_0)/\hbar^2}$ ; the value of the ground state energy of  $H_e$ ,  $E_0$ , is determined from the transcendental equation

$$\eta \tan(\zeta R) = -\zeta. \quad (70)$$

Note also that from this equation it follows that the smallest value of the QD radius  $R$  required for the existence of a bound state is  $R_c = (\pi^2 \hbar^2 / 8mV_0)^{1/2}$ .

After some calculations we can find the expectation energy  $E$  as a functional of the parameter  $\gamma$  in the form

$$E[\gamma] = \frac{2\pi\hbar^2 N^2}{m} [(\gamma^2 - \zeta^2)A + (\gamma + \eta)^2 B - \gamma \zeta C] + 4\pi N^2 V_0 B - \sum_{lmn} |\beta_{ln}^{(1)}|^2 \frac{|\langle \psi | V_{lmn}^{(1)}(\mathbf{r}) | \psi \rangle|^2}{\hbar \omega_{1\text{LO}}} - \sum_{lmn} |\beta_{ln}^{(2)}|^2 \frac{|\langle \psi | V_{lmn}^{(2)}(\mathbf{r}) | \psi \rangle|^2}{\hbar \omega_{2\text{LO}}}, \quad (71)$$

where  $C$  is given by

$$C = \frac{\zeta - e^{-2\gamma R} [\gamma \sin(2\zeta R) + \zeta \cos(2\zeta R)]}{2(\gamma^2 + \zeta^2)}. \quad (72)$$

In the above expression for the polaron energy functional  $E$ , the first two summands correspond to the energy of the bare electron confined in the QD, and the third and fourth ones describe the interaction of the electron with bulk LO phonons in media 1 and 2, respectively. Note also that in this equation the contribution from the electron-SO-phonon interaction is absent. This can be explained by the fact that in this case the electron has a spherically symmetrical wave function given by Eq. (65), and thus the value of the parameter  $f_{lm}^{(2)}$  is equal to zero. Physically this can be explained by noting that in the adiabatic approximation the electron is oscillating fast and since it is in the ground state with a spherically symmetrical charge distribution, the average surface ionic polarization charge is zero.

In the following calculations we will pay special attention to these quantities: total polaron energy  $E$ , given by Eq. (71), and contributions to it from the electron-bulk-phonon interaction in media 1 and 2,  $E_{\text{LO}}^{(1)}$  and  $E_{\text{LO}}^{(2)}$ , which can be cast in the following form:

$$E_{\text{LO}}^{(1)} = -\frac{[4eRN^2]^2}{R} \left( \frac{1}{\varepsilon_{1\infty}} - \frac{1}{\varepsilon_{10}} \right) \times \sum_{n=1}^{\infty} \frac{1}{n^2} \left[ \int_0^{\pi} dx \frac{\sin(nx)}{x} \sin^2 \left( \frac{\zeta R x}{\pi} \right) e^{-2\gamma R x / \pi} \right]^2, \quad (73)$$

$$E_{\text{LO}}^{(2)} = -\frac{[4e\pi N^2 \sin^2(\zeta R) e^{2\eta R}]^2}{R_2 - R} \left( \frac{1}{\varepsilon_{2\infty}} - \frac{1}{\varepsilon_{20}} \right) \times \sum_{k_{0n}} \frac{1}{k_{0n}^2} \left[ \int_R^{R_2} dr \frac{\sin[k_{0n}(r-R)]}{r} e^{-2\eta r} e^{-2\gamma r} \right]^2, \quad (74)$$

where  $k_{0n} = \pi n / (R_2 - R)$ ,  $n = 1, 2, \dots$ , is the solution of Eqs. (44) and (45).

Since we assume that the outer medium is infinitely large ( $R_2 \rightarrow \infty$ ), we can assert that the separation between the adjacent values of  $k_{0n}$  is infinitely small and thus replace the summation over  $k_{0n}$  in Eq. (74) by a one-dimensional integral over  $k$  which represents the transition from the discrete phonon modes to the continuum spectrum of phonons. The resulting expression does not depend on the particular value of radius  $R_2$  and can be rewritten as follows:

$$E_{\text{LO}}^{(2)} = -[4e\pi^{1/2} N^2 \sin^2(\zeta R) e^{2\eta R}]^2 \left( \frac{1}{\varepsilon_{2\infty}} - \frac{1}{\varepsilon_{20}} \right) \times \int_0^{\infty} \frac{dk}{k^2} \left[ \int_R^{R_2} dr \frac{\sin[k(r-R)]}{r} e^{-2\eta r} e^{-2\gamma r} \right]^2. \quad (75)$$

The energy of the bound polaron and electron-phonon interaction energies (73),(75) can then be found by minimizing numerically the functional  $E[\gamma]$  with respect to the parameter  $\gamma$ .

### B. Electron-phonon coupling

Numerical calculations have been carried out for  $\text{Zn}_{1-x}\text{Cd}_x\text{Se}/\text{ZnSe}$  QD systems with different values of  $x$  and for CuCl quantum dots embedded in NaCl. We start with

TABLE I. Physical parameters of two binary compounds:  $m$  is the mass of an electron (in units of a free electron mass),  $E_g$  is the energy band gap (in eV),  $\varepsilon_0$  and  $\varepsilon_{\infty}$  are the static and high-frequency dielectric constants,  $\hbar\omega_{\text{LO}}$  is the energy of the LO phonon (in meV).

Material	$\varepsilon_0$	$\varepsilon_{\infty}$	$\hbar\omega_{\text{LO}}$	$m$	$E_g$
CdSe	6.23	9.56	26.46	0.11	1.9
ZnSe	7.6	5.4	31.4	0.13	2.82
CuCl	3.61	7.9	25.64	0.5	3.4
NaCl	2.3	5.9	33.6	2.8	8.4

CdSe quantum dots. As was noted in Ref. 24, most of the necessary parameters are not very well known for ZnSe, CdSe, and their ternary alloys. Various theoretical studies use different values of these parameters. In this work we use the values of the material parameters adopted from Refs. 10,25 for ZnSe and CdSe (see Table I). The parameters for  $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$  are obtained by linear interpolation from the corresponding values for ZnSe and CdSe. For bandgap mismatch we use the simple relation  $\Delta E_g = 920x(\text{meV})$  for  $\text{Zn}_{1-x}\text{Cd}_x\text{Se}/\text{ZnSe}$  systems assuming that this approximation may have an effect only on quantitative properties, but not on qualitative conclusions. The value of the conduction band offset  $V_0$  is assumed to be 80% of  $\Delta E_g$ .<sup>24</sup>

In Fig. 1 we present the total polaron energy as a function of the QD radius. It is seen that all these energies approach the same negative value in the limit of large radius. Eventually the energy becomes negative in the limit of the large QD due to the fact that the electron-phonon interaction lowers the conduction band edge. For small values of the dot's radius these energies are smaller than the energy calculated for the QD with infinite barriers in the interface since the electron can spread out through the barrier, and when the radius is close to  $R_c$  the energies approach the values of  $V_0$  for the particular material.

In the next figure (Fig. 2) we present the total electron-phonon coupling energy  $E_{\text{LO}}$  given by the sum  $E_{\text{LO}}^{(1)} + E_{\text{LO}}^{(2)}$  for the  $\text{Zn}_{1-x}\text{Cd}_x\text{Se}/\text{ZnSe}$  QD system. The dependence of the electron-phonon interaction energy calculated for the case of perfect electron confinement ( $V_0 \rightarrow \infty$ ) is also shown

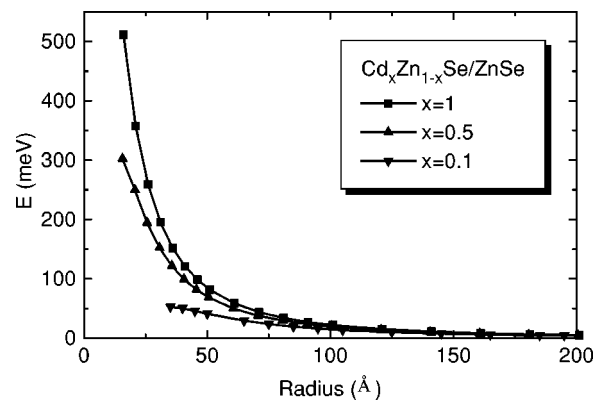


FIG. 1. The dependence of the total polaron energy  $E$  on the radius of the quantum dot.

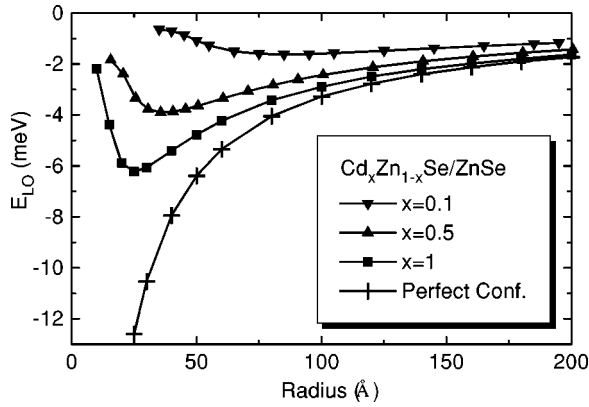


FIG. 2. The electron-phonon interaction energy  $E_{LO}$  as a function of the quantum dot's radius for the  $Zn_{1-x}Cd_xSe/ZnSe$  system.

(curve 4). It is seen that for large values of the dot's radius all curves obtained for the various values of Zn concentration approach the same value as calculated for the limiting case of the infinitely deep potential well. However, their behavior for smaller radii is rather different. When the radius decreases, the magnitude of the interaction energy first increases, as obtained earlier for the polaron confined perfectly in the QD:<sup>13</sup> for small values of  $R$ ,  $E_{LO} \propto 1/R$  since the radius of the dot now becomes the characteristic distance instead of the polaron radius in the bulk.<sup>18</sup> When the radius decreases further, the energy begins to deviate from the limiting  $1/R$  dependence due to the fact that the electron now can be present in the barrier as well, effectively increasing its localization radius. Note also that the smaller the value of  $x$  the smaller the interaction energy for all values of  $R$ . When the radius of the dot approaches the critical value  $R_c$  (the ground state level is close to the conduction band edge of the surrounding material) the electron-phonon interaction energy reaches its limiting value appropriate for the situation when the greatest part of the electronic density is in ZnSe.

In this situation the greatest contribution to the total value of the electron-phonon interaction comes from interaction of the electron with phonons in the surrounding ZnSe. This is clearly seen in Fig. 3 where we plotted separately the contributions from the internal LO phonons ( $E_{LO}^{(1)}$ ) and external phonons ( $E_{LO}^{(2)}$ ) for  $x=0.1$ . We see that for small radii the

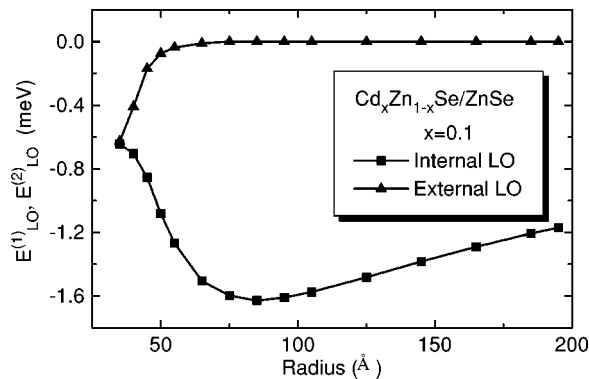


FIG. 3. The dependence of the interaction energy of the electron with internal and external LO phonons on the dot's radius.

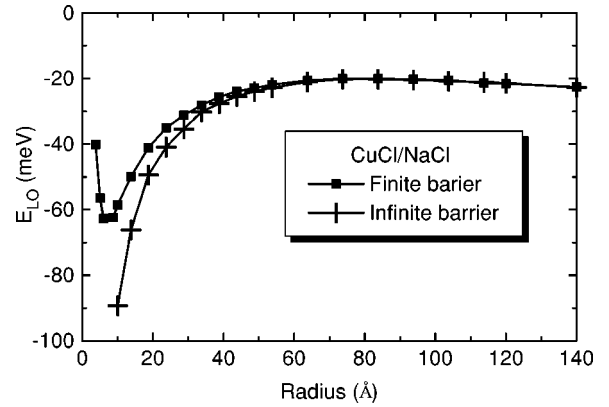


FIG. 4. The electron-phonon interaction energy  $E_{LO}$  as a function of the quantum dot's radius for the CuCl/NaCl system.

value of  $E_{LO}^{(1)}$  is much smaller than  $E_{LO}^{(2)}$ . As the radius increases the quantity  $E_{LO}^{(2)}$  exponentially quickly approaches zero since the energy level becomes significantly below the interface barrier so that the electron is localized in the QD. Then the interaction with internal QD phonons becomes dominant.

To demonstrate the behavior of the electron-phonon interaction in the limit of a very large confinement potential, we have also performed calculations for a CuCl quantum dot embedded in NaCl matrix. The parameters for this system are taken from Refs. 10,11,26 and also listed in Table I. For the conduction band offset we have assumed that it is 50% of  $\Delta E_g$ . From the dependencies shown in Fig. 4, it is seen that for most values of the QD radius the value of the electron-phonon interaction energy coincides with the limiting value obtained for perfect electron confinement, which is to be expected since the value of  $V_0$  here is 2.5 eV. Only for very small radii ( $R < 10 \text{ \AA}$ ), it deviates sharply from that curve. Thus it can be concluded that for this situation the model assuming an infinite value of the potential barrier on the interface produces reasonable results for almost all values of the QD radii.

#### IV. CONCLUDING REMARKS

In the present work we presented the Fröhlich Hamiltonian describing the electron-phonon interaction in spherical quantum dots. Such effects as the presence of a surrounding polar material in which the QD is embedded and the finite value of the band gap offset on the dot's interface are taken into account. Interactions with both bulk LO and SO phonons were also considered. This Hamiltonian was then applied to a study of the polaron confined in the quantum dot. The adiabatic variational method was used to treat the electron-phonon interaction. Generally speaking, this method gives valid results only for small quantum dots when effects of the quantum confinement predominate. It is in this range of QD radii that the most significant differences between the predictions of this Hamiltonian and the results obtained from the implementation of the model with perfect electron confinement<sup>9,10</sup> were found. As the radius of the dot decreases the magnitude of the electron-phonon interaction energy first



increases, passes through a maximum, and then gradually decreases to the value appropriate to the situation where the electron is weakly localized inside the dot. In this region the contribution from the interaction of the electron with phonons in the surrounding material, not considered in the previous study,<sup>10</sup> gives a significant contribution to the total electron-phonon coupling energy. As the height of the interface barrier decreases, the absolute value of the electron-phonon interaction energy also decreases. These results indicate that the dependence of the electron-phonon interaction on the radius of the dot is much smaller than can be predicted from the simplified model with infinite value of the band edge offset. The Hamiltonian obtained here should be useful to compare the predicted values of the electron-phonon coupling with experimentally observed values; it is known that the existing experimental results differ from each other significantly (see, e.g., Ref. 27, and references therein).

However, in order to make a quantitative comparison between the predictions of this model and available experimental data, the all-coupling variational scheme should be utilized to treat the electron-phonon interaction. This technique will allow us to obtain the correct values of the electron-phonon coupling in both weakly coupled systems such as GaAs/AlGaAs QD's and intermediate coupled materials where most of the compounds belong. The Hamiltonian derived here can also be quite easily extended for other interesting problems such as a polaron interacting with an impurity and confined in the QD (bound polaron problem), confined polaron exciton problem, and so on.

#### ACKNOWLEDGMENTS

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