Effect of the electron-phonon coupling on the ground state of a D^- center in a spherical quantum dot

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The influence of the electron-phonon coupling on the properties of a negatively charged donor center (D^-) confined in a semiconductor spherical quantum dot embedded in a glass matrix has been studied by variational means within the strong-coupling (Pekar) approach. A considerable enhancement of the binding is found for the D^- ground state, which results from the strong confinement of electrons and electron-phonon coupling. Numerical results are given for quantum dots made of CdSe nanocrystals of variable radii.
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Semiconductor quantum dots (QD) of spherical shapes formed by nanocrystals embedded in an isolating or semiconducting matrix have been widely studied[1] in the last years. The effect of the quantum confinement on the energy spectra has been studied[2–4] in the cases of neutral donors (D^0) and negatively charged (D^-) donors.[5–10] In particular, the present authors have shown that several excited states can be bound[8–10] in the case of a D^- center in a QD with a finite depth spherical confinement potential. The influence of the electron-LO phonon coupling on the properties of D^- centers in bulk crystals was studied by Adamowski.[11]

In the present paper, we consider the joint effects of the quantum confinement and the electron-phonon coupling on a D^- centers in a semiconductor QD embedded in a glass matrix. We use the effective-mass approximation for the excess electrons confined in the QD and the Fröhlich interaction Hamiltonian for the electron-LO phonon coupling. We assume that the donor impurity is located at the center of the spherical QD of radius R.

The Hamiltonian of the D^- center in the spherical QD including the coupling with LO phonons reads

$$H = H_{el} + H_{ph} + H_{int}. \tag{1}$$

The electronic Hamiltonian is given by

$$H_{el} = -\frac{\hbar^2}{2m_e^*}(\nabla_1^2 + \nabla_2^2) + \frac{e^2}{\varepsilon_\infty r_{12}} - \frac{e^2}{\varepsilon_\infty}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + V(r_1) + V(r_2), \tag{2}$$

where m_e^* is the electron effective band mass, ε_∞ is the high-frequency dielectric constant. r_1 and r_2 are the electron coordinates relative to the center of the sphere while r_{12} is the distance between the two particles. $V(r)$ is the confinement potential describing a spherical quantum well of radius R and infinite depth. The Hamiltonian of noninteracting spherically symmetric LO phonons is given by

$$H_{ph} = \sum_{lmq} \hbar\omega_{LO}\left(a_{lmq}^\dagger a_{lmq} + \frac{1}{2}\right), \tag{3}$$

where $a_{lmq}^\dagger$ (a_{lmq}) are the creation (annihilation) operators of the LO phonons with quantum numbers l,m,q and energy $\hbar\omega_{LO}$. The Hamiltonian of the electron -LO phonons interaction is given by:

$$H_{int} = -\sum_{lmq}\sum_{i=1}^{2}[V_l(q_l) j_l(q_l r_i) Y_{lm}(\theta_i,\phi_i) a_{lmq}^\dagger + \text{H.c.}] + \sum_{lmq}[V_l(q_l) j_l(0) Y_{lm}(\theta,\phi) a_{lmq}^\dagger + \text{H.c.}]. \tag{4}$$

The first and second terms describe, respectively, the interaction of the two electrons and of the positively charged donor center (D^+) with the LO phonons. $j_l(qr)$ and $Y_{lm}(\theta,\phi)$ are respectively the spherical Bessel functions and the spherical harmonics. The interaction amplitude $V_l(q_l)$ may be written in the form[3]

$$V_l(q_l) = e\left[\frac{4\pi\omega_{LO}}{q_l^2 R^3 j_{l+1}^2(q_l R)}\right]^{1/2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)^{1/2}, \tag{5}$$

where ε_0 is the static dielectric constant. In Eqs. (3) and (4), the summations run over $l=0,1,\ldots,\infty$, $m=-l,=l+1,\ldots,l$, and $q=q_l$, i.e., the roots of spherical Bessel functions.

In the first step of the calculations, we perform the Platzman transformation[12] of the Hamiltonian (1) in order to separate out the static lattice deformation induced by the positive donor center D^+, and to introduce a proper screening of the electron-donor Coulomb interaction.[3,13] The Platzman transformation operator reads

$$U_P = \exp\left[-\frac{V_l(q_l)}{\hbar\omega_{LO}} a^{\dagger}_{lmq} - \text{H.c.} \right]. \quad (6)$$

When applied to the Hamiltonian (1), it replaces the interaction of the positive donor center with LO phonons, the second term in Eq. (4), by the screening potential

$$V_{scr}(r_1, r_2) = \sum_{i=1}^{2} \frac{e^2}{r_i}\left(1 - \frac{r_i}{R}\right)\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right), \quad (7)$$

and additionally, introduces the self energy of the interaction of the donor center with the lattice polarization induced by the presence of the center. The self-energy term is independent of the quantum state of the system, and has no physical meaning. Therefore, we neglect it throughout the present paper. In the bulk-crystal limit, i.e., if $R \to \infty$, the screening potential $V_{scr}(r_1, r_2)$, added to the third term in Eq. (2), leads[12] to a screening of the electron-donor center interaction by the static dielectric constant ε_0.

In the second step of calculations, we apply the Pekar strong-coupling method[14] in order to get rid of the phonons from the problem. This approximation supposes that the motion of the electrons is much faster then that of the heavier ions. This may arise in the two following cases: (i) in the case of a microsphere with a small radius R, where the quantum confinement produces an orbital shrinking, which increases the electron speed; (ii) in the case of strong electron-phonon coupling, where an electron self-localization occurs, i.e., fast electron oscillations. According to this approach, the wave function of the electron-phonon system is given by the product *ansatz*

$$\Psi(\vec{r}_1, \vec{r}_2, \{a^{\dagger}_{lmq}, a_{lmq}\}) = \varphi(\vec{r}_1, \vec{r}_2)\chi(\{a^{\dagger}_{lmq}, a_{lmq}\}), \quad (8)$$

where φ is the electron part of the wave function. The phonon wave function χ is proposed in the form

$$\chi = \exp(S)|0\rangle, \quad (9)$$

where $|0\rangle$ is the phonon-vacuum state and S is an operator given by

$$S = -\sum_{lmq}\left[\frac{V_l(q_l)}{\hbar\omega_{LO}}(\rho^{(1)}_{lmq} + \rho^{(2)}_{lmq})a_{lmq} - \text{H.c.}\right]. \quad (10)$$

In Eq. (10), ρ_{lmq} is the one-electron density

$$\rho_{lmq} = \langle\varphi|j_l(qr)Y_{lm}(\theta,\varphi)|\varphi\rangle. \quad (11)$$

Owing to the indistinguishability of the electrons, $\rho^{(1)}_{lmq} = \rho^{(2)}_{lmq} = \rho_{lmq}$. The expectation value of the Hamiltonian, calculated with the use of the phonon function (9), yields the effective Hamiltonian

$$H_{eff} = \langle 0|\exp(-S)H\exp(S)|0\rangle = H_{el} + V_{scr} + V_{ep}, \quad (12)$$

where the effective electron phonon interaction term reads

$$V_{ep}[\varphi] = -4\sum_{lmq}\frac{V_l^2(q)}{\hbar\omega_{LO}}|\rho_{lmq}|^2. \quad (13)$$

Since the ground state is spherically symmetric, only the terms with $l = m = 0$ are nonzero. Moreover, the convergence of the summation over q is very fast due to the strong localization of the ground state.

In order to determine the reference energy for the charged donor D^- center, we have calculated the ground-state energies of the appropriate one-electron systems confined in the QD and interacting with LO phonons: the single-confined electron (polaron), and the neutral donor (D^0), which are described by the correspondingly simplified versions of Hamiltonian (1). The calculations for the confined polaron and the neutral donor D^0 have been performed with the use of the following trial wave function:

$$\varphi(r) = j_0(\pi r/R)\exp(-\alpha r)\sum_{i=0}^{N} c_i r^i, \quad (14)$$

where α and c_i are variational parameters and $j_0(\pi r/R)$ is the zero-order Bessel function, i.e., the exact ground-state solution of the problem of an electron confined in a spherical infinitely deep quantum well of radius R. For the ground state, the convergence has been reached for $N = 2$.

For the D^- center, we used a trial wave function, analogous to that we used previously[15] in the determination of the ground-state energy of an exciton-ionized-donor complex (D^+, X) in a spherical QD. It reads

$$\varphi(r_1, r_2, r_{12}) = j_0(\pi r_1/R)j_0(\pi r_2/R) \times \exp[-\alpha(r_1 + r_2)][1 + c_1(r_1 + r_2) + c_2 r_{12} + c_3(r_1^2 + r_2^2) + c_4 r_1 r_2], \quad (15)$$

where α and c_i are variational parameters. Due to the presence of the term dependent on r_{12}, the wave function (15) takes explicitly into account the electron-electron correlation. We have checked its accuracy by applying it to the problem of the hydrogen ion H^-, which provides an analog to the present problem without the electron-phonon coupling. The calculations performed with wave function (15) yield the H^- ground-state energy $E_{var} = -1.0514$ Ry, whereas the exact value[16] is $E_{exact} = -1.0555$ Ry (1Ry = 13.6 eV). If the coupling with phonons is included, the expectation value of the effective Hamiltonian (12) is a functional of the electron density (11). Therefore, the variational procedure cannot be linearized, and we have to minimize the expectation value of H_{eff} over all the variational parameters, which makes the problem numerically complicated. Nevertheless, we performed such a minimization for the ground-state energy as a function of R.

We have done our numerical calculations for material data corresponding to the CdSe nanocrystal in glass.[17] We have used the following material parameters[3] for the electron band mass, $m_e = 0.13m_0$, the dielectric constants, $\varepsilon_0 = 9.56$, and $\varepsilon_\infty = 6.23$, the LO-phonon energy, $\hbar\omega_{LO} = 26.46$ meV. The depth of the potential well for the CdSe nanocrystal in a glass matrix has recently been estimated[18] to be 1.3 eV. As a consequence of such a deep potential well value, the probability of penetration of the electrons into the barrier region

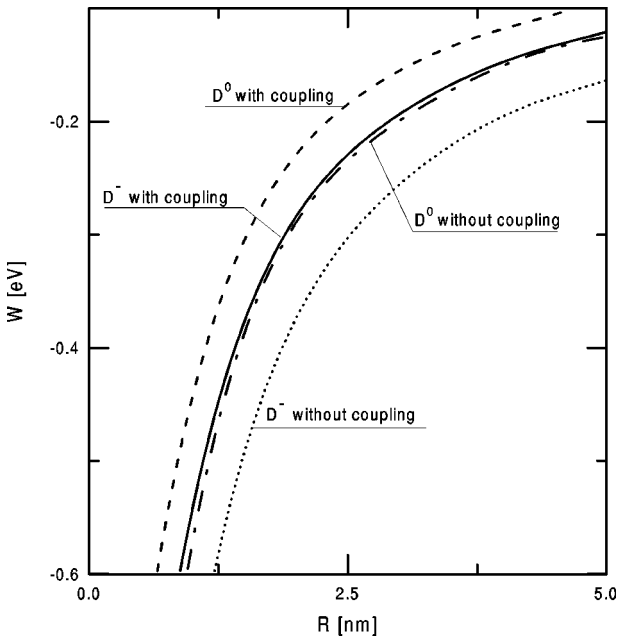

FIG. 1. Coulomb interaction energy as a function of radius R for a CdSe quantum dot for D^0 and D^- donor centers with and without electron-phonon coupling.

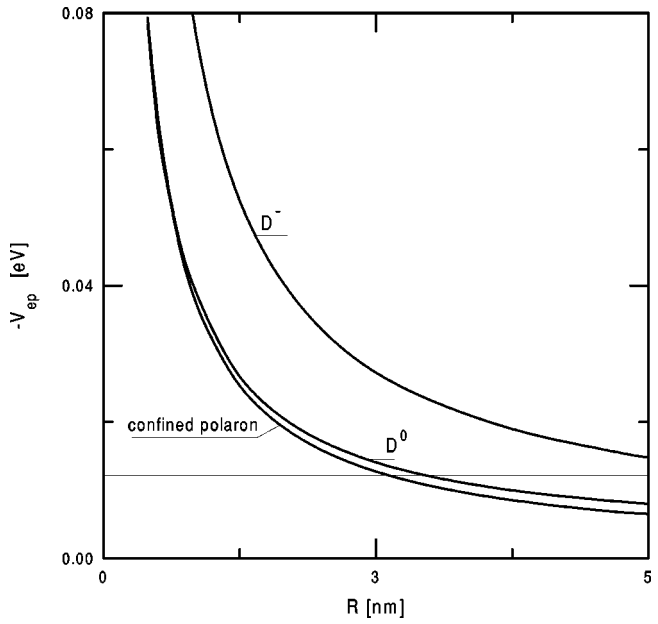

FIG. 2. Electron-phonon interaction energy for the confined polaron, D^0 and D^- donor centers as a function quantum-dot radius for a CdSe quantum dot. The thin line shows the self energy of a free polaron in a bulk crystal.

is negligibly small, at least for the D^- ground state, and for QD's of intermediate and large sizes. Therefore, in the case of CdSe QD's, the assumption of an infinitely deep potential well seems to be justified.

We have first determined the influence of the electron phonon coupling on the Coulomb ''interaction energies'' of the neutral and charged donors D^0 and D^-, defined respectively by $W_{D^0}=E_{D^0}-E_e$ and $W_{D^-}=E_{D^-}-2E_e$. Here, E_{D^0}, E_{D^-}, and E_e are the energies of the neutral and charged donors as well as of an electron in a QD. In Fig. 1, the interaction energies W are plotted as functions of the QD's radius for both the D^0 and D^- donor centers with, [Hamiltonian (12)], and without, [Hamiltonian (2)], the electron-phonon coupling. It appears that the electron phonon coupling shifts the interaction energies to higher values, i.e., smaller absolute values, which results from a larger screening of the electron-donor attraction. In Fig. 2, the electron phonon interaction energies V_{ep} for the electron (polaron), the neutral donor D^0, and the negatively charded donor D^-, are plotted against the QD's radius. For comparison, we have also plotted the free polaron ground-state energy in the bulk CdSe crystal. For QD's of small radii, there is no appreciable difference between the electron-phonon interaction energies of the confined polaron and of the neutral donor D^0. The electron-phonon interaction energy for the negatively charged donor is roughly equal to twice the value for the neutral donor.

Let us comment on the results of the present paper and compare them with those of other authors. The localization of the electrons in a semiconductor QD leads to an enhancement of the electron-phonon coupling. Indeed, the absolute value of the interaction energy rapidly increases with decreasing QD's radii. However, the present treatment of the electron-phonon coupling is based on the strong-coupling (Pekar) approach. The validity of this method has been recently studied[19] by Oshira *et al.* in the case of a polaron confined in a spherical QD embedded in a nonpolar material. The authors[19] concluded that in the case of CdSe QD's of small radii, ($R \lesssim 3$ nm), the Pekar method provides a good approximation to the electron-phonon coupling effect. Moreover, they[19] studied the effect of surface (SO) phonons and found that the effect of the coupling with the SO phonons is weak compared to that of the bulk LO phonons. Therefore, the SO phonons can be neglected in a first approximation.[20] Moreover, it was shown[21,3] that–due to the spherical symmetry–the on-center D^+ impurity is not coupled to the SO phonons.

The problem of electron-phonon coupling and its influence on the one-electron states in QD's have been studied by several authors.[21–23,3,24–26,19] These studies lead to the conclusion that the Pekar method[14] yields the correct results in the limit case of strong electron localization. For the QD's made of II-VI semiconducting compounds, the polaron radius is comparable to the radius of the QD. This is the case of the intermediate localization, for which we argue that we can extend the applicability of the strong-coupling method. However, for the III-V nanostructures with weak electron localization, a more general treatment of the electron-phonon coupling is needed. To our knowledge, we have presented the first calculations of electron-phonon coupling for a two-electron system confined in a quantum dot.

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