Exciton–optical phonon interaction in a spherical quantum dot embedded in nonpolar matrix

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(Received 12 November 2001; revised manuscript received 11 April 2002; published 7 October 2002)

Exciton–optical-phonon system in a spherical quantum dot embedded in a nonpolar matrix is studied with the consideration of the finite potential barrier and the image potential. The lowest energy of an exciton interacting with the bulk-type and the interface-type longitudinal-optical (LO) phonons is calculated by using a variational method. The virtual phonon number is also calculated in order to clarify the involvement of the LO phonon in exciton state. Our results show that with the decrease in the dot radius the LO-phonon effects on an exciton decrease gradually from the bulk value and then increase rapidly after taking the minimum. This is contrasted with the results calculated with the infinite potential barrier, where the monotonic decrease appears.

DOI: 10.1103/PhysRevB.66.153308 PACS number(s): 71.38.−k, 71.35.−y, 78.67.Hc

The effects of longitudinal-optical (LO) phonons on electrons and excitons in quasi-zero-dimensional semiconductor systems, called quantum dot systems, have attracted much attention theoretically[1–9] and experimentally.[2,4–6,10,11] However, different or even opposite conclusions have appeared, for example, in the size dependence of the exciton-phonon interaction.[1–11] It was pointed out that the exciton–LO-phonon coupling, mediated by the Fröhlich interaction, should vanish in small spherical nanocrystals.[1] Exciton–LO-phonon interactions have been discussed with the use of the adiabatic approximation by many authors.[2–6] There, some authors obtained that the exciton–LO-phonon interaction increases with the decrease in the dot radius in the strong confinement regime or weak confinement regime.[3–6] However, adiabatic approximation is valid only in the limit of strong confinement regime. This is because the differences between the lowest state and higher states are much larger than LO-phonon energy in the strong confinement case. On the other hand, when the confinement for an electron and a hole becomes weak, the energy difference between the lowest state and higher states becomes smaller than the LO-phonon energy. Then nonadiabatic effect becomes important. Therefore, we can say that both adiabatic and nonadiabatic processes should be taken into account for the exciton–LO-phonon system in general.[12]

In our previous works we studied the effect of LO phonons on the ground state of an electron[8] or an exciton[9] confined perfectly in a spherical quantum dot embedded in a glass matrix. The adiabatic and nonadiabatic effects of the LO phonons were taken into account and both effects were shown to be important in general. Following fundamental properties of the dot system were derived: (i) the LO-phonon effect on an electron increases rapidly with the decrease in the dot radius and (ii) the LO-phonon effect on an exciton decreases with the decrease in the dot radius because the LO-phonon effect on an electron and a hole cancel out each other. Our result showed that if the electron and the hole confined in the quantum dot have a similar distribution then the LO-phonon effects on an exciton vanish in the small dot limit, as pointed out in Ref. 1.

However, if the difference between the distributions of an electron and a hole becomes larger, the situation for exciton–LO-phonon system may be quite different. This situation occurs in the case of the finite confinement potential and the different masses for the electron and the hole. This problem has not been discussed theoretically up to now. Therefore, in the present paper, we study the effects of the exciton–LO-phonon interaction in a spherical quantum dot embedded in a nonpolar matrix with a finite potential barrier.

We consider a spherical semiconductor quantum dot with radius R, embedded in nonpolar matrix. The Hamiltonian for an exciton interacting with the LO-phonon is given by

$$H = H_{ex} + H_{ph} + H_{ex\text{-}ph}, \tag{1}$$

where H_{ex}, H_{ph}, and $H_{ex\text{-}ph}$ are the Hamiltonians of an exciton, LO phonons, and exciton–LO-phonon interaction, respectively. For the expressions of H_{ph} and $H_{ex\text{-}ph}$, one can refer to Ref. 9. Excitonic part H_{ex} with the effects of the finite potential barrier and the image charge is given by $H_{ex} = H_e + H_h + H_{e\text{-}h}$. H_j $(j = e,h)$ describes the Hamiltonian of an electron $(j = e)$ and a hole $(j = h)$ confined in the sphere, and is given by

$$H_j = \frac{\mathbf{p}_j^2}{2m_j} + V_{conf}^{(j)}(r_j) + H_S^j, \tag{2}$$

where $V_{conf}^{(j)}(r_j)$ is the confinement potential written as

$$V_{conf}^{(j)}(r_j) = \begin{cases} 0, & r_j \leqslant R \\ V_j, & r_j > R, \end{cases} \tag{3}$$

and the self-polarization term H_S^j is the interaction between the electron (hole) and its own image charge, and is given by (Ref. 13)

$$H_S^j = e^2 \sum_l \alpha_l h_l^S(r_j), \tag{4}$$

where we defined $h_l^S(r_j)$ as

$$h_l^S(r_j) = \begin{cases} (l+1) r_j^{2l} / (2\epsilon_\infty R^{2l+1}) & (r_j < R) \\ -l R^{2l+1} / (2\epsilon_d r_j^{2l+2}) & (r_j > R), \end{cases} \tag{5}$$

$$\alpha_l = \frac{\epsilon_\infty - \epsilon_d}{l\epsilon_\infty + (l+1)\epsilon_d}. \tag{6}$$

Here ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constant inside the sphere, respectively. ϵ_d is the dielectric constant of the nonpolar matrix that surrounds the dot.

The Coulomb interaction $H_{e\text{-}h}$ between the electron and the hole is given by (Ref. 13)

$$H_{e\text{-}h}=H^0_{e\text{-}h}+H_M, \tag{7}$$

where $H^0_{e\text{-}h}$ is the direct Coulomb interaction between the electron and the hole. H_M is a mutual polarization term that represents the interaction of one charge with the image charge created by the other charge. $H^0_{e\text{-}h}$ is given by

$$H^0_{e\text{-}h}=\begin{cases} -e^2/(\epsilon_\infty|\mathbf{r}_e-\mathbf{r}_h|) & (r_e<R,r_h<R)\\ -e^2\sum_{l,m} h^0_l(r_e,r_h)Y^m_l(\theta_e,\varphi_e)Y^{m*}_l(\theta_h,\varphi_h) & (r_e<R,r_h>R)\\ -e^2\sum_{l,m} h^0_l(r_h,r_e)Y^m_l(\theta_e,\varphi_e)Y^{m*}_l(\theta_h,\varphi_h) & (r_e>R,r_h<R)\\ -e^2/(\epsilon_d|\mathbf{r}_e-\mathbf{r}_h|) & (r_e>R,r_h>R). \end{cases} \tag{8}$$

Here we define $h^0_l(r_e,r_h)$ as

$$h^0_l(r_e,r_h)=\left(\frac{4\pi}{l\epsilon_\infty+(l+1)\epsilon_d}\right)\frac{r_e^l}{r_h^{l+1}}. \tag{9}$$

H_M is given by

$$H_M=-e^2\sum_l \frac{4\pi\alpha_l}{2l+1}h^M_l(r_e,r_h)Y^m_l(\theta_e,\varphi_e)Y^{m*}_l(\theta_h,\varphi_h), \tag{10}$$

where $h^M_l(r_e,r_h)$ is defined by

$$h^M_l(r_e,r_h)=\begin{cases}(l+1)r_e^l r_h^l/(2\epsilon_\infty R^{2l+1}) & (r_e<R,r_h<R)\\ -lR^{2l+1}/(2\epsilon_d r_e^{l+1}r_h^{l+1}) & (r_e>R,r_h>R)\\ 0 & (\text{otherwise}).\end{cases} \tag{11}$$

To treat the exciton–LO-phonon interaction we define an unitary operator U, including three variational parameters $f^{(e)}_{s\sigma}$, $f^{(h)}_{s\sigma}$, and $g_{s\sigma}$, as

$$U=\exp\left[\sum_{s\sigma} F^*_{s\sigma}(\mathbf{r}_e,\mathbf{r}_h)a_{s\sigma}-F_{s\sigma}(\mathbf{r}_e,\mathbf{r}_h)a^\dagger_{s\sigma}\right], \tag{12}$$

$$F_{s\sigma}(\mathbf{r}_e,\mathbf{r}_h)=v_{s\sigma}\{S_{s\sigma}(\mathbf{r}_e)f^{(e)}_{s\sigma}-S_{s\sigma}(\mathbf{r}_h)f^{(h)}_{s\sigma}+g_{s\sigma}\}. \tag{13}$$

The trial wave function $\tilde{\Psi}_\beta$ for the transformed Hamiltonian $\tilde{H}=U^{-1}HU$ is chosen as the product of exciton state $\Phi^\beta_{ex}(\mathbf{r}_e,\mathbf{r}_h)$ and zero-phonon state $|0\rangle$, that is,

$$\tilde{\Psi}_\beta(\mathbf{r}_e,\mathbf{r}_h)=\Phi^\beta_{ex}(\mathbf{r}_e,\mathbf{r}_h)|0\rangle. \tag{14}$$

Then the expectation value of the energy is given by $E=\langle\tilde{\Psi}_\beta|\tilde{H}|\tilde{\Psi}_\beta\rangle$. $\Phi^\beta_{ex}(\mathbf{r}_e,\mathbf{r}_h)$ including variational parameter β is chosen as (Ref. 14) $\Phi^\beta_{ex}(\mathbf{r}_e,\mathbf{r}_h)=\mathcal{N}_\beta\psi^e_g(r_e)\psi^h_g(r_h)e^{-\beta|\mathbf{r}_e-\mathbf{r}_h|}$ and

$$\psi^j_g(r_j)=\begin{cases}c_1\sin(k_jr_j)/k_jr_j & (r_j\leq R)\\ c_2\exp(-\kappa_jr_j)/\kappa_jr_j & (r_j>R),\end{cases} \tag{15}$$

where c_1, c_2, k_j, and κ_j are related to each other by the normalization condition and the continuous conditions. $\psi^j_g(r_j)$ is the ground state of an electron or a hole confined in the dot and is determined variationally from the minimization of the expectation value $E^j_g=\langle\psi^j_g|H_j|\psi^j_g\rangle$ with a variational parameter k_j $(j=e,h)$. It is noted that when the self-polarization term H^j_S in Eq. (2) is neglected, ψ^j_g is exact and then E^j_g takes $E^j_g=\hbar^2k_j^2/2m^{in}_j=V_j-\hbar^2\kappa_j^2/2m^{out}_j$, where m^{in}_j and m^{out}_j are masses of the particle j in the dot and the barrier matrix, respectively.

We can obtain the lowest energy of an exciton interacting with LO-phonon as the minimum value of $\langle\tilde{\Psi}_\beta|\tilde{H}|\tilde{\Psi}_\beta\rangle$ for β, that is, $E_g=\min_\beta\{\langle\tilde{\Psi}_\beta|\tilde{H}|\tilde{\Psi}_\beta\rangle\}=\langle\tilde{\Psi}_{\beta_g}|\tilde{H}|\tilde{\Psi}_{\beta_g}\rangle$. Then the lowest state is given by $\Psi_g(\mathbf{r}_e,\mathbf{r}_h)=U\Phi^{\beta_g}_{ex}(\mathbf{r}_e,\mathbf{r}_h)|0\rangle$.

Here it should be noted that both intermediate coupling method and adiabatic method are included in the present theory.[8,9] Actually if we set $f_{s\sigma}=0$ in Eq. (13) then this method reduces to the adiabatic method and $\Psi_g(\mathbf{r}_e,\mathbf{r}_h)$ reduces to a simple product of exciton state $\Phi^{\beta_g}_{ex}(\mathbf{r}_e,\mathbf{r}_h)$ and phonon state $U|0\rangle$ with $F_{s\sigma}=v_{s\sigma}g_{s\sigma}$ which is independent of $(\mathbf{r}_e,\mathbf{r}_h)$. On the other hand, if we set $g_{s\sigma}=0$ in Eq. (13), then this method reduces to the intermediate coupling method that takes into account the nonadiabatic effect.

Let us discuss LO-phonon effects on an exciton in a quantum dot. As a typical case of II-VI family, we choose the physical parameters of CdSe, that are, $m_e=0.11$, $m_h=0.44$, $\hbar\omega_{LO}=26.54$ meV, $\epsilon_0=9.3$, and $\epsilon=6.1$. For simplicity we set $m^{out}_j=m^{in}_j=m_j$ in the following calculation. The dielectric constant of the nonpolar dielectric matrix is chosen as a typical value of $\epsilon_d=3.6$, which is the value of SiO_2. The total band offset between the dot material and the nonpolar dielectric matrix is not known and is chosen simply as $\Delta=3$ eV for the both cases. By using the band offset ratio γ, the potential barriers for an electron and for a hole are written as $V_e=\gamma\Delta$ and $V_h=(1-\gamma)\Delta$, respectively. Here we note that when $\gamma=m_h/(m_e+m_h)$ and by neglecting the image charge effects, m_eV_e is just the same as m_hV_h, and then the wave functions of the electron and of the hole satisfy $\psi^e_g(r)=\psi^h_g(r)$ for any value of r.

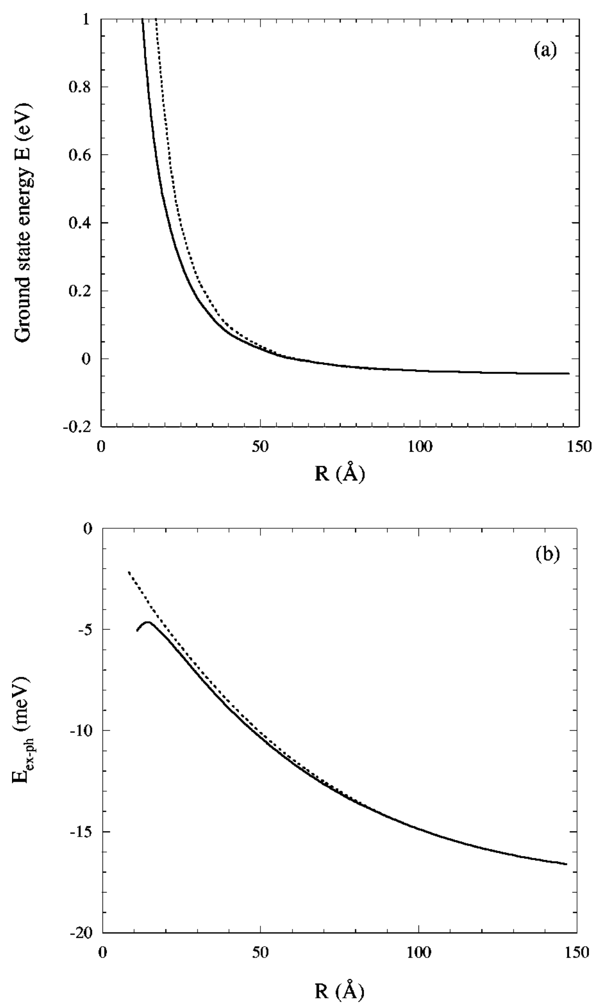

FIG. 1. (a) The ground-state energy of exciton and (b) the exciton-phonon interaction energy as a function of the dot radius R. The solid line stands for $\gamma=0.5$ and the dotted line infinite potential case.

In order to see the effect of the finite potential barrier on an exciton in the quantum dot we calculate the ground-state energy of the exciton with $\gamma=0.5$. The size dependence of the lowest exciton energy E_g and the exciton–LO-phonon interaction energy $E_{ex\text{-}ph}$ defined as $E_{ex\text{-}ph}=\langle\Phi_{ex}^{\beta_g}|H_{ex\text{-}ph}|\Phi_{ex}^{\beta_g}\rangle$ are plotted in Fig. 1, where the solid line stands for $\Delta=3$ eV and $\gamma=0.5$, and the dotted line stands for the infinite confinement potential ($\Delta\rightarrow\infty$). If we use the adiabatic method, then we obtain $E_{ex\text{-}ph}=-\hbar\omega_{LO}\Sigma_s v_{s1}^2 A_{s1}^2$. Here $\Sigma_s v_{s1}^2 A_{s1}^2$ is known as Huang-Rhys factor.[3] As shown in Fig. 1(a), with the decrease in the dot radius the differences between the results for infinite potential case and finite potential case become larger. In Fig. 1(b), it is seen that the magnitude of $E_{ex\text{-}ph}$ decreases with the decrease in the dot radius and then increases rapidly after taking minimum value. Here in order to explain this size dependence of the effect of LO phonon on the exciton, we consider the probability of finding the electron (hole) within the dot P_{in}^e (P_{in}^h). It is obvious that the polaron effects on the electron and the hole decrease with the decrease in P_{in}^e and P_{in}^h, respectively, because LO phonon does not exist in the

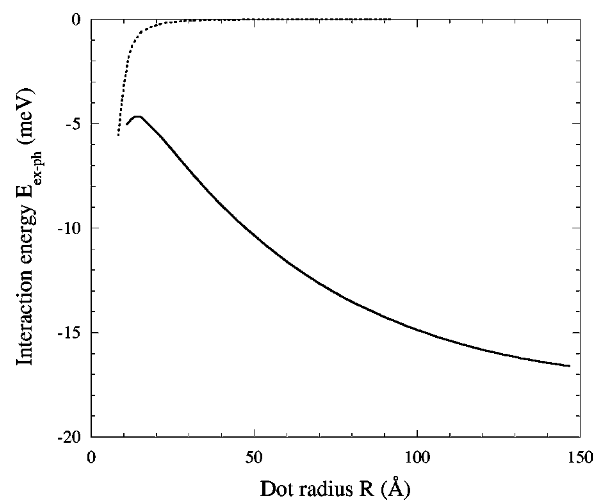

FIG. 2. The exciton-phonon interaction energy $E_{ex\text{-}ph}$ as a function of the dot radius R for $\gamma=0.5$. The solid line stands for our variational method and the dotted line stands for adiabatic method.

barrier matrix. Because $m_h V_h > m_e V_e$ with $\gamma < m_h/(m_e+m_h)$, P_{in}^h is larger than P_{in}^e with $\gamma=0.5$. Thus the rapid increase of $E_{ex\text{-}ph}$ with the decrease in the dot radius R in the region of $R<20$ Å shows that the larger polaron effect on the hole, comparing with that on the electron, appears in the polaron effect on an exciton. To make clear this point we calculate the difference between P_{in}^h and P_{in}^e. In the case of $R<20$ Å, $P_{in}^h - P_{in}^e$ increases rapidly with the decrease in the dot radius. In order to give a better understanding of the exciton–LO-phonon interaction, we calculate the virtual phonon number, defined as $N=\langle\Psi_g|\Sigma_{s\sigma}a_{s\sigma}^\dagger a_{s\sigma}|\Psi_g\rangle$, which shows the degree of the involvement of phonons in the exciton state Ψ_g. The calculated results show the following points:

(1) The virtual phonon number N decreases with the decrease in the dot radius and then increases rapidly after taking minimum value as the same as $E_{ex\text{-}ph}$. The rapid increase appears at $R<20$ Å.

(2) The contribution of the bulk phonon mode is dominant and the contribution of the interface phonon mode is very small.

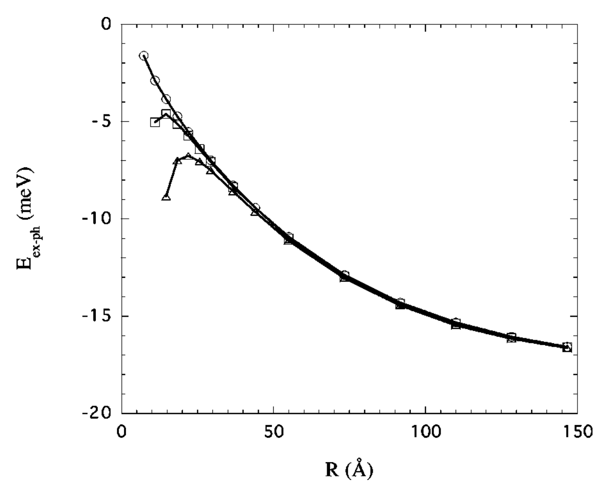

FIG. 3. The exciton-phonon interaction energy $E_{ex\text{-}ph}$ as a function of the dot radius R. ○ stands for $\gamma=0.8$, □ stands for $\gamma=0.5$, and △ stands for $\gamma=0.2$.

Here we consider the effect of LO phonons on an exciton in the small dot limit. Because LO phonon does not exist in the barrier matrix, the LO-phonon effect on the hole vanishes in the small dot limit. Thus in the finite potential barrier the effects of LO phonon on an exciton vanishes in this limit in a nonpolar matrix and *X* case.

In our previous works[8,9] with the infinite confinement potential, it was shown that (i) adiabatic process plays an important role for the large polaron effect on an electron (or a hole) with the decrease in the dot radius and (ii) the polaron effects on an exciton are very different and decrease with the decrease in the dot radius because the polaron effects on the electron and the hole cancel out each other. Especially, in exciton states the contributions due to the adiabatic processes for the electron and the hole cancel out each other very well. Actually with infinite potential, if we use the adiabatic method, that is, $f_{s\sigma}^{(j)}=0$ in Eq. (13), then there is no polaron effect on the exciton. Thus the variational parameter $g_{s\sigma}$ in Eq. (13) is not important when P_{in}^{h} nearly equals P_{in}^{e}. However, in the finite potential case, if we neglect the adiabatic effect and consider the nonadiabatic effect, that is, $g_{s\sigma}=0$ in Eq. (13), then the rapid increase in $E_{ex\text{-}ph}$ does not appear. Thus it is important in general that $F_{s\sigma}$ in Eq. (13) contains both $f_{s\sigma}^{(j)}$ term and $g_{s\sigma}$ term for the exciton–LO-phonon interaction in the finite quantum dots. Especially, nonadiabatic process is important. To show this importance we compare our result with that calculated by the adiabatic method in Fig. 2. It is clear that nonadiabatic process plays a dominant role for $R>15$ Å.

Next we study γ dependence for the polaron effect on an exciton. For the three values of $\gamma=0.2$, 0.5, and 0.8, the exciton–LO-phonon interaction energy $E_{ex\text{-}ph}$ is plotted as function of the dot radius *R*, in Fig. 3. ○, □, and △ stands for $\gamma=0.8$, $\gamma=0.5$, and $\gamma=0.2$, respectively. When $\gamma=0.88$, m_j and V_j satisfy the relation $m_e V_e = m_h V_h$. In the case of $\gamma=0.8$ we do not see the rapid increase in $E_{ex\text{-}ph}$ in the case of small dot because the difference between P_{in}^{e} and P_{in}^{h} is not large. On the other hand in the region of $\gamma<0.8$, $P_{in}^{h}-P_{in}^{e}$ and $E_{ex\text{-}ph}$ become larger with the decrease in γ. These results show that, when P_{in}^{h} becomes much larger than P_{in}^{e}, the cancellation of polaron effect on an electron and a hole decreases, and at the same times, the LO-phonon effect on an exciton increase rapidly.

We discuss the image charge effects. The ratio of the magnitudes of the self-polarization term and the kinetic term $\langle\Psi_g|H_S^j|\Psi_g\rangle/\langle\Psi_g|(H_j-H_S^j)|\Psi_g\rangle$ $(j=e,h)$ take a maximum value, ~ 0.6 at $R/a_B\sim 3$, where a_B is the exciton Bohr radius. Also the ratio of the magnitudes of the mutual polarization term and the direct Coulomb term $\langle\Psi_g|H_M|\Psi_g\rangle/\langle\Psi_g|H_{e\text{-}h}^0|\Psi_g\rangle$ take a maximum value, ~ 0.5 at $R/a_B\sim 0.5$. Thus the image charge effect is very important in magnitude for the total energy of the exciton. However, it is found that the qualitative behavior of $E_{ex\text{-}ph}$, discussed in the recent work, does not change even if the image charge effect is neglected.

We also calculate the size dependence of E_g, $E_{ex\text{-}ph}$, and $P_{in}^{(h)}-P_{in}^{(e)}$ for the III-V family by using the physical parameters of GaAs, that is, $m_e=0.067$, $m_h=0.51$, $\hbar\omega_{LO}=35.33$ meV, $\epsilon_0=12.4$, and $\epsilon=10.6$. It is found that almost the same qualitative behavior as in the II-VI family case is obtained, though the magnitudes are different.

In summary, we have studied the LO-phonon effects on the ground state of an exciton in a spherical quantum dot embedded in a nonpolar matrix with finite potential barrier. The ground-state energy of the exciton and the exciton–LO-phonon interaction energy are calculated by using the variational method and a typical II-VI, III-V semiconductor dot in mind. We found that the LO-phonon effect on the exciton decreases gradually from the bulk value with decrease in the dot radius and then increase rapidly after taking the minimum value. This rapid increase is caused by the large difference between polaron effects on the electron and the hole, i.e., the LO-phonon effect in QD appears if there is a large difference between the distributions of the electron and the hole (this occurs more strongly if the electron or the hole is localized). This natural result is helpful to understand some experiments, in which phonon sidebands and the relaxation process due to phonon have been discussed. In the limit of smaller QD the spherical shape approximation may not be good and the effect of QD shape need to be considered. However, the above qualitative property of the exciton–LO-phonon interaction effects will not change.

This work was supported by Yamaguchi University venture business laboratory. We would like to thank Dr. R. S. Zheng for useful discussions and suggestions.

[1] S. Schmitt-Rink, D.A.B. Miller, and D.S. Chemla, Phys. Rev. B **35**, 8113 (1987).
[2] M.C. Klein, F. Hache, D. Ricard, and C. Flytzanis, Phys. Rev. B **42**, 11 123 (1990).
[3] J.C. Marini, B. Stebe, and E. Kartheuser, Phys. Rev. B **50**, 14 302 (1994).
[4] S. Nomura and T. Kobayashi, Phys. Rev. B **45**, 1305 (1992).
[5] A.V. Fedrov, A.V. Baranov, and K. Inoue, Phys. Rev. B **56**, 7491 (1997).
[6] A.V. Baranov, S. Yamauchi, and Y. Masumoto, Phys. Rev. B **56**, 10 332 (1997).
[7] V.M. Fomin, V.N. Gladilin, J.T. Devreese, E.P. Pokatilov, S.N. Balaban, and S.N. Klimin, Phys. Rev. B **57**, 2415 (1998).
[8] K. Oshiro, K. Akai, and M. Matsuura, Phys. Rev. B **58**, 7986 (1998).
[9] K. Oshiro, K. Akai, and M. Matsuura, Phys. Rev. B **59**, 10 850 (1999).
[10] G. Scamarcio, V. Spagnolo, G. Ventruti, M. Lugara, and G.C. Righini, Phys. Rev. B **53**, R10489 (1996).
[11] A.M. de Paula, L.C. Barbosa, C.H.B. Cruz, O.L. Alves, D.A. Sanjurjo, and C.L. Cesar, Superlattices Microstruct. **23**, 1103 (1998).
[12] R. Englman and R. Ruppin, J. Phys. C **1**, 614 (1968).
[13] L.E. Brus, J. Chem. Phys. **80**, 4403 (1984).
[14] Y. Kayanuma, Solid State Commun. **59**, 405 (1986).