

# EXCITON-PHONON INTERACTION AND PHONON FREQUENCY SHIFT IN QUANTUM DOTS

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We present a theory of LO phonon renormalization by coupling with the exciton in semiconductor quantum dots. We find that the one phonon side band of the exciton ground state shows an anticrossing with the excited exciton states. Even away from such a resonant coupling, the phonon frequency shift is significant. For example, in CuCl quantum dots in the weak confinement regime, the phonon frequency in the presence of a single exciton is reduced by about 10% from its value in the ground state. Similar results are predicted for CdS and GaAs quantum dots in the strong confinement regime.

In quantum dots (QDs) of polar semiconductors, the longitudinal lattice vibrations interact strongly with the exciton and significant changes in the phonon modes upon electronic excitation may be expected. Recently a significant softening of the excited state LO phonon frequency in CuCl QDs was observed and explained as the renormalization of the phonon coupled to the exciton.<sup>1</sup> This behaviour is similar to that of molecular systems where it is known that electronic excitation can cause substantial changes in the lattice subsystem.<sup>2</sup> Here we present a theory of the LO phonon renormalization in semiconductor QDs both in the strong and weak confinement regimes.

We consider spherical QDs of radius  $R$  and describe the confined optical phonons using a macroscopic continuum model.<sup>3</sup> The electrostatic potential associated with the confined LO phonons is given by,

$$\Phi_{\nu lm}(\mathbf{r}) = \sqrt{\frac{8\pi\omega_{\text{LO}}^2}{\kappa R \xi_{\nu l}^2 j_{l+1}(\xi_{\nu l})^2}} j_l(\xi_{\nu l} r/R) Y_{lm}(\theta, \phi), \quad (1)$$

$\xi_{\nu l}$ 's are the zeros of the spherical Bessel function  $j_l(r)$  and  $\kappa = \epsilon_0\epsilon_\infty/(\epsilon_0 - \epsilon_\infty)$ . We neglect the dispersion of the LO phonon frequency  $\omega_{\text{LO}}$ .

The exciton-phonon Fröhlich coupling constant  $\gamma_{\nu lm}^{ij}$  is given by

$$\gamma_{\nu lm}^{ij} = -\sqrt{e^2/2\omega_{\text{LO}}} \int \psi_i^*(\mathbf{r}_e, \mathbf{r}_h) [\Phi_{\nu lm}(\mathbf{r}_e) - \Phi_{\nu lm}(\mathbf{r}_h)] \psi_j(\mathbf{r}_e, \mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h, \quad (2)$$

where  $\psi$ 's denote the exciton wave functions and  $i$  collectively stands for the quantum numbers of the exciton states.

Table 1. Parameters used in the calculation

	$\epsilon_0$	$\epsilon_\infty$	$m_e$	$m_h$	$\omega_{\text{LO}}(\text{meV})$
CuCl	7.9	4.5	0.5	1.8	25.6
CdS	9.4	5.5	.2	.8	38
GaAs	12.4	10.6	0.067	0.4	36.5

In spherical QDs, only the  $S$  ( $L = 0$ ) excitons are optically excited as zero phonon dipole allowed transitions. Further, from Eq. 2 it follows that only the  $l = 0$  phonons will appear as sidebands to the  $S$  excitons in the optical absorption and emission spectra. Here we consider the renormalization of these optically active states due to the exciton-phonon interaction. In what follows we denote all the zero angular momentum states by a single subscript, dropping  $lm$ .

We obtain the renormalized normal modes by degenerate second order perturbation theory which requires diagonalization of the matrix  $V_{\nu\nu'} = \omega_{\text{LO}} + \Pi_{\nu\nu'}$ , where the self energy  $\Pi$  is given by

$$\Pi_{\nu\nu'} = - \sum_{n \neq 1} \frac{\gamma_\nu^{1n} \gamma_{\nu'}^{n1} 2(E_n - E_1)}{(E_n - E_1)^2 - \omega_{\text{LO}}^2}. \quad (3)$$

The renormalized phonon frequencies are given by  $\tilde{\omega}_{\text{LO}}^\mu = \omega_{\text{LO}} + \tilde{\Pi}_\mu$ , where  $\mu$  denotes the (renormalized) phonon normal modes that diagonalize  $\Pi_{\nu\nu'}$ , and  $\tilde{\Pi}_\mu$ 's are the eigenvalues of  $\Pi$ .

In the strong confinement regime, we consider electrons and holes as independently confined, and include the Coulomb interaction in the first order perturbation theory. The  $n$ th electron-hole pair state ( $L = 0$ ) may now be labelled by the quantum numbers  $n_e$  and  $n_h$  of the electron and the hole states, respectively. As the phonon couples independently to the electron and the hole, for the renormalization of the  $l = 0$  phonons, we need to consider only the zero angular momentum single particle states. The relevant coupling constant  $\gamma_\nu^{1i}$  may be denoted by  $\gamma_\nu^{11;i_e i_h}$ , and is non-zero only if either  $i_e = 1$  or  $i_h = 1$ . Further, it can be shown that

$$\begin{aligned} \gamma_\nu^{11;i1} = -\gamma_\nu^{11;1i} = & -\sqrt{\frac{e^2 \omega_{\text{LO}}}{\kappa R}} \frac{1}{2\nu\pi} [\text{Si}((\nu + i - 1)\pi) - \text{Si}((\nu + i + 1)\pi) \\ & + \text{Si}((\nu - i + 1)\pi) - \text{Si}((\nu - i - 1)\pi)], \end{aligned} \quad (4)$$

where Si is the sine integral. In the above approximation, however, the diagonal matrix element  $\gamma_\nu^{11;11}$  is zero. This is a manifestation of the electron-hole symmetry in the lowest energy state which makes it a locally neutral excitation. More accurate treatment of the Coulomb interaction will break this

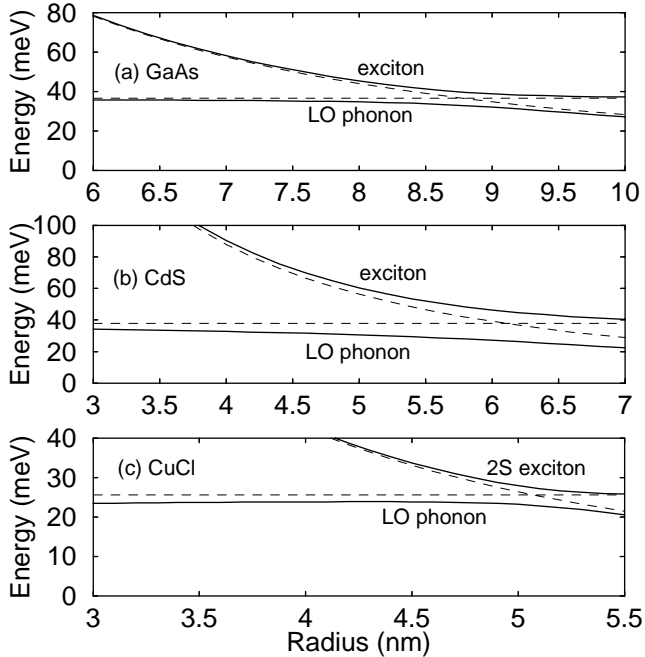


Figure 1. The size dependence of the renormalized LO phonon frequency for the mode most strongly coupled to the exciton ground state for (a) GaAs, (b) CdS and (c) CuCl quantum dots. The energy of the excited exciton state with which the phonon shows an anticrossing resonance is also shown. The dotted lines show the energies of these two states in the absence of the exciton-phonon coupling. For CdS and GaAs, the exciton state shown corresponds to the hole in the 2S state and the electron in the 1S state.

symmetry, and we evaluate  $\gamma_{\nu}^{11;11}$  using the second order perturbation theory for the electron-hole interaction. The parameters used are tabulated in Table I. We calculate the phonon self energy ( $\Pi$ ) by considering ten phonon modes and ten lowest energy  $l = 0$  electron and hole states.

We find that a single phonon mode is strongly shifted in frequency, and it is the same mode that has any significant coupling to the exciton ground state so as to be observed in the phonon-assisted absorption or luminescence spectra. In Fig. 1 we show the size dependence of the frequency of this mode for GaAs and CdS QDs. As  $R$  increases, the first excited state of the exciton becomes resonant with the LO phonon sideband of the exciton ground state, leading to an anticrossing. To take care of this resonance, we include the resonant exciton state in the subspace in which the degenerate perturbation calculation is done. The resulting renormalized energy of the exciton state is

also shown in Fig. 1. For smaller sizes, the phonon frequency is found to be reduced from its value in the ground state of the QD. In the size range shown in Fig. 1, the excited state that mixes with the phonon sideband involves the electron in the lowest state and the hole in the first excited state. The predicted changes in the phonon frequency for CdS and GaAs are significant and should be observable.

In the weak confinement regime, as a typical example, we consider CuCl QDs. We calculate the exciton states using a correlated basis set approach<sup>4</sup> and numerically obtain the coupling constants  $\gamma_{\nu}^{ij}$ . As seen from Fig. 1(c), the phonon frequency is decreased from its value in the ground state by about 10% for QDs with radius in the range 2 – 5 nm. The excited exciton state with which the phonon sideband anticrosses, as shown in Fig. 1(c), is the 2S state. These results are in excellent agreement with our experimental results reported in Ref. 1.

We have neglected the dispersion of the LO phonon frequency. In CuCl, the LO phonon frequency dispersion being positive, the confinement would lead to a slight increase in the LO phonon frequency. In GaAs and CdS an opposite effect would be expected. It may be noted that, in contrast to the confinement induced shift of the phonon frequency, the renormalization discussed here refers to the difference between the phonon frequencies in the ground and the excited electronic states of the QD.

In conclusion, we have presented a theory of LO phonon renormalization in semiconductor QDs in the presence of a single exciton. When the QD is small so that all the excited states of the exciton have energies exceeding the one phonon side band of the exciton ground state, the phonon frequency is found to be reduced. As the size of the QD is increased, the renormalized LO phonon sideband of the exciton ground state is shown to anticross with the excited excitonic state. For CuCl QDs, in a wide size range of  $R = 2 - 5$  nm, the phonon frequency is found to be reduced by about 2 meV in excellent agreement with the experimental results.<sup>1</sup> Significant changes in the phonon frequency upon electronic excitation are predicted for CdS and GaAs QDs.

## References

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