Resonance Raman scattering in semiconductor quantum dots: Adiabatic versus time-dependent perturbation theory

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The adiabatic theory of resonance one-phonon Raman scattering in semiconductor nanocrystals is revised and extended with perturbative nonadiabatic corrections, given by Albrecht's B term. This theory is confronted with the time-dependent perturbation approach, pointing at their differences and similarities. It is shown that both theories are equivalent in the limit of weak electron-phonon coupling and nondegenerate or uncoupled resonant states. Evaluations of the A and B terms for the confined LO phonon in CdSe and CdS nanocrystals are reported. These evaluations show that the B term can usually be neglected.

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I. INTRODUCTION

In the interpretation of resonant Raman scattering in quantum dots, two theories have been mostly used. The first one is based on the Albrecht's theory[1] of light scattering from small molecules, where the excited levels that contribute to the Raman polarizability are considered as vibron states in the adiabatic approximation. This theory also considered perturbative nonadiabatic corrections, but these later have been neglected in quantum dot studies.[2–9] Moreover, the exciton-phonon coupling factor has been identified with the Huang-Rhys factor, using this as a fitting parameter for the relative intensities of different orders in Raman spectra. However, the calculations of the Huang-Rhys parameter for intrinsic exciton states in PbS (Ref. 9) and CdSe (Refs. 10,11) nanocrystals have given values that are too small compared with those needed to explain the experimental results of multiphonon Raman scattering. Extrinsic mechanisms such as donorlike exciton,[12] surface hole traps,[13] or extra charges[10,14] have been invoked to resolve the discrepancy.

A different model of Raman scattering in quantum dots was conceived from a solid state point of view. In this approach, the Raman cross sections are calculated from third or higher order time-dependent perturbation theory (TDPT) (Refs. 15–17) and the intermediate virtual states are considered as tensorial products of electronic states, lattice vibrations, and photons. A nonperturbative calculation of multiphonon Raman spectra have been recently presented.[14] Not having adjustable parameters this model has scarcely been used by experimentalists to interpret their data. Moreover, up to now it is unclear the relation between the TDPT and the Albrecht's theory.

The purpose of the present article is (1) to establish the relation between Albrecht's theory and TDPT and (2) to investigate the importance of nonadiabatic corrections within Albrecht's theory. The structure of the paper is as follows. First, we give an overview of both theoretical approaches and show their interrelation. Next, we explain the calculation of the Albrecht's A and B terms for semiconductor nanocrystals. Finally we discuss the numerical results obtained for

several types of nanocrystals and present our conclusions. Several mathematical steps are given in the appendixes.

II. THE THEORIES

A. Time-dependent perturbation theory

For a one-phonon Raman process the differential cross section is given by[15]

$$\frac{d^2\sigma}{d\Omega_s d\omega_s} = \frac{V^2 \omega_s^3 \eta_l \eta_s^3}{4\pi^2 c^4 \omega_l \hbar} \sum_F |M_{FI}^{(1)}(p)|^2 \delta(\hbar\omega_l - \hbar\omega_s - \hbar\omega_p),$$
(1)

where η_l (η_s) is the refraction index at the incident (scattered) light frequency ω_l (ω_s), V is a normalization volume of the radiation field, and c is the velocity of light in vacuum. The one-phonon transition amplitude $M_{FI}^{(1)}(p)$ can be calculated by time dependent perturbation theory, considering the unperturbed Hamiltonian as the sum of the electronic, lattice, and radiation operators

$$H_0 = H_E + H_L + H_R,$$

while the perturbation is the sum of electron-lattice, electron-radiation, and lattice-radiation interactions (the last one is negligible in resonance conditions)

$$H_{\text{int}} = H_{E\text{-}L} + H_{E\text{-}R} + H_{L\text{-}R}.$$

The electron-lattice interaction can be expressed as

$$H_{E\text{-}L} = \sum_{\mu,\mu',\nu} \langle \mu | H_{E\text{-}L}^+(\nu) | \mu' \rangle \hat{D}_\mu^\dagger \hat{D}_{\mu'} \hat{b}_\nu^\dagger$$

$$+ \sum_{\mu,\mu',\nu} \langle \mu | H_{E\text{-}L}^-(\nu) | \mu' \rangle \hat{D}_\mu^\dagger \hat{D}_{\mu'} \hat{b}_\nu,$$
(2)

where $\hat{D}_{\mu'}$ ($\hat{D}_\mu^\dagger$) and $\hat{b}_\nu$ ($\hat{b}_\nu^\dagger$) are annihilation (creation) operators of electronic and vibrational excitations, respectively, while $H_{E\text{-}L}^+(\nu)$ and its Hermitian adjoint $H_{E\text{-}L}^-(\nu)$ are operators that act on the electronic system.[16] The operators $H_{E\text{-}R}$ and $H_{L\text{-}R}$ have a similar structure to that of $H_{E\text{-}L}$. The phonon states created by $\hat{b}_\nu^\dagger$ are those of the electronic ground state G. The electronic excitations $\mu \neq G$ can be considered as electron-hole pairs and confined excitons. Hence, the one-phonon Raman transition amplitude can be calculated by third order perturbation theory as

$$M_{FI}^{(1)}(p)=\sum_{\mu_1,\mu_2(\neq G)}\frac{\langle G|H_{E-R}^+|\mu_2\rangle\langle \mu_2|H_{E-L}^+(p)|\mu_1\rangle\langle \mu_1|H_{E-R}^-|G\rangle}{(\hbar\omega_l-E_{\mu_2}-\hbar\omega_p+i\Gamma_{\mu_2})(\hbar\omega_l-E_{\mu_1}+i\Gamma_{\mu_1})},\tag{3}$$

where Γ_μ are the lifetime broadenings of the electronic excitations. The interaction matrix elements $\langle \mu_2|H_{E-L}^+(p)|\mu_1\rangle,\langle G|H_{E-R}^+|\mu_2\rangle$, and $\langle \mu_1|H_{E-R}^-|G\rangle$ have been calculated under two approximations of solid state theory: the effective mass approximation and a long wave continuous model for the optical phonons (a field theory approach). Working expressions can be found elsewhere.[15–21] The conditions of validity of the above formalism can be summarized as (1) the scattering process is dominated by extended vibrational states, which are not affected by single-electron excitations, as is usual in large molecules and solids and (2) excited electronic states are well separated in energy from the ground state.

B. Albrecht's theory

In this scheme, the wave functions of the molecule (or the quantum dot) are considered in the adiabatic Born-Oppenheimer approximation

$$\Psi_{ev}(\{r\},\{Q\})=\Theta_e(\{r\},\{Q\})\Phi_{ev}(\{Q\}),$$

where e and v are the sets of electronic and vibrational quantum numbers, respectively, $\{r\}$ is the ensemble of electron coordinates of the molecule (or the quantum dot), and $\{Q\}$ is the ensemble of normal coordinates of the ions. The vibrational wave function Φ_{ev} is factored as a product of the wave functions of all the normal modes

$$\Phi_{ev}(\{Q\})=\varphi_{v_1}^e(Q_1)\varphi_{v_2}^e(Q_2)\cdots,\tag{4}$$

v_a being phonon occupation numbers. According to the dispersion theory, Albrecht obtained the Raman polarizability tensor for resonance scattering as

$$\overset{\leftrightarrow}{\boldsymbol{\alpha}}=\vec{\boldsymbol{A}}'''+\vec{\boldsymbol{B}}'''+\mathrm{HOT}+\mathrm{NRT},$$

where HOT means higher order terms and NRT nonresonant terms.

The A and B terms are given by

$$(\vec{\boldsymbol{A}}''')_{gi,gj}=\sum_{(e),v}\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,e}^0\frac{(gi|ev)(ev|gj)}{\hbar\omega_{ev,gi}-\hbar\omega_l+i\Gamma_e'}\tag{5}$$

and

$$(\vec{\boldsymbol{B}}''')_{gi,gj}=\sum_{(e),v,s,a}\frac{h_{se}^a\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,s}^0(gi|Q_a|ev)(ev|gj)+h_{es}^a\mathfrak{M}_{s,g}^0\mathfrak{M}_{g,e}^0(gi|ev)(ev|Q_a|gj)}{(\hbar\omega_{ev,gi}-\hbar\omega_l+i\Gamma_e')(\hbar\omega_{e,s})}.\tag{6}$$

In the above expression we follow Albrecht's notation,[1] but we use dyadic notation instead of tensor subindexes, $\hbar\omega_l$ instead of $h\nu_0$ for incoming photon energy, and $\hbar\omega_{\alpha,\beta}=E_\alpha-E_\beta$. $|gi),|ev),|gj)$ are the initial, intermediate and final vibrational states [Eq. (4)], respectively, in the potential energy fields of the electronic states g (ground) and e (excited). $\mathfrak{M}_{\alpha,\beta}^0$ and h_{se}^a are, respectively, dipole and electron-phonon interaction matrix elements (see Table I). Also, the order of some matrix element indexes is reversed in order to generalize the Albrecht's expressions for the case of complex wave functions. Note that the order of subindexes in matrix elements in this notation is the opposite of that in Dirac's notation. The summation on the index (e) can be restricted to the resonant state e. The s states in Eq. (6) appear from a perturbative expansion of $\Theta_e(\{r\},\{Q\})$ in terms of $\Theta_s(\{r\},\{0\})$.

The above formalism is valid if (1) the e states are non-degenerate or uncoupled to other states with the same energy and (2) excited electronic states are well separated in energy from the ground state.

1. The offset oscillators model

In this model, the vibrational states $\varphi_{i_a}^g(Q_a)$ and $\varphi_{v_a}^e(Q_a)$ are assumed to be localized in parabolic $V_{g(e)}(Q_a)$ potentials with the same curvature, but the origin of V_e shifted in $\Delta Q_a=\sqrt{2}x_{a0}\Delta_a=\sqrt{2}\sqrt{\hbar/\omega_a}\Delta_a$. In many cases, only one vibrational mode is assumed and Δ_a is employed as fitting parameter. Moreover, Δ_a^2 is identified as the Huang-Rhys factor.[2,10] The integrals appearing in the A and B terms are given by

$$(gl|ev)=\sqrt{\frac{v!}{l!}}e^{-\Delta_a^2/2}\Delta_a^{l-v}L_v^{l-v}(\Delta_a^2)\tag{7}$$

and

$$(ev|Q_a|gl)=x_{a0}\sqrt{\frac{l+1}{2}}(g,l+1|ev)+x_{a0}\sqrt{\frac{l}{2}}(g,l-1|ev)\tag{8}$$

$$=x_{a0}\frac{l-v+\Delta_a^2}{\sqrt{2}\Delta_a}(gl|ev),$$

TABLE I. Equivalence of Albrecht and TDPT notations.

Magnitude	Albrecht's	TDPT
Electron excited states	e,s	μ_2,μ_1
Electron ground state	g	G
Matrix element	$-i\sqrt{\dfrac{2\pi\hbar\omega_{s,g}}{V\eta_l^2}}\mathbf{e}_l\cdot\mathfrak{M}_{g,s}^0$	$\langle\mu_1|H_{E-R}^-(\mathbf{e}_l,\mathbf{0})|G\rangle$
Matrix element	$x_0 h_{se}^p$	$\langle\mu_2|H_{E-L}(p)|\mu_1\rangle$

where L_m^p are the Laguerre generalized polynomia and $x_{a0}=\sqrt{\hbar/\omega_a}$.

Several authors have used this model to study the electron-phonon coupling in nanocrystals.[2,5–9] All of them have considered only the term A and have used Δ_a^2 to fit the overtone/fundamental intensity ratios of Raman spectra. The fitted values of Δ_a^2 are near 1, in contradiction with microscopic calculations.[10,11]

2. The limit of weak electron-phonon coupling

In the limit of weak electron-phonon coupling the oscillator offset Δ_a should be small. Expanding Eqs. (7) and (8) in powers of Δ_a we find

$$(ev|gi)=\delta_{v,i}+\left[\sqrt{\frac{i!}{v!}}\delta_{v,i-1}-\sqrt{\frac{v!}{i!}}\delta_{v,i+1}\right]\Delta_a+O(\Delta_a^2) \tag{9}$$

and

$$
\begin{aligned}
(ev|Q_a|gi)=&\int\varphi_{i_a}(Q_a)\varphi_{v_a}(Q_a)Q_a\,dQ_a\\
=&\,x_{a0}\left[\sqrt{\frac{v_a}{2}}\delta_{v_a,i_a+1}+\sqrt{\frac{i_a}{2}}\delta_{v_a,i_a-1}\right]\\
&+\frac{x_{0a}\Delta_a}{\sqrt{2}}\left[\sqrt{\frac{i!}{v!}}[(i+1)\delta_{v,i}+\delta_{v,i-2}]\right.\\
&\left.-\sqrt{\frac{v!}{i!}}(i\delta_{v,i}+\delta_{v,i+2})\right]+O(\Delta_a^2). \tag{10}
\end{aligned}
$$

Replacing Eq. (9) in Eq. (5) we obtain

$$(\vec{A}''')_{gi,g,j}=\delta_{i,j}\frac{\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,e}^0}{E_{e,g}-\hbar\omega_l-\Delta_a^2\hbar\omega_a+i\Gamma_e'}+O(\Delta_a).$$

This means that $\vec{A}'''$ contributes mainly to Rayleigh scattering. Nevertheless, the term proportional to Δ_a is important for one-phonon Raman scattering. To first order in Δ_a we find that

$$(\vec{A}''')_{g0_a,g1_a}=\frac{-\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,e}^0\Delta_a\hbar\omega_a}{(E_{e,g}-\Delta_a^2\hbar\omega_a-\hbar\omega_l+i\Gamma_e')[E_{e,g}+(1-\Delta_a^2)\hbar\omega_a-\hbar\omega_l+i\Gamma_e']}.$$

On the other hand, substituting Eqs. (9) and (10) in Eq. (6) we obtain that, up to first order in the electron-phonon interaction, the B term is non-null only for one-phonon Raman processes. For Stokes processes at low temperature ($i_a=0,j_a=1$) we obtain

$$(\vec{B}''')_{g0_a,g1_a}=\sum_{(e),s}\left\{\frac{\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,s}^0 h_{se}^a x_{a0}/\sqrt{2}}{[E_{e,g}+(1-\Delta_a^2)\hbar\omega_a-\hbar\omega_l+i\Gamma_e'](E_e-E_s)}+\frac{\mathfrak{M}_{s,g}^0\mathfrak{M}_{g,e}^0 h_{es}^a x_{a0}/\sqrt{2}}{(E_{e,g}-\Delta_a^2\hbar\omega_a-\hbar\omega_l+i\Gamma_e')(E_e-E_s)}\right\}.$$

In the second term, one can exchange the indexes e and s. Next, under the condition $|E_e-E_s|\gg|\hbar\omega_a+i(\Gamma_e'-\Gamma_s')|$ one obtains

$$(\vec{B}''')_{g0_a,g1_a}=\sum_{e,s\ne e}\frac{-\mathfrak{M}_{e,g}^0\mathfrak{M}_{g,s}^0 h_{se}^a x_{a0}/\sqrt{2}}{[E_{e,g}+(1-\Delta_a^2)\hbar\omega_a-\hbar\omega_l+i\Gamma_e'](E_{s,g}-\Delta_a^2\hbar\omega_a-\hbar\omega_l+i\Gamma_s')}. \tag{11}$$

Noting that $\Delta_a^2\ll1$, $\Delta_a\hbar\omega_a=-\langle e|H_{E-L}(a)|e\rangle$, and $h_{se}^a x_{a0}/\sqrt{2}=\langle e|H_{E-L}(a)|s\rangle$ (see Appendixes A and B), we see that $\vec{A}'''+\vec{B}'''$ for one-phonon emission reduces to the same result that the TDPT.

TABLE II. Parameters used in the calculations. When not indicated, the source is Ref. 20 for CdS and Ref. 19 for CdSe.

Parameter	CdS	CdSe	CdSe (MBEMA)
E_g (eV)	2.6	1.865	1.841[a]
m_e/m_0	0.18	0.12	0.13[b]
m_h/m_0	0.51	0.45	
γ_1			1.66[b]
γ_2			0.41[b]
$2m_0 P^2$ (eV)	21[c]	20[c]	20[c]
κ	7.8	9.53	9.53
V_e (eV)	2.5	∞	0.6[b]
V_h (eV)	1.9	∞	∞[b]
ω_L (cm^{-1})	305	213	213
ω_T (cm^{-1})	238	165	165
ϵ_0	8.7[d]	9.53	9.53
ϵ_∞	5.3	5.72[d]	5.72[d]
β_L (10^{-6})	2.68	1.58	1.58
Γ_μ (meV)	5	5	5

[a]Reference 33.
[b]Reference 28.
[c]Reference 34.
[d]Calculated from the Lydanne-Sachs-Teller relation.

III. CALCULATION OF $\vec{A}'''$ AND $\vec{B}'''$

A. Effective mass approximation

We use the exciton wave functions and the electron-phonon operator of Ref. 20 to estimate the A and B terms in nanocrystals of several semiconductors. Using Table II and the effective mass approximation we have

$$\mathfrak{M}^0_{g,e} = \frac{ie}{m_0 \omega_{e,g}} \mathbf{p}_{s_z j_z ; e} f_{o_e},$$

where f_{o_e} is the envelope overlap integral (o_e being the set of envelope quantum numbers)

$$f_{o_e} = \int \Psi_{o_e}(\mathbf{r}, \mathbf{r})^* d^3\mathbf{r}.$$

$\mathbf{p}_{s_z J_z ; e}$ is the bulk momentum matrix element between the couple of bands to which the exciton e belongs. For the valence band $J_z = \pm 3/2, \pm 1/2$ and for the conduction band $s_z = \pm 1/2$.

We evaluate the relative importance of the terms A and B for semiconductor nanocrystals. Assuming only one vibrational mode and focusing on one-phonon creation processes at low temperature (i.e., $i=0$ and $j=1$), the resonant term in Eq. (5) is reduced to

$$(\vec{A}''')_{gi,gj} = \left(\sum_{s_z, J_z} \mathbf{p}^*_{s_z J_z ; e} \mathbf{p}_{s_z J_z ; e} \right) \left(\frac{e\hbar f_{o_e}}{m_0 E_{e,g}} \right)^2$$
$$\times \sum_v \frac{(gi|ev)(ev|gj)}{E_{e,g} + (v - \Delta^2)\hbar\omega_{LO} - \hbar\omega_l + i\Gamma'_e}. \quad (12)$$

The first term between parentheses is a band factor and is the responsible of the angular pattern of the scattered intensity. The summation over s_z, J_z, is performed to take into account the degeneracy of conduction and hole bands, giving[22]

$$\sum_{s_z, J_z} \mathbf{p}^*_{s_z J_z ; e} \mathbf{p}_{s_z J_z ; e} = \frac{(2J+1)}{3} (m_0 P)^2 \vec{\mathbf{I}}, \quad (13)$$

where $J = 3/2$ (1/2) if the upper valence band have Γ_8 (Γ_7) symmetry and $P = -i\langle S|\hat{p}_x|X\rangle/m_0$.

To evaluate the B term we also need to include the electron-phonon matrix elements $x_0 h_{se} = \sqrt{2}\langle e|H_{E-L}|s\rangle$ (see Appendix B). With these considerations we obtain

$$(\vec{B}''')_{gi,gj} = \left(\sum_{s_z J_z} \mathbf{p}^*_{s_z J_z ; e} \mathbf{p}_{s_z J_z ; s} \right) \left(\frac{e\hbar}{m_0} \right)^2 \sum_{v,os} \frac{f_{oe} f_{os} \sqrt{2}\langle e|H_{E-L}|s\rangle\{(gi|Q|ev)(ev|gj)/x_0 + (gi|ev)(ev|Q|gj)/x_0\}}{E_{e,g} E_{s,g} E_{e,s} [E_{e,g} + (v - \Delta^2)\hbar\omega_{LO} - \hbar\omega_l + i\Gamma'_e]}. \quad (14)$$

We evaluate $\langle e|H_{E-L}|s\rangle$ as in Ref. 20. Due to the Fröhlich interaction cannot cause intersubband transitions $\mathbf{p}^*_{s_z J_z ; s} = \mathbf{p}^*_{s_z J_z ; e}$ and the band factor in Eq. (14) is the same as that in Eq. (12). Intersubband transitions may occur via deformation potential interaction, but these are usually negligible in polar materials. It must be noticed that it is not possible to consider this mechanism within the Albrecht's theory, as the existence of degenerate hole states connected by the electron-phonon interaction means a breakdown of the adiabatic approximation, which is reflected in null denominators $E_{e,s}$ in Eq. (14). Nevertheless, TDPT can deal with it without trouble. From this result we conclude that the A and B terms are scalars (with small tensorial corrections for B) and the integration

over nanocrystal orientations and light polarization has no effect on the ratio between the A and B terms.

B. Multiband effective mass theory

In a multiband formalism, the essential effect of band mixing can be captured using the spherical approximation for the hole Hamiltonian[23]

$$H_h = \frac{\gamma_1}{2m_0} \left(\hat{\mathbf{p}}^2 - \frac{\mu}{9}(\mathbf{P}^{(2)} \cdot \mathbf{J}^{(2)}) \right) + V(r),$$

$V(r)$ being the confinement potential, $\mathbf{P}^{(2)}$ and $\mathbf{J}^{(2)}$ are spherical rank tensors built from linear and angular momen-

tum operators $\mu = 2\gamma_2/\gamma_1$, and γ_2 and γ_1 are Luttinger parameters.

Electron-hole pair states with well defined total (Bloch +orbital) angular momentum quantum numbers M and M_z can be obtained as

$$|e\rangle = \sum_{n,N,l,L,f,F} C^{(e)}_{nNlLsJfFMM_z} |nNlLsJfFMM_z\rangle$$

$$= \sum_{n,N,l,L,f,F,f_z,F_z} C^{(e)}_{nNlLsJfFMM_z}$$

$$\times (fFf_zF_z|MM_z)|nlsff_z\rangle \otimes |NLJFF_z\rangle,$$

where $(fFf_zF_z|MM_z)$ is a Clebsch-Gordan coefficient. Lowercase (uppercase) letters denote electron (hole) quantum numbers. $|nlsff_z\rangle$ and $|NLJFF_z\rangle$ are electron and hole states with well defined total angular momentum, their wave functions given by

$$\langle \mathbf{r}|nlsff_z\rangle = \sum_{l_z,s_z} (lsl_zs_z|ff_z)R_{nl}(r)Y_{ll_z}(\theta,\varphi)\langle \mathbf{r}|ss_z\rangle,$$

$$\langle \mathbf{r}|NLJFF_z\rangle = \sum_{K=L,L+2} \sum_{L_z,J_z} (KJL_zJ_z|FF_z)$$

$$\times R^{(F,L)}_{NK}(r)Y_{KL_z}(\theta,\varphi)\langle \mathbf{r}|JJ_z\rangle.$$

In the above expression $R_{nl}(r)$ are the radial wave functions of a particle in a spherical box and $R^{(F,L)}_{NK}(r)$ are the solutions of the MBEMA equations given elsewhere,[24,25] $Y_{ll_z}(\theta,\varphi)$ are the spherical harmonics,[26] $\langle \mathbf{r}|ss_z\rangle$ are Γ_6 Bloch function and $\langle \mathbf{r}|JJ_z\rangle$ are hole Bloch functions. The hole Bloch functions are related with the Γ_8 ($J=3/2$) electronic Bloch functions $|\overline{J,J_z}\rangle$ by the rule $|JJ_z\rangle = (-1)^{J-J_z}|\overline{J,-J_z}\rangle$ (derived from the time-reversal operation). Our $|JJ_z\rangle$ are $|3/2,\pm 3/2\rangle = \mp(i/\sqrt{2})(X\pm iY)|\pm\rangle$ and $|3/2,\pm 1/2\rangle = (i/\sqrt{6})[2Z|\pm\rangle \mp (X\pm iY)|\mp\rangle]$.

Within this basis, in the strong confinement regime, the Coulomb interaction can be treated by direct diagonalization of the Hamiltonian or even by simple perturbation theory. Using the theory of angular momentum,[27] compact expressions for the matrix elements can be obtained. The dipole matrix elements gives

$$\mathfrak{M}^0_{g,e} = i\hat{\mathbf{e}}^*_{M_z} \frac{2Pe\hbar}{E_{e,g}} \delta_{M,1}(-1)^{f+5/2}\sqrt{\frac{(2f+1)(2F+1)}{3}}$$

$$\times \begin{Bmatrix} 1 & 3/2 & 1/2 \\ l & f & F \end{Bmatrix}(\delta_{l,L} + \delta_{l,L+2})$$

$$\times \int R^{(F,L)}_{Nl}(r)R_{nl}(r)r^2 dr,$$

where R_{nl} and $R^{(F,L)}_{NL}$ are electron and hole radial functions, respectively, and

$$\hat{\mathbf{e}}_0 = \mathbf{k}, \quad \hat{\mathbf{e}}_{\pm 1} = \mp \frac{\mathbf{i} \pm i\mathbf{j}}{\sqrt{2}}.$$

In the A term we must sum over the degenerate e states with different M_z, which turns out in a term proportional to the diagonal tensor

$$(\vec{\vec{A}}''')_{gi,gj} = \vec{\vec{1}} \frac{4P^2e^2\hbar^2}{E^2_{e,g}} \delta_{M,1}(\delta_{l_e,L_e} + \delta_{l_e,L_e+2})$$

$$\times \frac{(2f_e+1)(2F_e+1)}{3}\begin{Bmatrix} 1 & 3/2 & 1/2 \\ l_e & f_e & F_e \end{Bmatrix}^2$$

$$\times \left[\int R^{(F_e,L_e)}_{N_el_e}(r)R_{n_el_e}(r)r^2 dr\right]^2$$

$$\times \sum_v \frac{(gi|ev)(ev|gi)}{E_{e,g} + (v-\Delta^2)\hbar\omega_{LO} - \hbar\omega_l + i\Gamma'_e}.$$

The B term for $l_p=0$ phonons gives

$$\vec{\vec{B}}'''|_{l_p=0} = \vec{\vec{1}}\delta_{M,1} \sum_{(e),s} \frac{4P^2e^2\hbar^2}{3E_{e,g}E_{s,g}}\begin{Bmatrix} 1 & 3/2 & 1/2 \\ l_e & f_e & F_e \end{Bmatrix}\begin{Bmatrix} 1 & 3/2 & 1/2 \\ l_s & f_s & F_s \end{Bmatrix}(-1)^{f_e+f_s+3}\sqrt{(2f_e+1)(2f_s+1)(2F_e+1)(2F_s+1)}$$

$$\times (\delta_{l_e,L_e} + \delta_{l_e,L_e+2})(\delta_{l_s,L_s} + \delta_{l_s,L_s+2})\int R^{(F,L_e)}_{N_el_e}(r)R_{n_el_e}(r)r^2 dr$$

$$\times \int R^{(F,L_s)}_{N_sl_s}(r)R_{n_sl_s}(r)r^2 dr\langle s|H^{(l_p=0)}_{E-L}|e\rangle \sum_v \frac{\sqrt{2}}{x_0}\frac{(gi|Q|ev)(ev|gj) + (gi|ev)(ev|Q|gj)}{(E_{e,s})(E_{e,g} + (v-i-\Delta^2)\hbar\omega_{LO} - \hbar\omega_l + i\Gamma'_e)}.$$

IV. DISCUSSION

Table III shows the Huang-Rhys parameter Δ^2, the A term absolute value, and the ratio $|A'''/B'''|$, calculated for typical nanocrystals 20 Å in radius. The photon energies, corresponding to incoming resonance with the lower exciton level are also indicated in the table. The incomplete exciton con-

finement in CdS nanocrystals has been considered with two different models. (1) Finite band offsets V_e and V_h (Ref. 21) and (2) an effective radius.[20] Moreover, for CdSe nanocrystals we have also considered two models: (1) effective radius[19] and (2) multiband effective mass approximation (MBEMA) along with finite conduction band offset V_e.[28]

TABLE III. Numerical results for typical QD's 20 Å in radius. The energies $\hbar\omega_l$ correspond to incoming resonance with the lower Raman active exciton level in each nanocrystal.

Nanocrystal	Δ^2	$\hbar\omega_l$ (eV)	$|A'''/B'''|$	$|A'''|$ (Å³)
CdS	0.08	2.870	13	8.1×10^4
CdS (R_{ef})	0.0013	2.878	8.4	1.2×10^4
CdSe	0.0008	2.592	27	7.9×10^3
CdSe (MBEMA)	0.2	2.280	32	6.4×10^4

As it has been noticed,[20,21] Raman scattering is quasiforbidden in quantum dots in the strong confinement regime. The scattering is possible through a *decompensation* between the electron and hole wave functions, which may appear due to (1) the Coulomb electron-hole interaction and difference between electron and hole masses, (2) difference in electron and hole confinement, (3) hole band mixing, (4) defects, and (5) nonadiabatic effects.[14] The electron-hole decompensation also has a direct relation with the Huang-Rhys parameter. This one is larger in the case of CdS, where incomplete confinement have been considered, and in CdSe when band mixing and incomplete electron confinement have been included. These ones are the cases where larger Raman polarizabilities are obtained. Notice that, due to the finite electron confinement assumed, our Huang-Rhys parameter for CdSe nanocrystals within MBEMA is larger than other reported theoretical values[10,11] and is within the order of magnitude of the experimental values.[2,3,29,30]

In all the cases examined, the *A* term determines the Raman polarizability. This means that the interpretation of one-phonon Raman cross section considering only the *A* term is consistent with the microscopic calculations using TDPT reported here and in Refs. 15, 20, 21. However, it is incorrect to fit the Huang-Rhys factor from the overtone to fundamental intensity ratios in multiphonon Raman spectra, as different scattering channels give substantial contributions to the overtones.[14,16,17]

Let us consider the participation of optical phonons with $l_p > 0$ in Raman scattering. These phonons connect degenerate band-mixed exciton states and breaks the adiabatic approximation. Hence, the Albrecht's theory cannot describe Raman scattering from these phonons. On the other hand, the TDPT, may deal with degenerate states and nonadiabatic processes. Calculations in Ref. 31 indicate that the role of $l_p > 0$ phonons in one-phonon Raman spectra is to cause a small shoulder near the interface phonon frequency, being unimportant for the principal peak. Nevertheless, the electron-lattice interaction breaks the degeneracy of the exciton states, causing a redistribution of the exciton-phonon energy levels and possibly originate exciton-phonon complexes. Both these factors could substantially alter the predicted Raman spectra. This effect can be considered by TDPT of higher order in the electron-lattice interaction, or by a nonperturbative calculation of the exciton-phonon complexes. Research on this direction is presently in progress.

V. CONCLUSIONS

We have established the connection between the two theories more used for resonance Raman scattering in semicon-ductor nanocrystals: the Albrecht's theory based on the adiabatic approximation and the time-dependent perturbative approach. In particular, we have shown that both theories are equivalent in the limit of weak electron-lattice interaction and when the resonant exciton level is nondegenerate or is a set of uncoupled degenerate states. We have evaluated the relative importance of the Albrecht's *A* and *B* terms (the last one not discussed in the literature) for CdSe and CdS nanocrystals, using different models for the electronic excitations. We have found that the A term is the leading coefficient in all the cases considered. Additionally, we have given the expressions of the matrix elements of the electron radiation and the electron-lattice interactions for a model of exciton considering the fourfold degeneracy of the Γ_8 valence band. In the framework of this model, we have obtained a theoretical Huang-Rhys parameter within the order of magnitude of experimental values.

APPENDIX A: THE OSCILLATOR OFFSET

The adiabatic vibrational eigenstates for the electronic state e are obtained from the Hamiltonian

$$\hat{H}^e_{\text{vibr}} = \langle e|H_L + H_{E\text{-}L}|e\rangle$$

$$= \sum_a \{\hbar\omega_a \hat{b}^\dagger_a \hat{b}_a + \langle e|H_{E\text{-}L}(a)|e\rangle(\hat{b}_a + \hat{b}^\dagger_a)\}.$$

We have considered the case of Hermitian $H_{E\text{-}L}(a)$. For non-Hermitian $H_{E\text{-}L}(a)$ see Appendix B. The unitary transformation $\hat{c}_a = \hat{b}_a - \alpha_a$, with $\alpha_a = -\langle e|H_{E\text{-}L}(a)|e\rangle/\hbar\omega_a$ diagonalize the Hamiltonian

$$H^e_{\text{vibr}} = \sum_a \hbar\omega_a(\hat{c}^\dagger_a \hat{c}_a - \alpha^2_a).$$

The new and old phonon coordinate operators are related by

$$Q^e_a = \sqrt{\frac{\hbar}{2\omega_a}}(\hat{c}_a + \hat{c}^\dagger_a) = Q^G_a - \sqrt{2}\sqrt{\frac{\hbar}{\omega_a}}\alpha_a.$$

This relation identifies α_a with the oscillator offset Δ_a.

APPENDIX B: THE CONNECTION BETWEEN THE CLASSICAL AND THE QUANTUM ELECTRON-PHONON INTERACTION

The Hamiltonian operator determining the electronic eigenstates can be expanded in Taylor series of the vibrational normal coordinates

$$H_E(Q) = H_E(0) + \sum_a \frac{\partial H_E}{\partial Q_a} Q_a.$$

The second term of the above formula is the electron-phonon interaction.

$$H_{E\text{-}L} = \sum_a \frac{\partial H_E}{\partial Q_a} Q_a. \qquad \text{(B1)}$$

The quantum Fröhlich-type interaction operator have the form[32]

$$H_{E\text{-}L} = \sum_a H_{E\text{-}L}^-(a)\hat{b}_a + H_{E\text{-}L}^+(a)\hat{b}_a^\dagger,$$

where $\hat{b}_a$ are annihilation operators of phonons in the normal modes a. $H_{E\text{-}L}^\pm(a)$ are operators that act on the electronic coordinates, e.g., $H_{E\text{-}L}^-(n,l,m) = \Phi_{n,l}(r)Y_{l,m}(\theta,\varphi)$ for the one-electron-phonon interaction in a semiconductor nanocrystal.[15] Making the transformation to coordinate and momentum operators

$$\hat{b}_a = \sqrt{\frac{\omega_a}{2\hbar}}\left(Q_a + \frac{i}{\omega_a}P_a\right),$$

the interaction operator becomes

$$H_{E\text{-}L} = \sum_a \sqrt{\frac{\omega_a}{2\hbar}}[H_{E\text{-}L}^-(a) + H_{E\text{-}L}^+(a)]Q_a$$

$$+ \frac{i}{\sqrt{2\hbar\omega_a}}[H_{E\text{-}L}^-(a) - H_{E\text{-}L}^+(a)]P_a. \qquad \text{(B2)}$$

If $H_{E\text{-}L}^-(a) = H_{E\text{-}L}^+(a) = H_{E\text{-}L}(a)$ then Eqs. (B1) and (B2) are equivalent and

$$h_{es}^a = \langle s|\frac{\partial H_{el}}{\partial Q_a}|e\rangle = \sqrt{\frac{2\omega_a}{\hbar}}\langle s|H_{E-L}(a)|e\rangle.$$

When the vibrational modes in a nanostructure are described by complex fields there are modes for which $H_{E\text{-}L}^-(a) \neq H_{E\text{-}L}^+(a)$. In this case, thanks to time reversal symmetry, complex modes are double degenerate and real fields can be obtained from the real and imaginary parts of the complex fields, which correspond to real normal coordinates. The new matrix elements can be obtained from the complex matrix elements as

$$\langle s|H_{E\text{-}L}^{(1)}(a)|e\rangle = \frac{\langle s|H_{E\text{-}L}^-(a) + H_{E\text{-}L}^+(a)|e\rangle}{\sqrt{2}}, \qquad \text{(B3a)}$$

$$\langle s|H_{E\text{-}L}^{(2)}(a)|e\rangle = i\frac{\langle s|H_{E\text{-}L}^-(a) - H_{E\text{-}L}^+(a)|e\rangle}{\sqrt{2}}. \qquad \text{(B3b)}$$

APPENDIX C: EXCITON PHONON MATRIX ELEMENTS WITH DEGENERATE BANDS

The matrix elements of the interaction of band-mixed excitons with the optical phonons in a spherical nanocrystal can be calculated following the procedure outlined in Ref. 19. We obtained the expression

$$\langle n'N'l'L'sJf'F'M'M_z'|H_{E-L}^-(n_p,l_p,m_p)|nNlLsJfFMM_z\rangle$$

$$= \langle nNlLsJfFMM_z|H_{E-L}^+(n_p,l_p,m_p)|n'N'l'L'sJf'F'M'M_z'\rangle$$

$$= (-1)^{M'-M_z'}\frac{C_F}{\sqrt{R}}\begin{pmatrix} M' & l_p & M \\ -M_z' & m_p & M_z \end{pmatrix}\sqrt{(2M+1)(2M'+1)(2l_p+1)/4\pi}$$

$$\times \left\{ -\delta_{F,F'}\delta_{N,N'}\delta_{L,L'}(-1)^{F+M+f+f'+s} \right.$$

$$\times \sqrt{(2f'+1)(2f+1)(2l'+1)(2l+1)}\begin{Bmatrix} f' & f & l_p \\ l & l' & s \end{Bmatrix}\begin{Bmatrix} M' & M & l_p \\ f & f' & F \end{Bmatrix}\begin{pmatrix} l' & l_p & l \\ 0 & 0 & 0 \end{pmatrix}\int R_{n'l'}(r)\Phi_{n_p,l_p}(r)R_{nl}(r)r^2 dr$$

$$+ \delta_{f,f'}\delta_{n,n'}\delta_{l,l'}(-1)^{M'+f+J+2F}\sum_{K=L,L+2}\sum_{K'=L',L'+2}\sqrt{(2F'+1)(2F+1)(2K'+1)(2K+1)}$$

$$\times \begin{Bmatrix} F' & F & l_p \\ K & K' & J \end{Bmatrix}\begin{Bmatrix} M' & M & l_p \\ F & F' & f \end{Bmatrix}\begin{pmatrix} K' & l_p & K \\ 0 & 0 & 0 \end{pmatrix}\int R_{N'K'}^{(F',L')}(r)\Phi_{n_p,l_p}(r)R_{NK}^{(F,L)}(r)r^2 dr \left. \right\},$$

where $\Phi_{n_p,l_p}(r)$ is the radial part of the optical phonons electrostatic potential.[15] The optical modes for $l_p > 0$ are described by complex fields, real field matrix elements can be obtained from Eq. (B3).

For the Coulomb electron-hole interaction we obtained the expression

$$\langle n'N'l'L'sJf'F'M'M'_z| \frac{1}{|\mathbf{r}_e - \mathbf{r}_h|} |nNlLsJfFMM_z\rangle$$

$$= \delta_{M,M'}\delta_{M_z,M'_z}(-1)^{s+J+2f+F+F'+M}\sqrt{(2f+1)(2f'+1)(2F+1)(2F'+1)} \sum_{K,K',p} \begin{Bmatrix} p & f & f' \\ s & l' & l \end{Bmatrix}$$

$$\times \begin{Bmatrix} p & F & F' \\ J & K' & K \end{Bmatrix} \begin{Bmatrix} p & f & f' \\ M & F' & F \end{Bmatrix} \sqrt{(2l+1)(2l'+1)(2K+1)(2K'+1)} \begin{pmatrix} l' & p & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K' & p & K \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \int \int R_{n'l'}(r_e)R_{nl}(r_e)R_{N'K'}^{(F',L')}(r_h)R_{NK}^{(F,L)}(r_h) \frac{r_<^{p+2}}{r_>^{p-1}}dr_e dr_h .$$

In the above expression, due to the properties of the $3j$ symbols, the summation on p runs from $\max(|l-l'|,|K-K'|)$ to $\min(l+l',K+K')$.

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