# Nonlocal electrodynamics of weakly confined excitons in semiconductor nanostructures

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The third order nonlinear optical response of semiconductor quantum dots is calculated in the limit of weak exciton confinement. We treat exactly the nonlocal photon–exciton interaction using Green function techniques, without invoking the long wavelength approximation. This procedure provides a unified treatment of systems with arbitrary size compared with the optical wavelength. Geometric confinement gives rise to quantized polariton modes with a finite radiative lifetime. The variation of optical nonlinearities with size, and the role of local field effects are analyzed. © 1994 American Institute of Physics.

# **I. INTRODUCTION**

Studies of geometric confinement effects on optical properties of semiconductor nanostructures have mainly focused on the quantization of the relevant elementary excitations (Wannier excitons or electron-hole pairs). An extensive effort has been devoted to characterizing the relation between the optical response and exciton confinement in III-V or II-VI compounds,<sup>1,2</sup> mainly because of practical device applications. The family of GaAs quantum wells (QW's) provides by far the best examples of 2D-confined systems. In these materials, the Wannier exciton Bohr radius  $a_0$  is typically larger than the QW width which defines the confinement direction and strength, and the quantization of excitons has a preponderant effect on the optical response via the strong modification of the exciton wave function and oscillator strength. Typical values of Bohr radii and binding energies for III-V, II-VI, and I-VII materials are summarized in Table I.

Due to the dominance of strongly confined structures in mesoscopic spectroscopy, most studies have focused on this limit, where the interaction with the light field can be treated in the long wavelength approximation (LWA). The emphasis, then, has been put on calculating the material states,<sup>3</sup> by neglecting the electromagnetic field degrees of freedom. This is reminiscent of atomic physics. Each atom can be viewed as a point dipole as far as the field is concerned, and polariton effects are completely neglected. This may be justified for systems such as GaAs-QW's, where the direct electronhole Coulomb interaction is small compared with the kinetic energy (which is increased by the confinement). Furthermore, in these materials the dipole-dipole (electron-hole exchange) interaction related to polariton formation which is much smaller than the Coulomb contribution, is negligible.

The situation is very different, however, when the size of the system is much larger than the exciton Bohr radius, as is the case, for example, in I–VII compounds such as CuCl (see Table I) or *a fortiori* in organic materials where the excitations are strongly localized (Frenkel excitons). In this case the optical properties are related to the coherence associated with the exciton center of mass. Indeed, these materials are characterized by a small bulk Bohr radius  $a_0$  and an intrinsically large oscillator strength (which is inversely proportional to  $a_0^3$ ):  $f \propto \mu_{cv}^2 / \pi a_0^3$ ,  $\mu_{cv}$  being the interbandtransition dipole moment. For strong confinement, the oscillator strength is no longer directly proportional to the volume of the system. The size dependence is more complex and enters via correlation between an electron and a hole characterized by a confined Bohr radius  $a_c$  which can differ substantially from its bulk value.<sup>4</sup> For example, in an ideal 2D-QW the exciton Bohr radius is half of that in 3D,  $a_c^{2D}$  $= a_0/2$ ,<sup>3</sup> which leads to a fourfold increase in the exciton binding energy  $E_R^{2D} = 4E_R (E_R = e^2/2a_0, e \text{ is the electron charge})$ . On the other hand, if confinement is weak,  $a_0$  is not affected by the confinement, the oscillator strength is simply proportional to the volume, and all interesting confinement effects are found in the coherence of the center of mass (CM) motion. In addition the effects of the dipole-dipole interaction (long wavelength longitudinal electromagnetic field) and radiative corrections due to the coupling with the transverse electromagnetic field, which are proportional to the oscillator strength, increase as the Bohr radius decreases. Furthermore, due to the large exciton binding energy (and small Bohr radius), excitons can be treated as point interacting particles, pretty much the same as Frenkel excitons.

The weak confinement limit is of great fundamental interest since it links confined and infinite systems through *confined polariton modes* (CPM). These are the eigenvalues of the nonlocal (in space and time) exciton equation (cf. Appendix E) which contains the retarded interaction with the transverse electromagnetic field through a self-energy. This self-energy adds a finite size-dependent radiative width to the quantized exciton levels. The procedure we employ in Appendix D to calculate the CPM is valid provided size is larger than the exciton Bohr radius, and for infinite size it reproduces the well known bulk polariton dispersion.

Polariton effects have clear signatures in nonlinear optical properties since they strongly renormalize the one and the two-exciton energies and oscillator strengths. The oscillator strength of each optically active exciton state, is proportional to the volume. This scaling law is exact as long as we can invoke the LWA and neglect the dipole-dipole interaction (i.e., local field effects). The possible increase of the magnitude of the third order resonant nonlinear susceptibility of a microcrystallite has been suggested in Ref. 5. This enhancement saturates for large radii and attains its maximum for

TABLE I. Bulk parameters for typical semiconductors.  $E_R$ : Exciton binding energy.  $a_0$ : Exciton Bohr radius.  $\Delta_{LT}$ : Longitudinal-transverse splitting as measured in the bulk.

	$E_R \; (\text{meV})$	a <sub>0</sub> (Å)	$\Delta_{LT} \ ({ m meV})^{ m a}$
(III–V) GaAs	4.2	120	0.075
(II-VI) CdS	27	30	1.9 to 2.6 (A exciton)
(I-VII) CuCl	190	7	5.5

<sup>a</sup>E. S. Koteles, *Excitons*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1982).

infinite volume if one uses the LWA and neglects local field corrections.<sup>6</sup>

In this paper we calculate the linear and nonlinear (third order) optical response of large semiconductor quantum dots. We assume that the confinement size L is large compared with the exciton Bohr radius  $a_0: L \gg a_0$ . Our calculation is based on a two-band model using the effective mass approximation. This approximation requires that the size be sufficiently large.

We provide a rigorous self consistent treatment of the interaction with the electromagnetic field, without invoking the long wavelength approximation, and consequently our formulation holds all the way to the limit of infinite size. In practice, as the size is increased we need to incorporate a larger number of exciton states, and the calculation becomes more computationally intensive. We further show that the dipole-dipole interaction, which is usually neglected in the calculation of optical properties of semiconductor nanostructures, is essential in order to calculate the exciton (or polariton) radiative-decay rates, as well as the correct exciton energies. Our calculation interpolates between weakly confined nanostructures and infinite systems in which the polaritonradiative decay vanishes, and the dipole-dipole interaction gives rise to the splitting between longitudinal and transverse exciton states.

Ishihara<sup>7</sup> used a numerical algorithm to solve the coupled Schrödinger and Maxwell equations based on a generalization of a model proposed by Cho.<sup>8</sup> This procedure involves the numerical calculation of the expansion coefficients of the electromagnetic field. Although these coefficients contain all the relevant information on exciton dynamics such as radiative corrections and coherence effects, these are implicit in the numerical expansion, which makes it difficult to interpret.

The present calculation is based on a Green function representation of the exciton dynamics and incorporates the nonlocality of the electromagnetic field resulting in a selfconsistent confined-polariton picture. We apply the Green function formalism of Chernyak and Mukamel<sup>9</sup> to a nondegenerate two-band semiconductor model. The relevant Green functions constitute the formal solutions of the linearized Heisenberg equations for the expectation values of the one and two electron-hole pair operators. We can thus describe the excitons as coupled anharmonic oscillators. In the weak exciton confinement limit, the two-exciton Green function coincides with the simple form obtained for the Frenkelexciton model.<sup>9</sup> Due to the difference in the starting Hamiltonian, our results, derived along the same lines as in Ref. 9, differ slightly in form, in particular in the treatment of the exciton anharmonicities giving rise to nonlinearities. By focusing on material operators with nonlocal retarded coupling to the electromagnetic field, we can pinpoint the polariton effects on the exciton Green function. Our procedure avoids the diverging terms which show up in a density matrix formulation. These divergencies cancel identically, but may pose some numerical difficulties. Our results show the importance of the size dependence of the radiative as well as nonradiative decay rates in the generation of optical nonlinearities. We found a local maximum in the nonlinearity versus size dependence whose position is determined by the relative magnitude of the exciton–exciton interaction and the decay rates. Ł

In Sec. II we present the Hamiltonian, and the corresponding equations of motion for exciton operators are derived in Sec. III for the linear case, and in Sec. IV for the nonlinear case. We then apply the present formalism to a large semiconductor sphere in Sec. V. The analogous application to a thick film geometry is outlined in Appendix F.

#### **II. THE TWO-BAND HAMILTONIAN**

We consider a semiconductor with two nondegenerate bands, whose Hamiltonian can be expressed in the effective mass approximation, and in the multipolar form (without magnetic terms) as<sup>3,10</sup>

$$\hat{H} = \hat{H}_0 + \hat{H}_{eh} + \hat{H}_{int}(t) + \hat{H}_{rad},$$
 (1)

where

$$\begin{aligned} \hat{H}_{0} &= \sum_{\alpha} \int d\mathbf{r} \ \Psi_{\alpha}^{+}(\mathbf{r}) \ \frac{\hbar^{2}}{2m_{\alpha}} \nabla_{\mathbf{r}}^{2} \Psi_{\alpha}(\mathbf{r}) + 2 \pi \int d\mathbf{r} |\hat{\mathscr{P}}^{\text{L}}(\mathbf{r})|^{2} \\ &+ \frac{1}{2} \sum_{\alpha,\beta=e,h} \int d\mathbf{r} \ d\mathbf{r}' \ \Psi_{\alpha}^{+}(\mathbf{r}) \Psi_{\beta}^{+}(\mathbf{r}') \\ &\times V_{\alpha\beta}(\mathbf{r}-\mathbf{r}') \Psi_{\beta}(\mathbf{r}') \Psi_{\alpha}(\mathbf{r}), \end{aligned}$$
(2)  
$$\hat{H}_{\text{eh}} &= - \int d\mathbf{r} \ d\mathbf{r}' \ \Psi_{e}^{+}(\mathbf{r}) \Psi_{h}^{+}(\mathbf{r}) T(\mathbf{r}-\mathbf{r}') \Psi_{e}(\mathbf{r}') \Psi_{h}(\mathbf{r}'). \end{aligned}$$
(3)

 $\Psi_{\alpha}^{+}(\mathbf{r})$  ( $\Psi_{\alpha}(\mathbf{r})$ ), with  $\alpha = e$ , h, is the creation (annihilation) operator for the quasiparticle  $\alpha$  (electron or hole). These operators satisfy the Fermi-anticommutation rules

$$[\Psi_{\alpha}(\mathbf{r}),\Psi_{\beta}^{+}(\mathbf{r}')]_{+} = \delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}').$$
(4)

The polarization operator is, in the dipole approximation

$$\mathscr{P}(\mathbf{r}) = \hat{\mu}_{cv} \{ \Psi_e^+(\mathbf{r}) \Psi_h^+(\mathbf{r}) + \Psi_e(\mathbf{r}) \Psi_h(\mathbf{r}) \}, \tag{5}$$

and  $\hat{\mu}_{cv}$  taken to be parallel to the z axis (see Appendix A) is the interband transition dipole moment calculated with Wannier functions.  $\hat{\mathscr{P}}^{\perp}$  is the transverse part of  $\hat{\mathscr{P}}$ .  $V_{\alpha\beta}(\mathbf{r}-\mathbf{r}')=e_{\alpha}e_{\beta}/|\mathbf{r}-\mathbf{r}'|$  is the Coulomb interaction between particles  $\alpha,\beta$ , which is assumed to be identical to that of an infinite system (no dielectric effects).  $e_{\alpha}=\pm e$  is the electric charge of the particle  $\alpha$ . In Eq. (1), we did not include intraband transitions. Furthermore, we explicitly separated, for clarity, the matter Hamiltonian into two parts,  $\hat{H}_0$  and  $\hat{H}_{eh}$ , the latter being the electron-hole exchange interaction.

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 $T(\mathbf{r}-\mathbf{r'})$  is a simplified form of this exchange interaction (cf. Appendix A) obtained by expanding the Coulomb potential in multipoles

$$T(\mathbf{r}-\mathbf{r}') = \Delta_{SR} \delta(\mathbf{r}-\mathbf{r}') + \hat{\mu}_{cv} \cdot \nabla_{\mathbf{r}} \nabla'_{\mathbf{r}} \cdot \frac{\mu_{cv}}{|\mathbf{r}-\mathbf{r}'|}.$$
 (6)

 $\Delta_{SR}$  is the short-range coupling.^{11} The ' symbol implies that the contribution arising from  $|\mathbf{r}-\mathbf{r}'| < \epsilon$  is excluded, where  $\epsilon$ is small compared to the dimensions of the system. The electron-hole exchange interaction strength is a measure of the significance of polariton effects. It is worth noting that  $\hat{H}_{eh}$  is equivalent to the dipole-dipole interaction of the Frenkel-exciton model. This contribution becomes more important in systems where the exciton Bohr radius  $a_0$  is of the order of the lattice constant a (e.g., CuCl where  $a_0=7$  Å, a=5.4 Å and the expectation value of  $\hat{H}_{\rm eh}$  on the fundamental exciton state is of the order of 5.5 mev<sup>11</sup>). In strongly confined semiconductor nanostructures (e.g., GaAs) this term is often neglected, since it is much smaller than the quantized kinetic energy.<sup>3</sup> However, we shall concentrate here on weakly confined systems where  $\langle \hat{H}_{eb} \rangle$  and the kinetic energy are comparable (around 1% or 2% of the exciton binding energy  $E_R$ ).

The electromagnetic field is treated quantum mechanically, and we adopt the multipolar Hamiltonian in the Coulomb gauge. (Eventually, we shall make a semiclassical approximation for the field, see Eq. (27).]  $\hat{H}_{rad}$  is the field Hamiltonian

$$\hat{H}_{\rm rad} = \frac{1}{8\pi} \int d\mathbf{r} [(\nabla \times \hat{A}(\mathbf{r}))^2 + (\hat{D}^{\perp}(\mathbf{r}))^2], \qquad (7)$$

where the vector potential field operator  $\hat{A}$  and its conjugate momentum  $\hat{D}$  satisfy the commutation rules

$$[D^{\perp}(\mathbf{r}), \hat{A}(\mathbf{r}')] = 4\pi i \delta^{\perp}(\mathbf{r} - \mathbf{r}'), \qquad (8)$$

and  $\delta^{L}$  is the transverse  $\delta$  function. These operators commute with all material operators. The retarded interaction with the transverse electromagnetic field is

$$\hat{H}_{\text{int}}(t) = -\int d\mathbf{r} \,\hat{\mathscr{P}}(\mathbf{r}) \cdot \hat{D}^{\perp}(\mathbf{r}, t), \qquad (9)$$

and the average electric (Maxwell) field is related to the displacement operator  $\hat{D}(\mathbf{r},t)$  by

$$\hat{E}(\mathbf{r},t) = \hat{D}(\mathbf{r},t) - 4\pi \hat{\mathscr{P}}(\mathbf{r},t).$$
(10)

# III. LINEAR OPTICAL PROPERTIES: CONFINED POLARITONS

We start our study of the optical properties in the excitonic region by introducing the following set of binary electron-hole operators which represent the single-electron reduced density matrix of the system

$$\hat{P}_{12}(t) = \Psi_{e}(\mathbf{r}_{1}, t) \Psi_{h}(\mathbf{r}_{2}, t),$$

$$\hat{P}_{12}^{+}(t) = \Psi_{e}^{+}(\mathbf{r}_{1}, t) \Psi_{h}^{+}(\mathbf{r}_{2}, t).$$
(11)

Their expectation values are denoted

$$P_{12}(t) = \langle \hat{P}_{12}(t) \rangle.$$
(12)

The polarization operator [Eq. (5)] as well as the linear and nonlinear optical properties of the system depend only on the diagonal operator with  $\mathbf{r}_1 = \mathbf{r}_2$ . However, by introducing this extended set of operators we can derive simple closed equations of motion. This is done in Appendix B.

To calculate the linear response using a confined polariton picture, we first connect the matter variable  $\hat{P}$  with the Maxwell field. Using the Heisenberg equation for **D**, we find that the electric field satisfies the Maxwell equation

$$\left(\nabla \wedge \nabla \wedge + \frac{1}{c^2} \frac{\partial^2}{\partial^2 t}\right) \hat{E}(\mathbf{r}, t) = 4\pi \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \hat{\mathscr{P}}(\mathbf{r}, t).$$
(13)

The formal solution of this linear equation is

$$\hat{E}(\mathbf{r},t) = \mathbf{E}_{0}(\mathbf{r},t) + \int_{-\infty}^{t} dt' \int d\mathbf{r}' \,\mathscr{G}(\mathbf{r},\mathbf{r}',t-t') \,\hat{\mathscr{F}}(\mathbf{r}',t'),$$
(14)

where  $\mathscr{G}(\mathbf{r},\mathbf{r}';t-t')$  is the dyadic Green function defined by

$$\mathscr{G}(\mathbf{r},\mathbf{r}',t) = \int d\omega \ \mathscr{G}(\mathbf{r},\mathbf{r}';q)e^{i\omega|t|},$$

$$\mathscr{G}(\mathbf{r},\mathbf{r}';q) = \{q^2 + \nabla \nabla \cdot\} \frac{e^{iq|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad q = \frac{\omega}{c}.$$
(15)

and  $\mathbf{E}_0$  is the external field. With these definitions, Eq. (B2) linearized to first order in  $\mathbf{E}_0$  becomes

$$\mathscr{L}_{ch}(\mathbf{r}_{1},\mathbf{r}_{2},t)P_{12}^{(1)}(t) - \int_{-\infty}^{t} \int d\mathbf{r}_{3} \,\mathscr{S}^{L}(\mathbf{r}_{1},\mathbf{r}_{3},t-t')\hat{\mu}_{cv}\{P_{33}^{(1)} \\ \times(t') + P_{33}^{(1)*}(t')\} - \int d\mathbf{r}_{3} \, T(\mathbf{r}_{1}-\mathbf{r}_{3})P_{33}^{(1)}(t) \\ = \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\hat{\mu}_{cv} \cdot \mathbf{E}_{0}(\mathbf{r}_{1}), \qquad (16)$$

 $\mathscr{L}_{eh}$  is the electron-hole Liouville operator [Eq. (B3)].  $\mathscr{P}^{I} = \mathscr{D} - \nabla \nabla \cdot 1/|\mathbf{r} - \mathbf{r}'|$  is the transverse part of the Maxwell equation Green function (15). Hereafter we apply the rotating wave approximation by neglecting  $P_{33}^{(1)*}$  in Eq. (16). The first-order polarization is related to the external field via the one-exciton Green function [kernel of Eq. (16)]

$$P_{12}^{(1)}(\omega) = \int d\mathbf{r}_3 \ G_{\text{exc}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_3, \mathbf{r}_3, \omega) \hat{\mu}_{cv} \cdot \mathbf{E}_0(\mathbf{r}_3, \omega).$$
(17)

Equation (17), together with Eqs. (14) which gives the scattered field outside the system, and Eq. (5) which connects the Maxwell equation source term with the matter variables, allow us to calculate all linear optical properties of the system. The right-hand side of the linear equation (16) only depends on the center of mass coordinate  $\mathbb{R}_{12} = (m_e \mathbf{r}_1 + m_h \mathbf{r}_2/M)$ ,  $M = m_e + m_h$ .

So far we did not specify the geometry or size of the system, but hereafter we specialize to the weak confinement limit

$$L/a_0 \gg 1,\tag{18}$$

where L is the smallest geometric dimension of the system and  $a_0$  the exciton Bohr radius in the bulk. In this limit the center of mass and relative motions of electron-hole pairs

J. Chem. Phys. Vol. 101, No. 11, 1 December 1994 Downloaded 07 Mar 2001 to 128.151.176.185. Redistribution subject to AIP copyright, see http://ojps.aip.org/jcpo/jcpcpyrts.html are decoupled. A discussion of the different confinement regimes can be found in Refs. 12 and 13. The following derivation holds for all sizes larger than  $a_0$ . This has important consequences since our expressions interpolate all the way from mesoscopic sizes (e.g., 40 Å for CuCl) to the bulk, where they describe the formation of 3D polaritons.

Only the CM motion is affected by the weak confinement and the relative electron-hole degrees of freedom do not depend on the long wavelength external field. We can then factorize the one-exciton amplitude as

$$\langle \hat{P}_{12}(t) \rangle = \varphi(\mathbf{r}_1 - \mathbf{r}_2) \psi(\mathbf{R}_{12}) \exp\left[\frac{-i}{\hbar} \epsilon_{\nu} t\right],$$
 (19)

where  $\varphi$ , the relative motion wave function, is assumed to be identical to that of the bulk. We consider only the first 1s level, so that  $\varphi_{1s}(x) = (\pi a_0^3)^{-1/2} e^{-x/a_0}$ . This is justified since the CM-kinetic energies are much smaller than the excitonic binding energy. Other states can be included if necessary.

The one-exciton CM-Green function can be constructed from the solution of the one-exciton equation derived from Eq. (16) by integrating over the relative motion and neglecting the antiresonant part of the polarization, resulting in

$$\left(\epsilon_{\nu} - \epsilon_{\rm ex} + \frac{\hbar^2}{2M} \nabla_{\rm R}^2\right) \psi_{\nu}({\rm R}) - \int d{\rm R}' \ \Sigma({\rm R}, {\rm R}'; \epsilon_{\nu}/\hbar) \psi_{\nu}({\rm R}') = 0, \qquad (20)$$

with the self-energy

$$\Sigma(\mathbf{R},\mathbf{R}';z) = \hat{d}_{cv} \cdot \mathscr{G}(\mathbf{R}-\mathbf{R}';z/c)\hat{d}_{cv}, \qquad (21)$$

where  $\epsilon_{ex} = E_g - E_R$  ( $E_g$  being the gap energy) is the bulkexciton energy for zero CM momentum (i.e., optically active transverse state in an infinite crystal) and **R** the CM coordinate. The eigenvalue  $\epsilon_v$  is the single exciton energy which fully incorporates retardation effects. In Eq. (20), we have introduced the dipole moment  $d_{cv}^2 \equiv \mu_{cv}^2 |\varphi_{1s}(0)|^2$  which is proportional to the experimentally measured longitudinaltransverse energy splitting in the bulk  $\Delta_{LT} = 4 \pi d_{cv}^2$ .<sup>3</sup> We have included the dipole-dipole interaction part arising from the electron-hole exchange interaction as the longitudinal part of the polarization [see Eq. (6)].

The linear polarization can then be written in terms of the eigenvalues and eigenfunctions of Eq. (20) as

$$P^{(1)}(\mathbf{R},\omega) = \sum_{\nu} \psi_{\nu}(\mathbf{R}) P^{(1)}_{\nu}(\omega), \qquad (22)$$

where we have defined

$$P_{\nu}^{(1)}(\omega) = \sum_{\nu'} \mathscr{B}_{\nu\nu'}^{(1)} \mathbf{E}_{\nu\nu'}^{0}(\omega), \qquad (23)$$

with the second rank tensor

$$\mathscr{H}_{\nu\nu'}^{(1)} = \delta_{\nu\nu'} \frac{\hat{d}_{cv}\hat{d}_{cv}}{\hbar\omega - \epsilon_{\nu}},\tag{24}$$

$$\mathbf{E}_{\nu}^{0}(\boldsymbol{\omega}) = \int d\mathbf{R} \ \psi_{\nu}^{*}(\mathbf{R}) \mathbf{E}_{0}(\boldsymbol{\omega}).$$
(25)

In Eq. (24),  $\epsilon_{\nu} = e_{\nu} - i(\Gamma_{\nu} + \gamma_{nr})$  is a complex quantity which contains the radiative width  $\Gamma_{\nu}$  of the exciton as well as the nonretarded width  $\gamma_{nr}$ . The form of the CM wave functions  $\psi_{\nu}(\mathbf{R})$  is discussed in the next sections and in Appendices D, E, and F.

In the long wavelength approximation we assume that the field varies very slowly inside the sphere and define the linear polarizability  $\alpha$  as

$$P_{LWA}^{(1)}(\omega) \equiv \frac{1}{V} \int d\mathbf{R} \ P_{LWA}^{(1)}(\mathbf{R}, \omega)$$
$$= \alpha(\omega) E_0(\omega), \qquad (26)$$

where

$$\alpha(\omega) = |\hat{d}_{cv}|^2 \sum_{\nu} \frac{f_{\nu}}{\hbar \omega - \epsilon_{\nu}},$$
$$f_{\nu} = \left| \int d\mathbf{R} \ \psi_{\nu}(\mathbf{R}) \right|^2.$$

Equations (22) and (24) which contain all the necessary information on the confined exciton states depend on the following parameters: The exciton binding energy  $E_R$  which is the natural energy scale, the exciton Bohr radius  $a_0$  as the natural length scale,  $\Delta_{\rm LT}$  which is a measure of the dipole moment  $\mu_{cv}$ ,  $\gamma_{\rm nr}$  a phenomenological nonradiative decay rate, *L* the confined dimension of the system (radius  $\mathcal{R}$  in the case of a sphere), and  $\zeta = m_e/m_h$  the ratio of the electron and hole effective masses.

#### IV. THE THIRD-ORDER POLARIZATION

The nonlinear optical properties are determined by higher order operators as described in Appendix B. We must take the expectation value of Eqs. (B2) and (B9) and close the hierarchy. We first make a semiclassical approximation by treating the electromagnetic field  $\hat{E}^{\perp}$  as a *c* number. We then have

$$\langle \hat{E}^{\perp} \hat{A} \rangle = E^{\perp} \langle \hat{A} \rangle, \tag{27}$$

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for all material operators  $\hat{A}$ . The third-order equation for the exciton polarization is

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$$\mathscr{L}_{eh}(\mathbf{r}_{1},\mathbf{r}_{2},t)P_{12}^{(3)}(t) = -\hat{\mu}_{cv} \cdot \int d\mathbf{r}_{3} P_{13}^{(1)}P_{23}^{(1)*}E^{\perp}(\mathbf{r}_{2},t) - \hat{\mu}_{cv} \cdot \int d\mathbf{r}_{3} P_{31}^{(1)}P_{32}^{(1)*}E^{\perp}(\mathbf{r}_{1},t) + \int d\mathbf{r}_{3} \int d\mathbf{r}_{4}(V_{14} - V_{13} - V_{24}) d\mathbf{r}_{4}(V_{14} - V_{13} - V_{14}) d\mathbf{r}_{4}(V_{14} - V_{14}) d\mathbf{r}_{$$

$$+V_{23}P_{34}^{(1)*}(t)Q_{3412}^{(2)}(t) - \int d\mathbf{r}_3 \int d\mathbf{r}_4 (D_{24}P_{23}^{(1)*}(t)Q_{1344}^{(2)}(t) + D_{14}P_{31}^{(1)*}(t)Q_{3244}^{(2)}(t)).$$
(28)

In Eq. (28) we have introduced the expectation value of the operator

$$\hat{Q}_{1234}(t) = \hat{P}_{12}(t)\hat{P}_{34}(t), \tag{29}$$

which corresponds to the annihilation of two excitons. This satisfies the following equation [see Eq. (B9)]:

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$$\mathscr{Z}_{2}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},\mathbf{r}_{4},t)\mathcal{Q}_{1234}^{(2)}(t) = \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\hat{\mu}_{cv}\cdot\hat{E}^{\perp}(\mathbf{r}_{1},t)P_{34}^{(1)} + \delta(\mathbf{r}_{3}-\mathbf{r}_{4})\hat{\mu}_{cv}\cdot E^{\perp}(\mathbf{r}_{3},t)P_{12}^{(1)} - \delta(\mathbf{r}_{1}-\mathbf{r}_{4})\hat{\mu}_{cv}\cdot\hat{E}^{\perp}(\mathbf{r}_{1},t)P_{32}^{(1)} - \delta(\mathbf{r}_{2}-\mathbf{r}_{3})\hat{\mu}_{cv}\cdot E^{\perp}(\mathbf{r}_{2},t)P_{14}^{(1)} + \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\int d\mathbf{r}_{5} D_{15}\mathcal{Q}_{5534}^{(2)} + \delta(\mathbf{r}_{3}-\mathbf{r}_{4})\int d\mathbf{r}_{5} D_{35}\mathcal{Q}_{1255}^{(2)} + \delta(\mathbf{r}_{1}-\mathbf{r}_{4})\int d\mathbf{r}_{5} D_{15}\mathcal{Q}_{3255}^{(2)} + \delta(\mathbf{r}_{2}-\mathbf{r}_{3})\int d\mathbf{r}_{5} D_{25}\mathcal{Q}_{1455}^{(2)}.$$
(30)

Here, Q is second order in the field. Equation (28) can be recast in an operator form

$$\mathscr{L}_{eh}(t)P^{(3)}(t) = \hat{\mu}_{cv} \cdot E^{\perp}(t)P^{(1)*}(t)P^{(1)}(t) + \mathbb{U}^{x}P^{(1)*}(t)Q^{(2)}(t).$$
(31)

The first contribution in the rhs comes from Pauli exclusion. It prohibits the optical creation of the same particle (electron or hole) at the same place, prevents the filling of already populated optically active exciton states, and induces transitions to initially forbidden states. This is usually denoted *phase space filling* (or band-filling effect).<sup>1</sup> The second term comes from the Coulomb interaction between excitons. The relative magnitude of these two contributions depends on the material and confinement size. The latter is much larger in compounds which have a large exciton binding energy (compared with dephasing rate) and a confinement size much larger than the exciton Bohr radius. We shall address this point in detail in the next section.

Equation (28), together with Eqs. (16) and (30) constitute a closed system which can be solved numerically. However, due to the large number (six) of continuous coordinates, an expansion in a basis set is preferable.

With the aid of the Green functions of the one- and two-exciton equations of motion, the third-order polarization at frequency  $\omega$ , obtained as the formal solution of Eq. (31) is given by

$$P_{12}^{(3)}(\omega) = -\int d\mathbf{r}_{3} d\mathbf{r}_{4} d\mathbf{r}_{5} G_{\text{exc}}(\mathbf{r}_{1}, \mathbf{r}_{2}; \mathbf{r}_{3}, \mathbf{r}_{4}, \omega) \Biggl\{ \int d\omega_{1} d\omega_{2} d\omega_{3} \, \delta(\omega - \omega_{1} - \omega_{2} - \omega_{3}) \int d\mathbf{r}_{5} \\ \times [\hat{\mu}_{cv} \cdot E^{\perp}(\mathbf{r}_{4}, \omega_{1}) P_{35}^{(1)*}(\omega_{2}) P_{45}^{(1)}(\omega_{3}) + \hat{\mu}_{cv} \cdot E^{\perp}(\mathbf{r}_{3}, \omega_{1}) P_{53}^{(1)*}(\omega_{2}) P_{54}^{(1)}(\omega_{3})] + \int d\omega_{1} d\omega_{2} \, \delta(\omega - \omega_{1} - \omega_{2}) \\ \times \int d\mathbf{r}_{5} \, d\mathbf{r}_{6} [(V_{36} - V_{35} - V_{46} + V_{45}) P_{56}^{(1)*}(\omega_{1}) Q_{5634}^{(2)}(\omega_{2}) - (D_{46} P_{45}^{(1)*}(t) Q_{3566}^{(2)}(t) + D_{36} P_{53}^{(1)*}(t) Q_{5466}^{(2)}(t))] \Biggr\}.$$
(32)

In the same way, we define the two-exciton Green function  $(G_{2exc})$  as the formal solution of Eq. (30)

$$Q_{1234}^{(2)}(\omega) = \int d\omega_1 \, d\omega_2 \int \Pi_i \, d\mathbf{r}'_i$$

$$\times \, \delta(\omega - \omega_1 - \omega_2) G_{2\text{exc}}(\mathbf{r}_i; \mathbf{r}'_i, \omega_1 + \omega_2)$$

$$\times \{ \delta(\mathbf{r}'_3 - \mathbf{r}'_4) \hat{\mu}_{cv} \cdot \mathbf{E}_0(\mathbf{r}'_3, \omega_1) P_{1'2'}^{(1)}(\omega_2)$$

$$+ \, \delta(\mathbf{r}'_1 - \mathbf{r}'_2) \hat{\mu}_{cv} \cdot \mathbf{E}_0(\mathbf{r}'_1, \omega_1) P_{3'4'}^{(1)}(\omega_2) \}.$$
(33)

We shall be interested in calculating the nonlinear scattered field outside the system

$$\mathbf{E}_{s}^{(3)}(\mathbf{r},\omega) = \int d\mathbf{r}_{1} \, \mathscr{T}(\mathbf{r},\mathbf{r}_{1};\omega) \hat{\mu}_{cv} [P_{11}^{(3)}(\omega) + P_{11}^{(3)*}(\omega)].$$
(34)

The evaluation of  $P^{(3)}$  requires the calculation of the two-exciton Green function. It is difficult to find an analytical solution for a Hamiltonian as general as Eq. (1). Indeed, even in the bulk, no analytical solutions are known for the four interacting particle system, and we shall introduce an approximate procedure for computing  $G_{2exc}$ . Our goal is to investigate the nonlinearities of a confined system at very low exciton density, and point out their scaling with size and other intrinsic parameters. Our approximation for the twoexciton Green function in based on the following argument: The relative electron-hole motion which is dominated by short range Coulomb forces, couples to the short wavelength longitudinal electromagnetic field, whereas the CM motion is affected by the long range dipole-dipole (i.e., electron-hole exchange) interaction, as well as by the transverse electromagnetic field. Therefore, if the short range Coulomb interaction can be separated from the center of mass motion, as is

the case in an infinite system, we can concentrate on confinement effects on the CM alone (weak confinement).

In Appendix C we show that, due to the small Bohr radius, we can invoke the point-dipole approximation for the exciton-exciton interaction, and neglect the correction due exchange between the same particles in the dipole-dipole interaction. This approximation, although rather crude, allows us to greatly simplify the problem for the following two reasons: (i) the interaction with the field becomes local, and may be evaluated at the exciton center of mass (hole and electron at the same site), and the nonlocality of the field enters through this CM variable and not through the relative motion; (ii) we can establish a direct correspondence with the Frenkel exciton model. We finally obtain

$$\mathbf{P}_{\nu_s}^{(3)}(\mathbf{R},\omega_s) = \sum_{\nu_s} \psi_{\nu_s}(\mathbf{R}) \mathbf{P}_{\nu_s}^{(3)}(\omega_s), \qquad (35)$$

where

$$\mathbf{P}_{\nu_{s}}^{(3)}(\omega_{s}) = \int d\omega_{1} \ d\omega_{2} \ d\omega_{3} \ \delta(\omega_{s} - \omega_{1} - \omega_{2} - \omega_{3}) \\ \times \left\{ \sum_{\nu_{1}\nu_{2}\nu_{3}} \mathscr{K}_{\nu_{s};\nu_{1}\nu_{2}\nu_{3}}^{(3),d}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3}) \\ \times \mathbf{E}_{\nu_{1}}^{0}(\omega_{1}) \mathbf{E}_{\nu_{2}}^{0}(\omega_{2}) \mathbf{E}_{\nu_{3}}^{0}(\omega_{3}) \\ + \sum_{\nu_{1}\nu_{2}} \mathscr{K}_{\nu_{s};\nu_{1}\nu_{2}}^{(3),x}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3}) \\ \times \mathbf{E}_{\nu_{2}}^{0}(\omega_{1}) \times \mathbf{E}_{\nu_{s};\nu_{1}\nu_{2}}^{0}(\omega_{2}) \mathbf{E}_{\nu_{1}}^{0}(\omega_{3}) \right\},$$
(36)

and the subscripts d and x refer to the contributions arising from the Coulomb interaction and Pauli exclusion, respectively. A complete real space expression for  $\mathcal{K}^{(3)}$  is given in Appendix B. When expanded using the eigenfunctions [Eq. (24)] we obtain

$$\mathcal{K}_{\nu_{s};\nu_{1}\nu_{2}\nu_{3}}^{(3),d}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3})$$

$$=\hat{\mu}_{cv}^{4}G_{\nu_{s}}^{(1)}(\omega_{s})G_{\nu_{1}}^{(1)}(-\omega_{3})^{*}\Gamma_{\nu_{s}\nu_{1},\nu_{2}\nu_{3}}(\omega_{1}+\omega_{2})$$

$$\times G_{\nu_{2}}^{(1)}(\overline{\omega}_{1})G_{\nu_{3}}^{(1)}(\omega_{2}), \qquad (37)$$

$$\mathscr{K}^{(3),x}_{\nu_{s};\nu_{1}\nu_{2}}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3}) = \hat{\mu}^{4}_{cv}G^{(1)}_{\nu_{s}}(\omega_{s})G^{(1)}_{\nu_{1}}(-\omega_{3})^{*}G^{(1)}_{\nu_{2}}(\omega_{1}), \qquad (38)$$

where

$$\Psi_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}} = v^{x} \int d\mathbf{R} \ \psi_{\nu_{1}}^{*}(\mathbf{R}) \psi_{\nu_{2}}^{*}(\mathbf{R}) \psi_{\nu_{3}}(\mathbf{R}) \psi_{\nu_{4}}(\mathbf{R}),$$
(39)

$$\mathbf{E}_{\nu_{1}\nu_{2}\nu_{3}}^{0} = g^{x} \int d\mathbf{R} \ \psi_{\nu_{1}}^{*}(\mathbf{R}) \psi_{\nu_{2}}(\mathbf{R}) \psi_{\nu_{3}}(\mathbf{R}) \mathbf{E}_{0}(\mathbf{R}), \quad (40)$$

$$G_{\nu}^{(1)}(\omega) = \frac{1}{\omega - \epsilon_{\nu}},$$

$$\Gamma_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}}(\omega) = \frac{V}{1 - G_{0}^{(2)}(\omega)V} \bigg|_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}}.$$
(41)

 $v^x$  and  $g^x$  are numerical constants given in Appendix C obtained by integrating the matrix elements over the relative motion.<sup>14</sup>  $G_0^{(2)}$  is given by

$$G_0^{(2)}(\omega)|_{\nu_1\nu_2} = \frac{1}{2i\pi} \int d\omega' \ G_{\nu_1}^{(1)}(\omega')G_{\nu_2}^{(1)}(\omega-\omega').$$
(42)

Equations (35)–(41) constitute our final expression for the third order response, and form the basis for the subsequent analysis. The nonlinear response contains two terms which reflect the contributions of the Coulomb interaction between excitons and of Pauli exclusion respectively. This differs from the result for the Frenkel-exciton model<sup>9</sup> which contains only the Pauli exclusion contribution. This is a direct consequence of the exciton–exciton interaction term which exists in our Hamiltonian but is absent in the Frenkelexciton model.

# **V. APPLICATION TO A LARGE SPHERE**

We consider a large semiconductor sphere with radius  $\mathscr{B} \ge a_0$ . We use parameters corresponding to CuCl which provides a beautiful example of a weakly confined nanostructure (cf. Table I). Using the symmetry, we decompose the Green function in spherical functions as described in Appendices D and E. The dipole-dipole interaction is by far stronger than the pure radiative corrections. We then diagonalize the exciton Hamiltonian by keeping only  $H_0 + H_{eh}$ . Using this partial diagonalization, we can express the one-exciton Green function as

$$G^{(1)}(\omega) = \sum_{\nu} |\nu\rangle G^{(1)}_{\nu}(\omega) \langle \nu|, \qquad (43)$$

where the states  $|\nu\rangle$  are defined in Eq. (20). The observed signal is calculated from the electromagnetic field, given by Eq. (14). Far from the sphere, it has the following form:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \mathbf{f}(\hat{r}, \hat{q}) \frac{e^{iqr}}{r}, \qquad (44)$$

where  $\mathbf{E}_0(\mathbf{r})$  is the incident field. The total cross section is related, by the optical theorem, to the forward scattering amplitude<sup>15</sup>

$$\sigma_{\text{tot}}(\omega) = \frac{4\pi}{q} \, \mathscr{F}m\{\boldsymbol{\epsilon}_0 \cdot \mathbf{f}(\hat{r} = \hat{q})\},\tag{45}$$

 $\epsilon_0$  is the direction of the incident field.  $\hat{r}$  is the direction of observation. **f** is calculated in Appendix E.

In Fig. 1, we plot the linear total-scattering cross section of a sphere of radius  $\mathcal{B}/a_0=40$ . We chose a relatively large radius in order to show a large number of levels and enhanced radiative width (proportional to the oscillator strength). The figure shows the positions of the optically active states as well as their relative strength. The inset

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FIG. 1. Total linear scattering cross section of a sphere of radius  $\mathcal{B}/a_0=40$ . We have included a small nonradiative damping  $\gamma_{nr} = 10^{-4} E_R (E_R)$  is the bulk exciton binding energy). Inset: Linear total scattering cross section of a sphere of radius  $\mathcal{R}/a_0 = 10$ .

shows the linear spectrum of a  $10a_0$  sphere. When the radius is small (stronger confinement), the mixing between states induced by the dipole-dipole interaction (i.e. local field effects) can be neglected, and the linear spectrum shows only s-exciton states (l=0) whose energies are approximately given by  $\epsilon_n = \epsilon_{ex} + \Delta_{LT}/3 + \hbar^2 n^2 \pi^2/2M \mathscr{R}^2$  and oscillator strengths  $f_n \propto \mathcal{R}^3/n^2$ , *n* being the radial quantum number (*n* =1,2,3,...). When the size is increased and the spacings between the quantized levels decrease, the local field effect becomes more important and gives rise to a strong mixing of s and d exciton levels (cf. Appendix E). Therefore, the strongest oscillator strength is no longer associated with the lowest exciton state. The maximum of the linear absorption is found at  $\epsilon = \epsilon_{ex} + \Delta_{LT}/3$ , and is connected to higher excited states. The importance of the local field is well known from the classical Mie theory.<sup>15</sup> For not too large radii, i.e., when  $\omega/c \gg \mathscr{R}$  still holds, the optical resonances of the sphere are determined by the following equation (for  $\omega$ ):

$$\frac{l}{l+1} \left( 2M\Delta_{\rm LT}/\hbar^2 - k_+(\omega)^2 \right) \frac{j_{l-1}(k_-(\omega)\mathscr{B})}{j_{l+1}(k_-(\omega)\mathscr{B})} - k_+^2 \frac{j_{l-1}(k_+(\omega)\mathscr{B})}{j_{l+1}(k_+(\omega)\mathscr{B})} = 0, \tag{46}$$

obtained from Eq. (D9) by setting  $c \to \infty$ .  $j_l$  are the spherical Bessel functions of order l. Here,  $k_+(\omega)^2 = 2M(\hbar\omega - \epsilon_{ex})/\hbar^2$ and  $k_{-}(\omega)^2 = k_{+}^2 - 2M\Delta_{\rm LT}/\hbar^2$ . We shall see that Eq. (46) gives for large radius (but still small compared to the external wavelength) the well known Mie theory. When  $\mathscr{B} \rightarrow \infty$ , asymptotic properties of the Bessel functions the  $(j_l(x) \rightarrow \sin(x - l\pi/2)/x \text{ for } x \rightarrow \infty)$  give

$$\frac{l}{2l+1} \Delta_{\rm LT} - \frac{\hbar^2}{2M} k_+^2 = 0 \tag{47}$$



FIG. 2. Panels a to d show the dimensionless exciton radiative decay rate  $\gamma_{\text{exc}} \equiv \Gamma_{\text{exc}} / ((\mathscr{R}/a_0)^3 E_R)$ , as a function of  $\mathscr{R}/a_0$  for the four lowest exciton levels, respectively. The solid line is the exact radiative decay and the long dashed line has been calculated without dipole-dipole interaction. The short dash curve in panels a and c is the LWA (levels l=0, n=1, 2) without dipole-dipole interaction.

The scattered field in Mie theory, to first order in  $q\mathcal{R}$ , gives a pole in the total cross section of the form<sup>17</sup>

$$\frac{1}{\epsilon(\omega)+2},\tag{48}$$

where only terms with l=1 contribute, and  $\epsilon(\omega)$  is the bulk dielectric function<sup>3</sup>

$$\epsilon(\omega) = 1 + \frac{\Delta_{\rm LT}}{\epsilon_{\rm ex} - \omega}.$$
(49)

Since  $k_{\pm}^2 = \hbar \omega - \epsilon_{ex}$ , the identity between Eq. (46) with l=1and the pole of Eq. (48) is evident. Therefore, there exists an intermediate range of sizes where the classical Mie theory holds. For smaller sizes, quantum confinement effects on the energy levels and wave functions are preponderant, and the complete description in terms of quantized exciton states is necessary. In the opposite limit, when the radius is comparable or larger than the wavelength, one cannot ignore polariton effects (c is finite) and again the full nonlocal description (20) is required.

In Fig. 2 we plot the radiative decay rate per unit volume, i.e., the imaginary part of the exciton energy divided by  $(\mathcal{R}/a_0)^3$ , of the four lowest exciton levels, using different approximations. The solid curve represents the exact calculation while the long-dashed curve is obtained by neglecting the dipole-dipole interaction. The short-dashed curve in Figs. 2(a) and 2( $\tilde{c}$ ) is the LWA (levels l=0, n=1,2) without dipole-dipole interaction. In this approximation the radiative decay rate is given by  $\Gamma_{nlm} \propto (\mathscr{R}^3 ln^2) \delta_{l0}^6$  and the decay rate is simply proportional to the volume of the sphere. The nonlocal calculation without the local field effects, differs only at large radii ( $\geq$ 30) since the interaction with the transverse

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FIG. 3. (a) Energy of the six lowest exciton levels (real part of the  $\epsilon_{\nu}$ ). (b) The exact dimensionless radiative decay rate  $\gamma_{exc}$ , defined in Fig. 2.

field is rather weak. The combined contribution of the longitudinal+transverse (i.e., local field+pure radiative corrections) results in a much stronger dependence on the radius (solid curves). It is interesting to compare the size dependence of the real and imaginary parts of the energy, shown in Fig. 3. Panel b shows the radiative decay rate, of the six lowest exciton levels. Their variation with size is to be compared with panel a which shows the real part of the exciton energy and its scaling with size. Inflection points in the damping rate curves correspond to level anticrossings of the real part of the energy. Similar results have been obtained in Ref. 16.

The strong variation of the radiative decay rate with size, which may be clearly attributed to the dipole—dipole interaction (as seen, for example, Fig. 2) is due to the mixing of different states. Our numerical diagonalization does not allow us to pinpoint which unperturbed quantized state corresponds to a particular radiative decay rate depicted in Fig. 2. However, we can provide a physical explanation for the bellshaped  $\gamma(\mathcal{R})$ . The exciton-field interaction-matrix element is proportional to

$$\langle 0|\hat{P} \cdot \mathbf{E}|nlm \rangle \propto \mathscr{R}^{3/2} \frac{\kappa_{nl}}{\kappa_{nl}^2 - (q\mathscr{R})^2} j_l(q\mathscr{R}) \quad q = \frac{\omega}{c}.$$
 (50)

The quantized exciton wave vectors are  $k_{nl} = \kappa_{nl}/\mathcal{R}$  which vanish when  $\mathcal{R} \to \infty$  for fixed quantum numbers n,l. Therefore, when  $\mathcal{R}$  increases, the optically active states (with a nonvanishing radiative decay) will have higher quantum numbers in order to keep a finite  $k_{nl}$ . For an infinite system, the selection rule  $k_{nl} = q$  corresponds to  $n \to \infty$  and  $k_{nl}$  finite [for large  $n, k_{nl} \approx \pi(n+l/2)/\mathcal{R}$ ]. This shows the successive resonant character of higher quantum states and explains the shape of Fig. 3(b). It should be noted also that the sum rule  $\sum_{\nu} \gamma_{\nu} = C = \text{constant}$ , should hold for each radius. In our calculation this was verified to within 1%, and "C" slightly decreases for larger  $\mathcal{R}$ . This is because the oscillator strength redistributes to higher quantum states  $l = 1, 3 \cdots$  which are not included in our truncated calculation.

We shall now apply our expressions for the nonlinear response of a sphere, calculate a stationary pump-probe signal, and study its scaling with size. We look for the resonant third-order polarization generated at probe frequency  $\omega_T$  by the interaction with a pump field with frequency  $\omega_P$ . The signal field outside the sphere is given by Eq. (14). Since we expand the polarization in the external field, we can express the scattering of the incident fields in terms of a cross section, as discussed in Appendix E. The measured signal is the difference between the cross sections at the probe frequency with and without the pump

$$\delta\sigma(\omega_T, \omega_P) = \sigma(\omega_T, E_P \neq 0) - \sigma(\omega_T, E_P = 0)$$

$$\propto \int d\mathbf{R} \ e^{i\mathbf{q}\cdot\mathbf{R}} \mathbf{P}^{(3)}(\mathbf{R}, \omega_s). \tag{51}$$

As indicated in Sec. IV, the nonlinear polarization has two contributions related to different physical processes, namely, phase space filling and Coulomb interactions. The former is proportional to  $g^{x}$  [cf. Eq. (40)] and the latter to  $v^{x}$  [cf. Eq. (39)]. As discussed in Ref. 6, the former is much smaller than the Coulomb contribution in the weak confinement limit, when the exciton binding energy is much larger than the damping parameters (as in CuCl). We shall therefore neglect the  $g^{x}$  contribution to the third-order polarization in the following calculations. The present calculation does not hold for materials such as GaAs, where phase space filling is significant, and the calculation requires a much larger number of quantized levels.

In our calculations, we have approximated the Coulomb matrix element by its diagonal value

$$V_{\nu_1\nu_2\nu_3\nu_4} \simeq V_{\nu_1\nu_2} \delta_{\nu_1\nu_3} \delta_{\nu_2\nu_4}.$$
 (52)

We have verified that the calculation with the complete matrix elements (39) gives a very small correction. The different matrix elements have the following scaling with size  $V_{\nu\nu'} \propto \mathscr{R}^{-3}$ ;  $g^{x} \propto \mathscr{R}^{-3/2}$ ;  $E_{\nu} \propto \mathscr{R}^{-2}$ ;  $\mu_{\nu} \propto \mathscr{R}^{3/2}$  and  $\Sigma_{\nu} \propto \mathscr{R}^{3}$  (for small radii).  $\Sigma_{\nu}$  reflects the correction due to the pure retarded interaction. Using these matrix elements, the approximation (52) and integrating Eq. (32) to calculate the cross section, we can show that at resonance, the third-order polarization scales as

$$P^{(3)} \propto V_{\nu\nu'} |\mu_{\nu'}|^2 |\mu_{\nu'}|^2 \propto \mathscr{R}^3.$$
(53)

Therefore, the polarization per unit volume is independent on size in the limit of infinite radius, and the result has the proper thermodynamic limit. Calculating the nonlinear response using the density matrix as in Ref. 6 leads to an expression which contains two diverging contributions in  $P^{(3)}/\mathscr{R}^3$  (when  $\mathscr{R} \rightarrow \infty$ ). These contributions interfere destructively, yielding a size-independent  $\chi^{(3)}$ .<sup>18,19</sup> Our present calculation gives directly the correct scaling since the whole



FIG. 4. Linear absorption cross section (upper panels) and pump-probe signal (lower panels) as a function of probe frequency and size. Frames a to d correspond to  $\mathcal{R}/a_0=12$ , 20, 30, and 40. The pump frequency  $\omega_P$  is resonant with the maximum of the linear spectrum for each case. The pump-probe signal curves are given relative to the (a) curve which was normalized to unity. The dimensionless detuning of the probe beam is defined as  $\Delta\omega_T = (\hbar\omega_T - \epsilon_{ex})/E_R$ . The nonradiative damping parameter is  $\gamma_{trr} = 10^{-4}E_R$ .

nonlinear polarization arising from the Coulomb interaction is proportional to  $V_{\nu\nu'}$ . The band-filling contribution contains no divergence, as was shown in Ref. 6.

We shall now study the coherent enhancement of the third order polarization, defined as the increase of the nonlinear response magnitude (at resonance) with the radius. It is mainly determined by the above scaling rules and in particular it is proportional to the inverse of Coulomb matrix element V, as long as it is larger than the decay rate. When these two quantities become comparable, the enhancement is canceled. For small radii,  $V \ge \gamma$  and the maximum of  $\delta \sigma$ scales as  $(\gamma^2 V)^{-1} v^x / \gamma$ , where  $\gamma$  is the total damping rate. When  $V \ll \gamma$  (i.e., for larger radius) we have  $\delta \sigma \propto \gamma^{-3} v^x / \gamma$ . Therefore, the maximum value is reached when  $V \ll \gamma$  provided  $\gamma$  does not depend on  $\mathscr{P}$ . However, our nonlocal procedure includes the radiative decay which depends on  $\mathcal{R}$ , as seen on Fig. 2. Then,  $\gamma = \gamma_{nr} + \gamma_{rad}(\mathcal{R})$ , and the maximum of  $\delta\sigma$  decreases when  $\gamma_{nr} \leq \gamma_{rad}(\mathscr{R})$ . The model can be improved by incorporating a size dependent nonradiative damping rate  $\gamma_{nr}$ , e.g., due to coupling with phonons or surface impurities<sup>20</sup>). In Fig. 4, we show  $\delta\sigma$  (lower panels) as a function of probe frequency and radius together with the linear spectra (upper panels) for reference. All  $\delta\sigma$  have been normalized to the curve in panel a. The pump frequency is at the maximum of the linear spectrum. This corresponds to higher exciton levels as  $\mathscr{B}$  is increased. As discussed above, it converges towards  $E_p = \epsilon_{ex} + \Delta_{LT}/3$ . We give a global per-



FIG. 5. Variation of the pump-probe spectrum with size. All parameters other than the sizes are identical to Fig. 4. Sizes  $\Re a_0$  vary from 12.5 to 47.5 in increments of 4.

spective of the same calculation in Fig. 5. Figure 6 shows the corresponding maximum of  $\delta\sigma$  as a function of size. The dashed curve was calculated by keeping the pump frequency at the lowest exciton state. The difference between the two curves is due to the redistribution of the oscillator strength among the higher exciton states, as  $\mathcal{R}$  is increased.

Additional important properties of such systems can be treated using the same formalism. For example it would be essential to incorporate the size dependence of the nonradiative decay channels due, e.g., to coupling with con-



FIG. 6. Maximum of the pump-probe signal  $\delta\sigma$  as a function of size. The full curve is calculated with the pump frequency as in Fig. 4. For the dashed curve,  $\omega_P$  is equal to the energy of the lowest exciton state for each size. The nonradiative damping is  $\gamma_{\rm nr} = 10^{-4} E_R$ .

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strongly depend on size.

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# APPENDIX A: DERIVATION OF THE DIPOLE-DIPOLE INTERACTION

In this Appendix, we derive the dipole–dipole approximation for the electron–hole exchange interaction. The original electron–hole exchange part  $\hat{H}_{eh}$  of the Hamiltonian (1)<sup>21</sup>

$$\hat{H}_{eh} = -\int d\mathbf{r} d\mathbf{r}' \Psi_{e}^{+}(\mathbf{r})\Psi_{h}^{+}(\mathbf{r}')V(\mathbf{r}-\mathbf{r}')\Psi_{e}(\mathbf{r}')\Psi_{h}(\mathbf{r}),$$
(A1)

can be rewritten by expanding the operators  $\Psi_\alpha^+$  and  $\Psi_\alpha$  in terms of Wannier functions

$$\Psi_{\alpha}^{+}(\mathbf{r}) = \sum_{l} w_{\alpha}^{*}(\mathbf{r}-\mathbf{l})a_{\mathbf{l}}^{+}, \qquad (A2)$$

where  $a_1^+$  is the creation operator of an electron  $(\alpha = e)$  hole  $(\alpha = h)$  at site **l**, as

$$\hat{H}_{eh} = -\sum_{l_1...l_4} c_{l_1}^+ d_{l_2}^+ d_{l_4} c_{l_3} \int d\mathbf{r} \, d\mathbf{r'} \, w_c^*(\mathbf{r} - \mathbf{l}_1) \\ \times w_v^*(\mathbf{r'} - \mathbf{l}_2) \, \frac{e^2}{|\mathbf{r} - \mathbf{r'}|} \, w_c(\mathbf{r'} - \mathbf{l}_4) w_v(\mathbf{r} - \mathbf{l}_3). \quad (A3)^{-1}$$

Here,  $w_c(\mathbf{r}-\mathbf{l})$  is the conduction-band Wannier function at site l and  $w_v(\mathbf{r}-\mathbf{l}')$  the valence-band Wannier function at site l'. Due to the localization of the Wannier functions only the combinations  $l_1 = l_4$  and  $l_2 = l_3$  survive in Eq. (A3). In the same way, the integrations over  $\mathbf{r}$  and  $\mathbf{r}'$  are restricted to the extension of the Wannier functions near the sites  $l_1$ ;  $l_2$ . We then have

$$\hat{H}_{eh} = -\sum_{l_1, l_2} c_{l_1}^+ d_{l_2}^+ d_{l_1} c_{l_2} \int d\tau \, d\tau' \, w_c^*(\tau) w_v(\tau)$$
$$\times \frac{e^2}{|\mathbf{l}_1 - \mathbf{l}_2 + \tau - \tau'|} \, w_v^*(\tau') w_c(\tau').$$

We now separate the sum over  $l_1, l_2$  into two contributions; a short range interaction with  $l_1 = l_2$ , and a second term with all the other contributions  $l_1 \neq l_2$ ,

$$I_{\rm SR} = \Delta_{\rm SR} \sum_{l_1} c_{l_1}^+ d_{l_1}^+ d_{l_1} c_{l_1},$$

$$I_{LR} = \sum_{l_1 \neq l_2} c_{l_1}^+ d_{l_1} c_{l_2} d_{l_2}^+ \int d\tau \, d\tau' \, w_c^*(\tau) w_v(\tau)$$
$$\times \frac{e^2}{|\mathbf{l}_1 - \mathbf{l}_2 + \tau - \tau'|} \, w_v^*(\tau') w_c(\tau'), \tag{A4}$$

with

$$\Delta_{\rm SR} = \int d\boldsymbol{\tau} \, d\boldsymbol{\tau}' \, w_c^*(\boldsymbol{\tau}) w_v(\boldsymbol{\tau}) \, \frac{e^2}{|\boldsymbol{\tau} - \boldsymbol{\tau}'|} \, w_v^*(\boldsymbol{\tau}') w_c(\boldsymbol{\tau}'). \tag{A5}$$

We expand the integral in Eq. (A4) in multipoles, bearing in mind that  $l_1 \neq l_2$  and that the Wannier functions are strongly localized. The first two terms vanish by charge neutrality and the first nonzero term is

$$\frac{\hat{\mu}_{cv}\cdot\hat{\mu}_{cv}^{*}}{|\mathbf{l}_{1}-\mathbf{l}_{2}|^{3}} - 3 \frac{(\hat{\mu}_{cv}\cdot(\mathbf{l}_{1}-\mathbf{l}_{2}))^{2}}{|\mathbf{l}_{1}-\mathbf{l}_{2}|^{5}}, \quad l_{1} \neq l_{2},$$
(A6)

where

$$\hat{\mu}_{cv} = e \int d\tau \, w_c^*(\tau) \, \tau w_v(\tau). \tag{A7}$$

In the continuous form we then obtain the dipole-dipole interaction Hamiltonian (3).

# APPENDIX B: EQUATIONS OF MOTION FOR $\hat{P}$ AND $\hat{Q}$

We detail, in this Appendix, the equations of motion for the operators  $\hat{P}$  and  $\hat{Q}$ . The Heisenberg equation of motion

$$i\hbar \frac{\partial}{\partial t} \hat{A} = [\hat{A}, \hat{H}],$$
 (B1)

applied to  $\hat{P}_{12}(t)$  with the Hamiltonian (1), gives (we denote  $[\hat{A}, \hat{B}]_{+} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}$ ):

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$$\mathscr{L}_{eh}(\mathbf{r}_{1},\mathbf{r}_{2},t)\hat{P}_{12}(t) = \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\left(\hat{\mu}_{cv}\cdot\mathbf{E}^{\perp}(\mathbf{r}_{1},t) + \int d\mathbf{r}_{3} T(\mathbf{r}_{1}-\mathbf{r}_{3})\hat{P}_{33}(t)\right) - \{[\hat{n}_{e}(\mathbf{r}_{2},\mathbf{r}_{1},t),\mathbf{E}^{\perp}(\mathbf{r}_{2},t)]_{+} \\ + [\hat{n}_{h}(\mathbf{r}_{1},\mathbf{r}_{2},t),\mathbf{E}^{\perp}(\mathbf{r}_{1},t)]_{+}\} - \left\{\hat{n}_{e}(\mathbf{r}_{2},\mathbf{r}_{1},t)\int d\mathbf{r}_{3} T(\mathbf{r}_{2}-\mathbf{r}_{3})\hat{P}_{33}(t) + \hat{n}_{h}(\mathbf{r}_{1},\mathbf{r}_{2},t) \\ \times \int d\mathbf{r}_{3} T(\mathbf{r}_{1}-\mathbf{r}_{3})\hat{P}_{33}(t)\right\} + \sum_{\alpha=e,h} \sigma_{\alpha} \int d\mathbf{r}_{3}[V(\mathbf{r}_{1}-\mathbf{r}_{3})-V(\mathbf{r}_{2}-\mathbf{r}_{3})]\hat{n}_{\alpha}(\mathbf{r}_{3},\mathbf{r}_{3})\hat{P}_{12}(t).$$
(B2)

Here,  $\sigma_e = 1$ ,  $\sigma_h = -1$ , and the operator  $\mathcal{L}_{eh}$  is defined by

$$\mathscr{L}_{\rm eh}(\mathbf{r}_1,\mathbf{r}_2,t) = \left\{ i\hbar \,\frac{\partial}{\partial t} - \frac{\hbar^2}{2m_e} \,\nabla_{\mathbf{r}_1}^2 - \frac{\hbar^2}{2m_h} \,\nabla_{\mathbf{r}_2}^2 - V(\mathbf{r}_1 - \mathbf{r}_2) \right\}. \tag{B3}$$

The two-point density

$$\hat{n}_{\alpha}(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_{\alpha}^+(\mathbf{r}_1, t)\Psi_{\alpha}(\mathbf{r}_2, t), \tag{B4}$$

satisfies the following equation of motion (taking  $\alpha = e$ ):

$$i\hbar \frac{\partial}{\partial t} \hat{n}_{e}(\mathbf{r}_{1},\mathbf{r}_{2},t) = -\frac{\hbar^{2}}{2m_{e}} (\nabla_{\mathbf{r}_{1}}^{2} - \nabla_{\mathbf{r}_{2}}^{2}) \hat{n}_{e}(\mathbf{r}_{1},\mathbf{r}_{2},t) + \hat{\mu}_{cv} \cdot \{ [\hat{P}_{12}(t), \mathbf{E}^{\perp}(\mathbf{r}_{1},t)]_{+} - [\hat{P}_{21}^{+}(t), \mathbf{E}^{\perp}(\mathbf{r}_{2},t)]_{+} \} \\ + \hat{P}_{21}^{+}(t) \int d\mathbf{r}_{3} \ T(\mathbf{r}_{2} - \mathbf{r}_{3}) \hat{P}_{33}(t) - \hat{P}_{12}(t) \int d\mathbf{r}_{3} \ T(\mathbf{r}_{1} - \mathbf{r}_{3}) \hat{P}_{33}^{+}(t) + \sum_{\alpha = e,h} \sigma_{\alpha} \int d\mathbf{r}_{3} [V(\mathbf{r}_{1} - \mathbf{r}_{3}) - V(\mathbf{r}_{2} - \mathbf{r}_{3})] \Psi_{e}^{+}(\mathbf{r}_{1}) \hat{n}_{\alpha}(\mathbf{r}_{3}, \mathbf{r}_{3}, t) \Psi_{e}(\mathbf{r}_{2}).$$
(B5)

The operator equation (B2) needs to be linearized in order to derive a closed equation for the expectation values of the relevant operators,  $\hat{P}$  and  $\hat{n}_{\alpha}\hat{P}$ .

If the density of excited particles is sufficiently high, one has to keep these two equations and find a proper factorization procedure for the expectation value of  $\hat{n}_{\alpha}\hat{P}$ , as is done for example in the time-dependent Hartree–Fock procedure.<sup>22</sup> Since we are interested only in nonlinearities up to third order, and the system is subject to transitions from zero-exciton states to oneand two-exciton states, we shall introduce a new operator representing two-exciton quasiparticles

$$\hat{Q}_{1234}(t) = \hat{P}_{12}(t)\hat{P}_{34}(t), \tag{B6}$$

which appears in Eq. (B2) in the term that contains  $\hat{n}_{\alpha}$ . We could as well use the equation of motion for the operator  $\hat{n}_{\alpha}$ , however, for the present case of strongly bound states, it is advantageous to work with this variable instead of the density of electrons and holes.<sup>23</sup>

In order to calculate the third-order nonlinearities, we need consider only the space spanned by the zero, one and two exciton states. The time-dependent wave function can then be expanded as

$$|\psi(t)\rangle = |0\rangle + \int d\mathbf{r}_{1} d\mathbf{r}_{2} \ \psi_{\text{exc}}(\mathbf{r}_{1}, \mathbf{r}_{2}, t) \Psi_{e}^{+}(\mathbf{r}_{1}) \Psi_{h}^{+}(\mathbf{r}_{2}) |0\rangle$$
  
+ 
$$\int d\mathbf{r}_{1} d\mathbf{r}_{2} d\mathbf{r}_{3} d\mathbf{r}_{4} \ \psi_{2 \text{ exc}}(\mathbf{r}_{1}, \mathbf{r}_{2}, \mathbf{r}_{3}, \mathbf{r}_{4}, t) \Psi_{e}(\mathbf{r}_{1})^{+} \Psi_{h}^{+}(\mathbf{r}_{2}) \Psi_{e}(\mathbf{r}_{3})^{+} \Psi_{h}^{+}(\mathbf{r}_{4}) |0\rangle + \cdots$$
$$= |\psi_{0}(t)\rangle + |\psi_{1}(t)\rangle + |\psi_{2}(t)\rangle + \cdots$$
(B7)

When calculating the expectation value of  $\hat{n}_{\alpha}P_{\rm eh}$  using this state, only states up to  $|\psi_2(t)\rangle$  contribute at third order. Furthermore, since the Hamiltonian does not allow the separate creation of electrons or holes [i.e., the density of electrons (or holes) is equal to the exciton density], we can use the identity

$$\hat{n}_{e}(\mathbf{r}_{3},\mathbf{r}_{3})\hat{P}_{12}(t) = \int d\mathbf{r}_{4} \, \hat{P}_{34}^{+}(t)\hat{Q}_{3412}(t), \tag{B8}$$

which allows us to consider the operator  $\hat{Q}$  instead of  $\hat{n}_{\alpha}$ . The advantage of working with  $\hat{Q}$  instead of  $\hat{n}$  is that it enables us to point out the transitions from one- to two-exciton states. Hereafter we introduce the abbreviated notation

$$V_{12} \equiv V(\mathbf{r}_1 - \mathbf{r}_2), \quad D_{12} \equiv T(\mathbf{r}_1 - \mathbf{r}_2).$$

The equation of motion for  $\hat{Q}$  is

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$$\mathscr{L}_{2}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},\mathbf{r}_{4},t)\hat{Q}_{1234}(t) = \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\hat{\mu}_{cv}\cdot\hat{E}^{\perp}(\mathbf{r}_{1},t)\hat{P}_{34} + \delta(\mathbf{r}_{3}-\mathbf{r}_{4})\hat{\mu}_{cv}\cdot\hat{P}_{12}E^{\perp}_{\mathbf{r}_{3},t} + \delta(\mathbf{r}_{1}-\mathbf{r}_{2})\int d\mathbf{r}_{5} D_{15}\hat{Q}_{5534} + \delta(\mathbf{r}_{3}-\mathbf{r}_{4})\int d\mathbf{r}_{5} D_{35}\hat{Q}_{1255} + \delta(\mathbf{r}_{1}-\mathbf{r}_{4})\int d\mathbf{r}_{5} D_{15}\hat{Q}_{3255} + \delta(\mathbf{r}_{2}-\mathbf{r}_{3})\int d\mathbf{r}_{5} D_{25}\hat{Q}_{1455} - \sum_{\alpha} \sigma_{\alpha}\int d\mathbf{r}_{5}(V_{15}-V_{25}+V_{35}-V_{45})\hat{n}_{\alpha}(\mathbf{r}_{5},\mathbf{r}_{5})\hat{Q}_{1234} - \int d\mathbf{r}_{5}[\hat{n}_{e}(\mathbf{r}_{2},\mathbf{r}_{1})D_{25} + \hat{n}_{h}(\mathbf{r}_{1},\mathbf{r}_{2})D_{15}]\hat{Q}_{5534} - \int d\mathbf{r}_{5}[\hat{n}_{e}(\mathbf{r}_{4},\mathbf{r}_{3})D_{45} + \hat{n}_{h}(\mathbf{r}_{3},\mathbf{r}_{4})D_{35}]\hat{Q}_{1255} - \frac{1}{2}\hat{\mu}_{cv} \cdot([\hat{n}_{e}(\mathbf{r}_{2},\mathbf{r}_{1}),\hat{E}^{\perp}_{\mathbf{r}_{2}}] + \hat{P}_{34} + [\hat{n}_{h}(\mathbf{r}_{1},\mathbf{r}_{2}),\hat{E}^{\perp}_{\mathbf{r}_{1}}] + \hat{P}_{12} - \frac{1}{2}\hat{\mu}_{cv} \cdot([\hat{n}_{e}(\mathbf{r}_{4},\mathbf{r}_{3}),\hat{E}^{\perp}_{\mathbf{r}_{4}}] + \hat{P}_{12} + [\hat{n}_{h}(\mathbf{r}_{3},\mathbf{r}_{4}),\hat{E}^{\perp}_{\mathbf{r}_{3}}] + \hat{P}_{12},$$
(B9)

where we have defined

$$\mathscr{L}_{2}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},\mathbf{r}_{4},t) = i\hbar \frac{\partial}{\partial t} + \frac{\hbar^{2}}{2m_{e}} \nabla_{\mathbf{r}_{1}}^{2} + \frac{\hbar^{2}}{2m_{h}} \nabla_{\mathbf{r}_{2}}^{2} + V(\mathbf{r}_{1}-\mathbf{r}_{2}) + \frac{\hbar^{2}}{2m_{e}} \nabla_{\mathbf{r}_{3}}^{2} + \frac{\hbar^{2}}{2m_{h}} \nabla_{\mathbf{r}_{4}}^{2} + V(\mathbf{r}_{3}-\mathbf{r}_{4}) - V(\mathbf{r}_{1}-\mathbf{r}_{3}) - V(\mathbf{r}_{2}-\mathbf{r}_{4}) + V(\mathbf{r}_{1}-\mathbf{r}_{4}) + V(\mathbf{r}_{2}-\mathbf{r}_{3}).$$
(B10)

Equations (B2), (B8), and (B9) form the basis for the following calculations.

Since our Hamiltonian does not contain relaxation (in particular pure dephasing), we can write<sup>18</sup>

$$\langle \hat{P}^+ \hat{Q} \rangle \equiv \langle \hat{P}^+ \rangle \langle \hat{Q} \rangle, \tag{B11}$$

and get a closed equation for the third-order component  $P_{12}(t)$  and second order  $Q_{1234} = \langle \hat{Q}_{1234} \rangle$ . Note that the exchange among the same particles (fermions) is correctly included in the equation of motion for  $\hat{Q}$ . The above equations are valid for an arbitrary size and geometry. Our Hamiltonian uses the effective mass approximation which assumes that the system size is much larger than the lattice constant.<sup>13</sup>

Since it is straightforward to calculate the one-exciton Green function in the weak confinement limit, we shall express the two-exciton Green function in terms of this Green function. We first write  $G_{2 exc}$  in the form

$$G^{(2)} = G_0^{(2)} + G_0^{(2)} V G^{(2)}.$$
(B12)

When the ground state is the vacuum of excitons, the solution of Eq. (B12) gives the true two-exciton states, and only ladder diagrams contribute to the expansion. The operator V contains the Coulomb as well as the dipole-dipole interaction. For the continuous part of the spectrum (weakly interacting excitons and no bound excitons) we search for an approximate function for the zero-order Green function. We assume the following form:

$$G_0^{(2)} = \mathscr{A}G^{(1)}G^{(1)}$$
(B13)

where  $G^{(1)}$  is the solution of Eq. (16), and  $\mathcal{A}$  assures the proper antisymmetrization between fermions of the same species. Note that  $G^{(1)}$  contains the radiative corrections in the one-exciton level.

Using these definitions and Eq. (32), we finally obtain

$$P^{(3)}(\mathbf{R},\omega) = \int d\omega_1 \ d\omega_2 \ d\omega_3 \ \delta(\omega - \omega_1 - \omega_2 - \omega_3) \mathscr{K}^{(3)}(\mathbf{R},\omega_1,\omega_2,\omega_3), \tag{B14}$$

where

(2)

$$\mathcal{K}^{(3)}(\mathbf{R},\omega_{1},\omega_{2},\omega_{3}) = g^{x} \int d\mathbf{R}_{1} d\mathbf{R}_{2} d\mathbf{R}_{3} G^{(1)}(\mathbf{R},\mathbf{R}_{1},\omega) G^{(1)}(\mathbf{R}_{1},\mathbf{R}_{2},-\omega_{2})^{*} G^{(1)}(\mathbf{R}_{1},\mathbf{R}_{3},\omega_{3}) \hat{\mu}_{cv} \mathbf{E}_{0}(\mathbf{R}_{1},\omega_{1}) \hat{\mu}_{cv} \\ \cdot \mathbf{E}_{0}(\mathbf{R}_{2},\omega_{2}) \hat{\mu}_{cv} \cdot \mathbf{E}_{0}(\mathbf{R}_{3},\omega_{3}) \\ + v^{x} \int d\mathbf{R}_{1} \cdots d\mathbf{R}_{5} G^{(1)}(\mathbf{R},\mathbf{R}_{1},\omega) G^{(1)}(\mathbf{R}_{1},\mathbf{R}_{3},-\omega_{3})^{*} \Gamma(\mathbf{R}_{1};\mathbf{R}_{2},\omega_{1}+\omega_{2}) \\ \times G^{(1)}(\mathbf{R}_{2},\mathbf{R}_{4},\omega_{1}) G^{(1)}(\mathbf{R}_{2},\mathbf{R}_{5},\omega_{2}) \hat{\mu}_{cv} \cdot \mathbf{E}_{0}(\mathbf{R}_{4},\omega_{1}) \hat{\mu}_{cv} \cdot \mathbf{E}_{0}(\mathbf{R}_{5},\omega_{2}) \hat{\mu}_{cv} \cdot \mathbf{E}_{0}(\mathbf{R}_{3},\omega_{3}).$$
(B15)

The self-energy  $\Gamma$  has the following expansion:

$$\Gamma(\mathbf{R};\mathbf{R}',\omega) \equiv \delta(\mathbf{R}-\mathbf{R}') + v^{x} G_{0}^{(2)}(\mathbf{R};\mathbf{R}',\omega) + v^{x2} \int [d\mathbf{R}_{1} G_{0}^{(2)}(\mathbf{R};\mathbf{R}_{1},\omega) G_{0}^{(2)}(\mathbf{R}_{1};\mathbf{R}',\omega) + \dots,$$
(B16)

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and

$$G_0^{(2)}(\mathbf{R};\mathbf{R}',\omega) = \frac{1}{2i\pi} \int d\omega' \ G^{(1)}(\mathbf{R},\mathbf{R}',\omega')$$
$$\times G^{(1)}(\mathbf{R},\mathbf{R}',\omega-\omega'). \tag{B17}$$

Recasting this in the eigenfunction basis, we obtain Eq. (42).

# APPENDIX C: POINT INTERACTION APPROXIMATION FOR THE COULOMB AND DIPOLE-DIPOLE TERMS

The direct and exchange interaction matrix elements can be written as

$$V_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}}^{x} = -e^{2} \int d\mathbf{r}_{e} d\mathbf{r}_{e'} d\mathbf{r}_{h} d\mathbf{r}_{h'} \psi_{\nu_{1}}^{*}(\mathbf{R}_{eh})\psi_{\nu_{2}}^{*}(\mathbf{R}_{e'h'}) \\ \times \psi_{\nu_{3}}(\mathbf{R}_{eh'})\psi_{\nu_{4}}(\mathbf{R}_{e'h})\varphi_{1s}(\mathbf{r}_{eh})\varphi_{1s}(\mathbf{r}_{e'h'})\varphi_{1s} \\ \times (\mathbf{r}_{eh'})\varphi_{1s}(\mathbf{r}_{e'h}) \bigg\{ \frac{1}{r_{ee'}} + \frac{1}{r_{hh'}} - \frac{1}{r_{eh'}} - \frac{1}{r_{e'h}} \bigg\},$$
(C1)

$$V_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}}^{d} = e^{2} \int d\mathbf{r}_{e} d\mathbf{r}_{e'} d\mathbf{r}_{h} d\mathbf{r}_{h'} |\psi_{\nu_{1}}(\mathbf{R}_{eh})|^{2} \\ \times |\psi_{\nu_{2}}(\mathbf{R}_{e'h'})|^{2} \varphi_{1s}(\mathbf{r}_{eh})^{2} \varphi_{1s}(\mathbf{r}_{e'h'})^{2} \\ \times \left\{ \frac{1}{r_{ee'}} + \frac{1}{r_{hh'}} - \frac{1}{r_{eh'}} - \frac{1}{r_{e'h}} \right\},$$
(C2)

where  $\mathbf{R}_{ij} = (m_e \mathbf{r}_i + m_h \mathbf{r}_j)/(m_e + m_h)$ ;  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ . It can be shown<sup>14</sup> that the exchange part of the Coulomb interaction is much larger than the direct contribution. In fact the direct part vanishes identically in the bulk and we shall ignore it. The exchange term vanishes unless the exciton CM's are at the same site (overlap of the functions  $\varphi$ ).  $V^x$  can then be factorized into two independent integrals

$$V_{\nu_{1}\nu_{2},\nu_{3}\nu_{4}}^{\mathbf{x}} = -e^{2} \int d\mathbf{R} \ \psi_{\nu_{1}}^{*}(\mathbf{R}) \psi_{\nu_{2}}^{*}(\mathbf{R}) \psi_{\nu_{3}}(\mathbf{R}) \psi_{\nu_{4}}(\mathbf{R})$$

$$\times \int d\mathbf{x}_{1} \ d\mathbf{x}_{2} \ d\mathbf{x}_{3} \ f(\mathbf{x}_{1},\mathbf{x}_{2},\mathbf{x}_{3}),$$

$$= E_{R} \ \frac{26 \pi a_{0}^{3}}{3} \int d\mathbf{R} \ \psi_{\nu_{1}}^{*}(\mathbf{R}) \psi_{\nu_{2}}^{*}(\mathbf{R}) \psi_{\nu_{3}}(\mathbf{R}) \psi_{\nu_{4}}(\mathbf{R}).$$
(C3)

Finally, the Coulomb exchange interaction between two excitons will be written as

$$V(\mathbf{R}_1\mathbf{R}_2;\mathbf{R}_3\mathbf{R}_4) = v^x \delta_{\mathbf{R}_1\mathbf{R}_2\mathbf{R}_3\mathbf{R}_4},\tag{C4}$$

with  $\mathbf{R}_i$  representing the exciton center of mass.  $v^x$  is explicitly given by  $a_0^3 26 \pi/3 E_R$ . Proceeding along the same way, we can approximate the Pauli exclusion contribution as in Eq. (40) [or Eq. (B15)] and obtain  $g^x = -7 \sqrt{\pi/2} a_0^{3/2}$ . We have thus reduced the many coordinate interaction to a point interaction among the CM. The evaluation of the exchange correction to the dipole-dipole interaction in terms of center of mass alone leaves a nonlocal operator as can be seen from Eq. (B9). We shall however neglect this term since it is proportional to

$$\frac{\mu_{cv}^2}{a_0^3} \frac{g}{(\mathscr{B}/a_0)^3} \propto \Delta_{LT} \frac{g}{(\mathscr{B}/a_0)^3},$$
 (C5)

where g is a numerical dimensionless parameter, and  $\Delta_{LT}$  the longitudinal-transverse splitting in the bulk. In most semiconductors the ratio  $E_R/\Delta_{LT}$  is very large (almost 40 in CuCl), which justifies this approximation.

# APPENDIX D: THE DIPOLE-DIPOLE INTERACTION AND RADIATIVE CORRECTIONS FOR A SPHERE

In this Appendix we derive the nonlocal exciton eigenvalue equation for a sphere in the weak confinement limit, and show how quantized polariton modes are obtained. The link with bulk polaritons is established.

The equation of motion for the exciton center of mass, including dipole-dipole interactions as well as radiative corrections, can be written as

$$\left(\epsilon_{\nu} - \epsilon_{\rm ex} + \frac{\hbar^2}{2M} \nabla_{\rm R}^2\right) \psi_{\nu}({\bf R}) - \int d{\bf R}' \ \Sigma({\bf R}, {\bf R}'; \epsilon_{\nu}/\hbar) \psi_{\nu}({\bf R}') = 0, \qquad (D1)$$

with the self-energy

$$\Sigma(\mathbf{R},\mathbf{R}';z) = \hat{d}_{cv} \cdot \mathscr{G}(\mathbf{R}-\mathbf{R}';z/c)\hat{d}_{cv}.$$
 (D2)

The eigenvalues of this equation  $\epsilon_{\nu}$  give the excitonpolariton quantized energies. For a finite system, they contain a Lamb shift and an imaginary correction related to finite sample size. Let us first discuss an infinite system. Equation (D1) can be solved directly by looking for plane wave solutions

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}.\tag{D3}$$

The solution is straightforward and immediately leads to the polariton dispersion

$$(q^{2}-k^{2})\left(\hbar\omega - \epsilon_{\rm ex} - \frac{\hbar^{2}}{2M}k^{2}\right) = 4\pi (d_{cv}^{2}q^{2} - d_{cv}d_{cv}k_{i}k_{j}),$$
(D4)

where i, j are the Cartesian coordinates. It is well known that polaritons in an infinite homogenous system are stable (no imaginary part of the eigenvalues<sup>3,24</sup>).

In the case of a finite sphere, we can choose the  $\hat{z}$  axis along the dipole moment and express the product  $\hat{z}\psi(\mathbf{R})$  on a vectorial basis of the form

$$\hat{z}\psi(\mathbf{R}) = \sum_{klm\epsilon} c_{klm\epsilon} \rho_{klm\epsilon}(\mathbf{R}),$$

$$\rho_{klm\epsilon}(\mathbf{R}) = j_{l+\epsilon}(kR) \mathbf{Y}_{l,l+\epsilon}^{m}(\hat{R})$$
(D5)

 $j_l$  are the spherical Bessel functions and  $\mathbf{Y}_{l,l+\epsilon}^m$  the vector spherical harmonics.<sup>25</sup> k is the eigenvalue to be determined.

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The quantum numbers  $lm\epsilon$  are given by  $l \ge 1, -l \le m \le l$  and  $\epsilon = 0, \pm 1$ . The angular functions  $\mathbf{Y}_{l,l+\epsilon}^m(\hat{r})$  constitute the basis of the subgroups of the operator  $\mathbf{I} \otimes \mathbf{1}$ , where  $\mathbf{I}$  is the angular momentum operator. It is important to note that due to the dipole-dipole interaction, l is no longer a good quantum number. This is of paramount importance for the scaling dependence with size. Substituting expression (D5) in Eq. (D1), we obtain a set of equations for the unknown quantities  $c_{klm\epsilon}$ , which is equivalent to the scalar eigenvalue equation (D1) ( $\lambda = klm\epsilon$ )

$$\sum_{\lambda} c_{\lambda} \left[ \left( \hbar \omega - \epsilon_{ex} + \frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \right) \delta_{\mathbf{R}\mathbf{R}'} - \int d\mathbf{r}' \ \Sigma(\mathbf{R}, \mathbf{R}'; \omega) \right] \boldsymbol{\rho}_{\lambda}(\mathbf{R}') = 0.$$
 (D6)

This system is diagonal in l,m. Furthermore, the subgroups  $\epsilon=0$  and  $\epsilon=\pm 1$  are not connected. The states lm0 are transverse in the sense that  $\nabla \cdot \hat{d}_{cv} \psi(\mathbf{r})=0$ . The subspaces lm,  $\epsilon=\pm 1$  contain both transverse and longitudinal components.

This equation allows us to establish the link with the infinite size limit, since the boundary conditions occur only at the end of the calculation, when one determines the eigenvalues. Introducing the functions (D5) in Eq. (D6), we find that the expansion holds provided one of the following conditions is met:

$$\frac{k^2}{q^2} = 1 + \frac{\Delta_{\rm LT}}{\hbar\omega - \epsilon_{\rm ex} - \frac{\hbar^2}{2M} k^2}$$
(D7)

$$k^2 = (\hbar \omega - \Delta_{\rm LT}) 2M/\hbar^2.$$
 (D8)

These two equalities define the polariton solutions for each  $\omega$ . There exist then only three possible k values,  $k_1$  and  $k_2$  for the first, and  $k_3$  for the second equation. We further have the following conditions:

$$c_{k_{1,2}lm,-1} = -\sqrt{\frac{l+1}{l}} c_{k_{1,2}lm,1},$$
$$c_{k_3,lm,-1} = \sqrt{\frac{l}{l+1}} c_{k_3,lm,1},$$

which show the transverse (solutions  $k_{1,2}$ ) or longitudinal (solution  $k_3$ ) character of the solutions since they assure  $\nabla \cdot \hat{d}_{cv} \psi(\mathbf{r}) = 0$  or  $\nabla \wedge \hat{d}_{cv} \psi(\mathbf{r}) = \mathbf{0}$ . The final system determining the coefficients (together with the boundary conditions) for the states  $\{lm, \epsilon = \pm 1\}$  is

$$\begin{pmatrix} j_{l+1}(k_{1}\mathscr{B}) & j_{l+1}(k_{2}\mathscr{B}) & \frac{j_{l+1}(k_{3}\mathscr{B})}{d_{cv}^{2}} \\ j_{l-1}(k_{1}\mathscr{B}) & j_{l-1}(k_{2}\mathscr{B}) & -\frac{l}{l+1}\frac{j_{l-1}(k_{3}\mathscr{B})}{d_{cv}^{2}} \\ \frac{I_{l+1}(q,k_{1}) + \frac{l+1}{l}I_{l+1}(q,k_{1})}{k_{1}^{2} - q^{2}} & \frac{I_{l+1}(q,k_{2}) + \frac{l+1}{l}I_{l+1}(q,k_{2})}{k_{2}^{2} - q^{2}} & \frac{I_{l+1}(q,k_{3}) - I_{l+1}(q,k_{3})}{k_{3}^{2} - q^{2}} \end{pmatrix} \begin{pmatrix} c_{k_{1}} \\ c_{k_{2}} \\ c_{k_{3}} \end{pmatrix} = 0, \quad (D9)$$

where

$$I_{l}(q,k) = [qh_{l+1}^{(1)}(k\mathcal{R})j_{l}(q\mathcal{R}) - kj_{l+1}(k\mathcal{R})h_{l}^{(1)}(q\mathcal{R})].$$
(D10)

The eigenvalues  $\omega_{nlm\epsilon}$  of the coupled exciton+field system are then obtained when the determinant of Eq. (D9) vanishes. For each quantum number  $|lm\rangle$  there exists an infinite series of discrete complex values  $k_{nlm}$  as discussed in Ref. 16.

The link to an infinite system is easily established if we note that the integrations in Eq. (D6) give automatically a diagonal matrix in k, and we recover the same dispersion relation [Eqs. (D7), (D8) as in Eq. (D4)]. The only difference between the two is the basis chosen to expand the fields (Cartesian+plane waves in the former case and vector-spherical functions in the latter).

# APPENDIX E: EIGENFUNCTION EXPANSION OF THE EXCITON EQUATION FOR A SPHERE

Following Appendix D, we introduce here an alternate treatment of Eq. (D1) which was used in the calculations of Sec. V. Indeed, the form of the solutions obtained above is

not convenient for computing the Green function since the expressions in Appendix D depend on complex arguments. Therefore, we shall expand all the wave functions in a complete set of eigenfunctions.

We first expand Eq. (D6) in the basis set of the operator  $\nabla^2$ 

$$\psi_{nlm_l}(\mathbf{r}) = \chi_{nl}(r) Y_{lm_l}(\hat{r}),$$

$$\chi_{nl}(r) = \sqrt{\frac{2}{\mathcal{B}^3}} \frac{j_l(\kappa_{nl}x)}{j_{l+1}(\kappa_{nl})}, \quad x = r/\mathcal{R},$$
(E1)

where the quantum numbers are  $l \ge 0$ ,  $-l \le m_l \le l$  and n=1,2,.... The boundary conditions

$$\psi_{nlm_l}(\mathbf{r})|_{|\mathbf{r}|=\mathscr{R}}=0,\tag{E2}$$

determines the parameter  $\kappa_{nl}$  via the equation

$$i_l(\kappa_{nl}) = 0, \tag{E3}$$

and the one-exciton energies (without dipole-dipole interaction) are

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$$\epsilon_{nl}^{0} = \epsilon_{\text{ex}} + \frac{m_{e}m_{h}}{\left(m_{e} + m_{h}\right)^{2}} \frac{\kappa_{nl}^{2}}{\left(\mathcal{R}/a_{0}\right)^{2}}.$$
(E4)

Using this basis set and the transformation discussed in Appendix D  $(l=l+\epsilon)$ , we can recast the eigenvalue equation (D1) as an infinite system  $(\lambda\lambda'=nlm\epsilon)$ 

$$\hbar \omega - E_{\lambda} - \sum_{\lambda'} A_{\lambda\lambda'}(\mathcal{R}, \omega) = 0, \qquad (E5)$$

where

$$A_{\lambda\lambda'}(\mathscr{R},\omega) = d_{cv}^2 \int d\mathbf{r} \boldsymbol{\rho}_{\lambda}^*(\mathbf{r}) \cdot \int d\mathbf{r}' \ \mathscr{G}(\mathbf{r},\mathbf{r}';\omega) \boldsymbol{\rho}_{\lambda'}(\mathbf{r}'),$$
(E6)

$$\begin{split} A_{\lambda\lambda'}(\mathscr{B},\omega) &= i4\pi\tilde{q}d_{cv}^{2} \left[ \frac{2\kappa_{n'l+\epsilon'}\kappa_{nl+\epsilon}\tilde{q}^{2}}{(\kappa_{n'l+\epsilon'}^{2}-\tilde{q}^{2})(\kappa_{nl+\epsilon}^{2}-\tilde{q}^{2})} j_{l+\epsilon}(\tilde{q})h_{l+\epsilon}^{(1)}(\tilde{q}) \frac{\lambda_{\epsilon}^{-}}{2l+1} - i\frac{\delta_{nn'}}{\tilde{q}(\kappa_{nl+\epsilon}^{2}-\tilde{q}^{2})} \left(\tilde{q}^{2}-\kappa_{nl+\epsilon}^{2}\frac{\lambda_{\epsilon}^{+}}{2l+1}\right) \right] \quad \epsilon = \epsilon', \\ &= -i4\pi\tilde{q}d_{cv}^{2} \frac{\sqrt{\lambda_{\epsilon}^{-}\lambda_{\epsilon}^{+}}}{2l+1} \left[ \frac{2\kappa_{n'l+\epsilon'}\kappa_{nl+\epsilon}\tilde{q}^{2}}{(\kappa_{n'l+\epsilon'}^{2}-\tilde{q}^{2})(\kappa_{nl+\epsilon}^{2}-\tilde{q}^{2})} j_{l-\epsilon}(\tilde{q})h_{l+\epsilon}^{(1)}(\tilde{q}) \frac{\lambda_{\epsilon}^{-}}{2l+1} \right. \\ &+ \epsilon i\frac{2\kappa_{n'l+\epsilon'}\kappa_{nl+\epsilon}(2l+1)}{\tilde{q}(\kappa_{nl+\epsilon}^{2}-\tilde{q}^{2})(\kappa_{n'+\epsilon'}^{2}-\kappa_{nl+\epsilon}^{2})} \right] \quad \epsilon = -\epsilon', \\ &= i4\pi\tilde{q}^{3}d_{cv}^{2} \left[ \frac{2\kappa_{n'l}\kappa_{nl}}{(\kappa_{n'l}^{2}-\tilde{q}^{2})(\kappa_{nl}^{2}-\tilde{q}^{2})} j_{l}(\tilde{q})h_{l}^{(1)}(\tilde{q}) - i\frac{\delta_{nn'}}{\tilde{q}(\kappa_{nl}^{2}-\tilde{q}^{2})} \right] \quad \epsilon = \epsilon' = 0, \\ \lambda_{\epsilon}^{\pm} = l + \frac{1\pm\epsilon}{2} \quad \tilde{q} = q\mathscr{B}. \end{split}$$

$$\tag{E7}$$

In the above equations  $l \ge 1$  and  $A_{lml'}m' = \delta_{ll'}\delta_{mm'}$ since the angular functions  $\mathbf{Y}_{l,l+\epsilon}^m(\hat{r})$  are orthonormal. The dipole-dipole interaction-Hamiltonian matrix elements are given by taking the limit  $q \rightarrow 0$  in Eq. (E6)

A dip-dip

$$= \begin{cases} 4\pi d_{cv}^2 \delta_{nn'} \frac{\lambda_{\epsilon}^+}{2l+1} & \epsilon = \epsilon' \\ -4\pi d_{cv}^2 \frac{\sqrt{\lambda_{\epsilon}^- \lambda_{\epsilon}^+}}{2l+1} \frac{2\kappa_{nl+\epsilon}}{\kappa_{n'l+\epsilon'} (\kappa_{n'l+\epsilon'}^2 - \kappa_{nl+\epsilon}^2)} & \epsilon \neq \epsilon' \end{cases}$$

A remarkable feature is that  $A_{dip-dip}$  does not depend on size. It cannot be neglected for symmetry reasons as was suggested in Ref. 26. The only parameter which may justify the neglect of the dipole-dipole interaction is the relative magnitude of  $\epsilon_{nl}^0$  and  $d_{cv}^2$ . For CuCl,  $4\pi d_{cv}^2 \approx 0.025$  and  $\epsilon_{10}(\mathcal{B}=10)\approx 0.015$  (in 3D exciton Rydberg units) which shows the importance of this contribution in large spheres. In our calculations we start with the eigenvectors of this Hamiltonian, and express  $A^{\perp} = A - A_{dip-dip}$  via an unitary transformation. The exciton-exciton interaction matrix elements are also calculated in this basis. The details have been discussed previously in Ref. 14.

In the numerical calculations we use the following formula for the eigenvalues

$$\epsilon_{\nu} = e_{\nu} + \Sigma_{\nu}(e_{\nu}), \tag{E8}$$

where  $e_{\nu}$  are the eigenvalues of  $H = H_0 + H_{eh}$  and the selfenergy operator is

$$\Sigma_{\nu}(z) = \langle \nu | H_q | \nu \rangle + \left\langle \nu \left| H_q \frac{Q}{z - Q \tilde{H} Q - Q H_q Q} H_q \right| \nu \right\rangle.$$
(E9)

Q is the projection operator on the complementary space of  $\{\nu\}$ , and  $H_q$  contains the radiative corrections. Here, we have made the Markov approximation, but this can be relaxed by calculating the exact eigenvalues.

The resulting eigenfunctions and eigenvalues are used in Sec. V to construct the one-exciton Green function (24).

The total cross section (45) can now be calculated from

$$\mathbf{f}(\mathbf{r},\mathbf{q}) = \sum_{l \ge 1,m} \{ a_{lm} \mathbf{Y}_{l,l}^m(\hat{r}) \wedge \hat{r} + c_{lm} \mathbf{Y}_{l,l}^m(\hat{r}) \}, \quad (E10)$$

where the coefficients are defined by

$$\begin{cases} a_{lm} = \sum_{n \ge 1} \left\{ \frac{l}{2l+1} \lambda_{nlm,1} f_{nlm,1} - \frac{l+1}{2l+1} \lambda_{nlm,-1} f_{nlm,-1} \right\} \\ c_{lm} = \sum_{n \ge 1} \lambda_{nlm,0} f_{nlm,0} \end{cases}$$
$$\lambda_{nlm,\epsilon} = iq \sqrt{2\mathscr{R}^3} \sqrt{\frac{(2-|\epsilon|)\left(l+\frac{1-\epsilon}{2}\right)}{2l+1}} \\ \times \begin{cases} \frac{\kappa_{nl+\epsilon}}{(\kappa_{nl+\epsilon}^2 - q\mathscr{R}^2)} j_{l+\epsilon}(q\mathscr{R}) & q\mathscr{R} \neq \kappa_{nl+\epsilon} \\ \frac{1}{2} j_{l+1+\epsilon}(\kappa_{nl+\epsilon}) & q\mathscr{R} = \kappa_{nl+\epsilon}. \end{cases}$$

The f's are the coefficients of the calculated linear +nonlinear polarization expressed in the  $Y_{l,l+\epsilon}^m$  basis.

# APPENDIX F: APPLICATION TO A THICK FILM

In this Appendix we briefly show how the present formalism can be applied to a thick film (i.e., a large quantum

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well). We consider a quantum well whose width L is much larger than the exciton Bohr radius  $(a_0)$ , and let z be the coordinate along the growth direction. In this case, the exciton wave function can be written

$$\psi_{\mathbf{k}_{\parallel},n}(\mathbf{r}) = e^{\imath \mathbf{k}_{\parallel} \cdot \mathbf{R}} f(z) \quad \mathbf{R} = (\mathbf{x}, \mathbf{y}), \tag{F1}$$

with the boundary conditions  $\psi(z=0) = \psi(z=L) = 0$ , and

$$f_{\mathbf{k}_{\parallel}}(z) = \frac{1}{\sqrt{L}} \sum_{n} c_{\mathbf{k}_{\parallel},n} \sin(k_{n}z) \quad k_{n} = n \pi/L$$
 (F2)

The nonlocal operator in two dimensions is  $(q_z = \sqrt{q^2 - k_{\parallel}^2}, q = \omega/c)$ 

$$\mathscr{T}(\mathbf{r},\mathbf{r}';q) = \frac{1}{2iq_z} \left(q^2 + \nabla \nabla \cdot\right) \int \frac{d\mathbf{k}_{\parallel}}{(2\pi)^2} e^{i\mathbf{k}_{\parallel} \cdot \mathbf{R}} e^{iq_z|z-z'|}.$$
(F3)

The equation of motion for the exciton reduces to  $(0 \le z \le 1)$ 

$$\left(\tilde{\omega} + \frac{d^2}{dz^2}\right) e^{i\mathbf{k}_{\parallel} \cdot \mathbf{R}} f_{\mathbf{k}_{\parallel}}(z) = \frac{1}{2i\alpha q_z} \hat{\mu} \cdot (q^2 + \nabla \nabla \cdot) \hat{\mu} e^{i\mathbf{k}_{\parallel} \cdot \mathbf{R}} \\ \times \int_0^L dz' \ e^{iq_z|z-z'|} f_{\mathbf{k}_{\parallel}}(z'), \qquad (F4)$$

where  $\tilde{\omega} = (\hbar \omega - \dot{E}_{exc})/\alpha - k_{\parallel}^2 (\alpha = \hbar^2/2M)$ . By integrating Eq. (F4) on both sides with  $\sin(k_n z)$ , we obtain a linear system for the coefficients  $c_{\mathbf{k}_{\parallel},n}$ . Let us assume, for simplicity, that  $\hat{\mu} \perp \hat{z}$ . From the solutions  $c_{\mathbf{k}_{\parallel},n}$  we can express, by a resummation of the infinite series, the one-exciton Green function in a compact form

$$G_{\text{exc}}^{(1)}(z, z', \omega, \mathbf{k}_{\parallel}) = \frac{1}{(k_1^2 - k_2^2)} \sum_{k_i} \frac{k_i^2 - q_z^2}{k_i \sin k_i} \sin(k_i z_{<})$$

$$\times \sin(k_i (1 - z_{>})) + \sum_{\pm} \frac{h^{\pm}(z) h^{\pm}(z')}{1 - \lambda_{\pm}},$$
(F5)

 $k_i \equiv \mathbf{k}_i(\mathbf{k}_{\parallel}, \omega)$  are the confined exciton polariton wave vectors, given by the solutions of the equation

$$(\tilde{\omega}^2 - k^2)(q_z^2 - k^2) = dq_z^2 \quad \left(d = \frac{\mu_{cv}^2}{\alpha}\right),$$
 (F6)

and

$$\lambda_{\pm} = \sum_{n=2p-(1\pm1)/2, p \ge 1} \frac{\xi_n^2(\mathbf{k}_{\parallel})}{\hbar \,\omega - E_n(\mathbf{k}_{\parallel})},$$
$$h^{\pm}(z) = \sum_{n=2p-(1\pm1)/2} \frac{\xi_n(\mathbf{k}_{\parallel})}{\hbar \,\omega - E_n(\omega, \mathbf{k}_{\parallel})} \sin(k_n z).$$

We have defined the following quantities:

$$E_n = E_{\text{exc}} + \alpha (k_{\parallel}^2 + k_n^2) + \frac{\mu_{cv}^2 q_z^2}{(q_z^2 - k_n^2)},$$
  
$$\xi_n(\mathbf{k}_{\parallel}) = \sqrt{\mu_{cv}^2 q_z (1 \pm e^{iq_z})/i} \frac{k_n}{(q_z^2 - k_n^2)}.$$

Alternatively, we can write  $G_{\text{exc}}^{(1)}$  in the following form:

$$G_{\text{exc}}^{(1)}(z,z',\omega,\mathbf{k}_{\parallel}) = \sum_{nn'} \sin(k_n z) H_{nn'}^{-1}(\omega,\mathbf{k}_{\parallel}) \sin(k_{n'} z'),$$
(F7)

which is more suitable for numerical evaluations. The principal contribution comes from the diagonal elements of the Green function. Near a particular pole  $E_n$ , we can write

$$G_{\text{exc}}^{(1)}(z, z', \omega, \mathbf{k}_{\parallel}) \simeq \sum_{n=2p-(1\pm1)/2} \sin(k_n z) \times \frac{1}{\hbar \omega - E_n(\omega, \mathbf{k}_{\parallel}) - \Sigma_n(\omega, \mathbf{k}_{\parallel})} \sin(k_n z'),$$
(F8)

where  $\Sigma_n$  is given by

$$\Sigma_{n}(\omega, \mathbf{k}_{\parallel}) = \frac{\xi_{n}^{2}(\mathbf{k}_{\parallel})}{1 - \Sigma_{n \neq n'}} \frac{\xi_{n'}^{2}(\mathbf{k}_{\parallel})}{\omega - E_{n'}(\mathbf{k}_{\parallel})}.$$
 (F9)

This expression for the diagonal element is exact. At this point we make the following approximations: We only keep the diagonal part and neglect the energy dependence of  $E_n$  and  $\Sigma_n$ . Equation (F8) contains the exact poles of the system, determined by the equation

$$1 = \sum_{n} \frac{\xi_{n}^{2}(\mathbf{k}_{\parallel})}{\hbar \omega - E_{n}(\mathbf{k}_{\parallel})}.$$
 (F10)

Our approximation is certainly justified as long as we are close to the one-exciton resonance.

The approximate expression for the scattering matrix is then

$$\Gamma_{NN'}(\boldsymbol{\omega}, \mathbf{k}_{\parallel}) \simeq \frac{V}{1 - VG_0^{(2)}(\boldsymbol{\omega}, \mathbf{k}_{\parallel})} \bigg|_{NN'} \qquad N, N' = \{n, n'\},$$
(F11)

where

$$(VG_0^{(2)}(\omega, \mathbf{k}_{\parallel}))_{n_1 n_2; n_3 n_4}$$
  
=  $V_{n_1 n_2; n_3 n_4} \int d\mathbf{k}' \times \frac{1}{\omega - \tilde{E}_{n_3}(\mathbf{k}') - \tilde{E}_{n_4}(\mathbf{k}_{\parallel} - \mathbf{k}')},$ 

 $V_{n_1n_2;n_3n_4}$ 

$$= v^{x}/L \int_0^L dz \, \sin(k_{n_1}z) \sin(k_{n_2}z) \sin(k_{n_3}z) \sin(k_{n_4}z)$$

and

$$\tilde{E}_{n}(\mathbf{k}_{\parallel}) \simeq E_{n}(\mathbf{k}_{\parallel}) + \sum_{n} (E_{n}(\mathbf{k}_{\parallel}), \mathbf{k}_{\parallel}), \qquad (F12)$$

where, as above  $\Sigma_n$  contains the radiative corrections. With these definitions, Eq. (32) may be used to calculate the non-linear response.

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