Third-order nonlinear susceptibility of large semiconductor microcrystallites

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We show that the theory of the third-order nonlinear susceptibility of semiconductor microcrystallites with a radius much greater than the exciton radius ("weak confinement") has big intrinsic uncertainties due to the unknown volume dependence of the phenomenological relaxation times. These dependencies are actually sources of another type of optical nonlinearity. The third-order susceptibility increases strongly with the increasing radius of the microcrystallite in the range between 10 and 100 exciton Bohr radii and approaches a well-defined infinite radius limit.

I. INTRODUCTION

The optical properties of small semiconductor crystallites were the subject of extended experimental and theoretical investigations during the last decade. In their pioneering theoretical work, Efros and Efros[1] have distinguished several confinement regimes. Of outermost interest are, of course, the very small quantum dots, whose radius is less than a_B—the Bohr radius of the exciton in the bulk (strong confinement). The theoretical treatments exploit here the smallness of the parameter R/a_B. Another extreme case is that of large dots, for which the inverse parameter $\lambda \equiv a_{B_0}/R$ is the small entity (weak confinement). Unfortunately, no systematic expansion is possible here, the parameter λ playing effectively the role of Planck's constant in the Schrödinger equation. Nevertheless, there is an increased experimental[2–6] and theoretical[7–14] interest toward the nonlinear optics of such big quantum dots. The theoretical interest was partly motivated by the apparent increase as $\lambda^{-3/2}$ of the polarization matrix element between vacuum and the exciton state predicted within the weak confinement model.[7] Although recent theoretical studies of Frenkel excitons on linear chains[10,11] predict an enhancement only in a restricted range of radii, the subject is still worthy of a detailed discussion.

We would like to base our discussion on a consequent formulation of the theory of the third-order susceptibility, in which the decay parameters (phenomenological width) are introduced from the beginning in a consistent manner. The formal theory is developed in Sec. II and applied to the weak confinement model of the excitons in a quantum dot in Sec. III. A related discussion of the asymptotic volume dependence of the third-order susceptibility and of the radiative decay is given in Sec. IV. The last section contains several numerical examples of calculated third-order susceptibilities to illustrate the frequency dependence, dependence on the radius, and the instability against very small variations of the width parameters.

II. FORMAL THEORY OF NONLINEAR SUSCEPTIBILITY

The knowledge of the low-lying eigenvalues and wave functions of a quantum-mechanical system with a discrete spectrum (such as electrons and holes in a microcrystal) allows, in principle, the calculation of the lowest optical nonlinearities at low temperatures. In what follows we describe here the formal theory of the third-order nonlinear susceptibility χ_3.

Let us admit that the system, described by the Hamiltonian H, is exposed to the interaction with a classical optical electric field in the dipole approximation according to the electromagnetic (em), time-dependent, interaction Hamiltonian

$$H_{\rm em}(t) = -PE(t) , \tag{2.1}$$

where P is the projection of the interband dipole operator onto the polarization direction of the em field E.

We are, generally speaking, interested in calculating the quantum statistical average of the polarization supposed to coincide with the dipole operator P, but P has no diagonal matrix elements between the eigenstates of H (for example, in a semiconductor quantum dot it changes the number of electron-hole pairs with one, while H commutes with the number of electron-hole pairs) and therefore in thermal equilibrium its average vanishes. A nonvanishing average value of P can only be induced by the electromagnetic field $E(t)$. Then, admitting that the field is introduced at the time $t = t_0$, one has the development in the powers of the applied field

$$\frac{1}{\Omega}\langle P(t)\rangle = \int_{t_0}^{t} dt_1 \chi_1(t,t_1)E(t_1) + \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \chi_3(t,t_1,t_2,t_3)E(t_1)E(t_2)E(t_3) + \cdots . \tag{2.2}$$

[Even power terms are excluded, because P has the same space-reflection property as the field E, but also explicitly because any power of the field in this expansion is associated through the explicit form of the perturbation according to Eq. (2.1) with the same power of the P operator, and only averages of even powers of the P operator are nonvanishing.] The volume of the system Ω was introduced for a correct definition of the susceptibilities.

The time-dependent susceptibilities χ_1 and χ_3 may be computed using perturbation theory in the Liouville equation for the density matrix

$$i\hbar\frac{\partial}{\partial t}\rho=[H+H_{\rm em}(t),\rho]-iK\{\rho\} \tag{2.3}$$

with the initial equilibrium condition

$$\rho(t_0)=\rho_0(H) \ . \tag{2.4}$$

The "superoperator" K, acting directly on the matrix elements of the density matrix, represents all the dissipative, irreversible processes which ensure the existence of asymptotically stationary solutions (after an infinite time) for harmonically oscillating fields.

A simple phenomenological "superoperator" satisfying the requirements of (i) conserving the hermiticity, trace, and positivity of the density matrix as well as (ii) bringing the system back to equilibrium in the absence of the perturbation, is given by[15]

$$K\{\rho\}=\tfrac{1}{2}\{\Gamma,\rho\}-\frac{1}{2\,\mathrm{Tr}(\Gamma\rho_0)}\{\Gamma,\rho_0\}\,\mathrm{Tr}(\Gamma\rho) \ , \tag{2.5}$$

where $\{,\}$ is the anticommutator and Γ is a positive (Hermitian) operator. This is the generalization of the simple relaxation term

$$\frac{\hbar}{\tau}(\rho-\rho_0)$$

which can be obtained if Γ is taken to be just the constant $\hbar/\tau$. Therefore $(1/\hbar)\Gamma$ is just to be interpreted as the inverse relaxation time operator. In what follows we shall restrict ourselves to operators Γ that commute with the Hamiltonian H.

We shall stress here an important property,[16] namely, that although formally one can develop a susceptibility theory by a straightforward application of the time-dependent adiabatic perturbation theory, introducing an adiabatic factor $e^{t/\tau}$ in the field, the result coincides with the introduction of a relaxation time τ in the Liouville equation only for the linear susceptibility, but for the third-order susceptibility it gives wrong coefficients for the different terms and for the damping parts of the denominators. Beyond linear response adiabatic introduction of a perturbation and relaxation are physically and mathematically completely unequivalent. This implies that in the nonlinear theory one must be very careful and cannot introduce arbitrary dampings in an adiabatically obtained formula. The damping mechanism described by dissipative superoperators assures that all the important general physical properties of the original quantum-mechanical system are still conserved.

For the irreversible behavior of a quantum-mechanical system coupled to a "thermal bath," one may derive under certain conditions more general superoperators (see, for example, Ref. 17) expressed in terms of the bath-induced transition rates W_{ij} between the eigenstates $|i\rangle$ and $|j\rangle$ of the system Hamiltonian H,

$$K\{\rho\}_{ij}=\begin{cases}\sum_l(\rho_{ii}W_{il}-\rho_{ll}W_{li}) & \text{for } i=j\\ \frac{1}{2}\sum_l(W_{il}+W_{jl}) & \text{for } i\neq j \ .\end{cases}$$

The superoperator Eq. (2.5) is just a peculiar case of this more general class of superoperators. Its main advantage for phenomenological applications is that it depends only on the "single index" parameters (eigenvalues) Γ_i having the interpretation of inverse lifetimes of the eigenstate $|i\rangle$. These are directly accessible experimentally through the interpretation of the homogeneous linewidth of the linear susceptibility. Whenever the damping mechanism is known and a simple expression for the transition rates is available it is, however, desirable to work with the last more general expression giving rise to a much richer spectrum of population decay rates. In the case of the quantum dots the less ambitious approach seems more appropriate, but the formalism might be developed easily also for the more general case.

Now we proceed to obtain the formal solution of the generalized Liouville equation. To simplify the notations we shall introduce the superoperator (Liouvillian) L as

$$L\{\rho\}\equiv-\frac{i}{\hbar}[H,\rho]-\frac{1}{\hbar}K\{\rho\} \ . \tag{2.6}$$

Then it is convenient to write down the integral equation equivalent to Eqs. (2.3) and (2.4),

$$\rho(t)=\rho_0+\frac{1}{i\hbar}\int_{t_0}^{t}dt'e^{L(t-t')}[P,e^{L(t'-t)}\rho(t')]E(t') \ . \tag{2.7}$$

This form is very adequate for iterative solutions in powers of the field E. We give here directly the results of the first and third iterations for the susceptibilities. They are most conveniently expressed in terms of the transposed Liouvillian L^T defined through the identity

$$\mathrm{Tr}(AL\{B\})\equiv\mathrm{Tr}(BL^T\{A\}) \tag{2.8}$$

for any operators A and B. A further useful notation is for the equilibrium average

$$\langle A\rangle_0\equiv\mathrm{Tr}(\rho_0 A) \ . \tag{2.9}$$

With these notations we have

$$\chi_1(t,t_1)=-\frac{1}{i\hbar\Omega}\langle[P,e^{L^T(t-t_1)}P]\rangle_0 \tag{2.10}$$

and

$$\chi_3(t,t_1,t_2,t_3)=\frac{-1}{\Omega(i\hbar)^3}\langle[P,e^{L^T(2t_2-t_1-t_3)}\times[P,e^{L^T(2t_1-t-t_2)}\times[P,e^{L^T(t-t_1)}P]]]\rangle_0 \tag{2.11}$$

where we also took into account that $L\{\rho_0\}=0$. This formula is actually valid also for any superoperator K.

It is important to notice that the susceptibilities are invariant with respect to a common choice of the time origin and therefore have only three independent time variables. It is then useful to define explicitly a susceptibility depending only on three independent time variables

$$\chi_3(\tau_1,\tau_2,\tau_3)\equiv\chi_3(t,t-\tau_1,t-\tau_1-\tau_2,t-\tau_1-\tau_2-\tau_3) \tag{2.12}$$

and to set $t_0=-\infty$, which does not affect the expressions since $E(t)$ vanishes for $t<t_0$. We remark that $\tau_1,\tau_2,\tau_3>0$.

The important steps needed to make the formulas for the time-dependent susceptibilities explicit [with the choice of the superoperator Eq. (2.5)] are the following: the introduction of the complete set of eigenstates $|n\rangle$ of H in the intermediary states ($\sum_n|n\rangle\langle n|=1$) and the use of the assumed diagonality of Γ, which enables us to write for any operator A

$$\langle n|L^T\{A\}|n'\rangle=\frac{i}{\hbar}\left[E_n-E_{n'}+i\frac{\Gamma_n+\Gamma_{n'}}{2}\right]A_{nn'}+\frac{1}{\hbar}\delta_{nn'}\Gamma_n\frac{\langle\Gamma A\rangle_0}{\langle\Gamma\rangle_0}\ . \tag{2.13}$$

In particular, for operators for which $\langle\Gamma A\rangle_0=0$, the action of the superoperator L^T is very simple and we may write generally, due to the positivity of Γ

$$L^T\{A\}=L^T\left\{A-\frac{1}{\Gamma}\langle\Gamma A\rangle_0\right\}+L^T\left\{\frac{1}{\Gamma}\right\}\langle\Gamma A\rangle_0$$
$$=\frac{1}{\hbar}\left[i\left[H,A-\frac{1}{\Gamma}\langle\Gamma A\rangle_0\right]-\left\{\Gamma,A-\frac{1}{\Gamma}\langle\Gamma A\rangle_0\right\}+\left[\frac{\Gamma}{\langle\Gamma\rangle_0}-1\right]\langle\Gamma A\rangle_0\right]\ . \tag{2.14}$$

This last equation also enables the explicit use of the exponent of the superoperator L^T through the same decomposition trick

$$e^{L^T t}\{A\}=e^{(iH-\Gamma)/\hbar t}\left[A-\frac{1}{\Gamma}\langle\Gamma A\rangle_0\right]e^{(-iH-\Gamma)/\hbar t}+\langle\Gamma A\rangle_0 e^{L^{T*}t}\left\{\frac{1}{\Gamma}\right\}\ . \tag{2.15}$$

The exponential of the superoperator applied on $1/\Gamma$ can be treated separately, but can be eliminated through other tricks from the total expression. Special care has to be devoted to the time integration. The exponents are so that only the negative (decaying at $-\infty$) exponentials are surviving and therefore the convergence of all the integrations is assured.

The time-dependent third-order susceptibility is important in the treatment of experiments with very short pulses. A useful entity for the discussion of quasistationary light fields (very long laser pulses) is obtained by the introduction of Fourier transforms,

$$\frac{1}{\Omega}\langle\tilde{P}(\omega)\rangle=\tilde{\chi}_1(\omega)\tilde{E}(\omega)+\int d\omega_1\int d\omega_2\int d\omega_3\tilde{\chi}_3(\omega_1,\omega_2,\omega_3)\delta(\omega-\omega_1-\omega_2-\omega_3)\tilde{E}(\omega_1)\tilde{E}(\omega_2)\tilde{E}(\omega_3)+\cdots\ . \tag{2.16}$$

The expression of $\tilde{\chi}_3(\omega_1,\omega_2,\omega_3)$ is easily obtained from the previous definitions

$$\tilde{\chi}_3(\omega_1,\omega_2,\omega_3)=\frac{-1}{\Omega(i\hbar)^3}\left\langle\left[P,\frac{1}{L^T+\omega_1+\omega_2+\omega_3}\left[P,\frac{1}{L^T+\omega_2+\omega_3}\left[P,\frac{1}{L^T+\omega_3}P\right]\right]\right]\right\rangle_0\ . \tag{2.17}$$

Actually, only the symmetrical part $\tilde{\chi}_3(\omega_1,\omega_2,\omega_3)^{\rm sym}$ of $\tilde{\chi}_3(\omega_1,\omega_2,\omega_3)$ contributes under the integral.

A different kind of experimental situation with several beams of different frequencies may be discussed in terms of these susceptibilities. For example, in a one-beam experiment the entity

$$3\tilde{\chi}_3(\omega,\omega,-\omega)^{\rm sym}$$

is relevant, while in a pump and test setting the entity

$$6\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)^{\rm sym}$$

appears, where ω_P,ω_T are the frequencies of the pump and test fields, respectively. The explicit form of the frequency-dependent susceptibility is obtained again through the introduction of a complete set of eigenstates of the Hamiltonian H in the intermediate states.

We did insist on the technical details related to the theory of nonlinear susceptibilities because in the case of the microspheres having discrete energy levels, unlike in bulk semiconductors with continuous spectrum, this theory is relatively well formulated, although not widely known. The delicate point by the infinite volume limit (in the presence of a continuous spectrum) is the fact that although the whole susceptibility is an intensive entity, by the decomposition through the intermediate states one gets a lot of terms, each of them being proportional to the volume or even its second power and one has to face a very subtle cancellation mechanism.

III. THIRD-ORDER SUSCEPTIBILITY OF SEMICONDUCTOR MICROCRYSTALLITES IN THE WEAK CONFINEMENT LIMIT

Let us consider here for the sake of definiteness the pump and test case at zero temperature in a confined electron-hole system (semiconductor quantum dot). The polarization operator has nonvanishing matrix elements P_{0e} between the vacuum and one pair ("exciton") states as well as P_{eb} between the one-pair and two-pair ("biexciton") states. Its explicit expression has been derived in Ref. 18,

$$
\begin{aligned}
\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)^{\mathrm{sym}} = -\frac{i}{6\Omega}\Bigg[& \sum_{ee'} \frac{|P_{e0}|^2 P_{e'0}|^2}{\Gamma_{e0}+i(\epsilon_e-\hbar\omega_T)} \\
& \times \Bigg[\frac{2\Gamma_{e'0}/\Gamma_{e'e'}}{\Gamma_{e'0}^2+(\epsilon_{e'}-\hbar\omega_P)^2} \\
& + \left[\frac{1}{\Gamma_{e'0}-i(\epsilon_{e'}-\hbar\omega_P)} + \frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_T)} \right] \frac{1}{\Gamma_{e'e'}-i(\hbar\omega_T-\hbar\omega_P)} \\
& + \frac{1}{\Gamma_{e'0}-i(\epsilon_{e'}-\hbar\omega_P)} \left[\frac{1}{\Gamma_{ee'}+i\epsilon_{ee'}} + \frac{1}{\Gamma_{ee'}+i(\epsilon_{ee'}-\hbar\omega_T+\hbar\omega_P)} \right] \\
& + \frac{1}{\Gamma_{e0}+i(\epsilon_e-\hbar\omega_P)} \frac{1}{\Gamma_{ee'}+i\epsilon_{ee'}} + \frac{1}{\Gamma_{e0}+i(\epsilon_e-\hbar\omega_T)} \frac{1}{\Gamma_{ee'}+i(\epsilon_{ee'}-\hbar\omega_T+\hbar\omega_P)} \Bigg] \\
& + \sum_{bee'} P_{0e}P_{eb}P_{be'}P_{e'0} \Bigg\{ \frac{1}{\Gamma_{b0}+i(\epsilon_b-\hbar\omega_P-\hbar\omega_T)} \\
& \times \left[\frac{1}{\Gamma_{e0}+i(\epsilon_e-\hbar\omega_T)} - \frac{1}{\Gamma_{be}+i(\epsilon_{be}-\hbar\omega_T)} \right] \\
& \times \left[\frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_P)} + \frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_T)} \right] \\
& - \frac{1}{\Gamma_{be}+i(\epsilon_{be}-\hbar\omega_T)} \\
& \times \Bigg[\frac{1}{\Gamma_{e0}-i(\epsilon_e-\hbar\omega_P)} \\
& \times \left[\frac{1}{\Gamma_{ee'}-i\epsilon_{ee'}} + \frac{1}{\Gamma_{ee'}-i(\epsilon_{ee'}+\hbar\omega_T-\hbar\omega_P)} \right] \\
& + \frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_P)} \frac{1}{\Gamma_{ee'}-i\epsilon_{ee'}} \\
& + \frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_T)} \\
& \times \frac{1}{\Gamma_{ee'}-i(\epsilon_{ee'}+\hbar\omega_T-\hbar\omega_P)} \Bigg] \Bigg\} \Bigg] . \qquad (3.1)
\end{aligned}
$$

Here, $i=e,b$ runs over the exciton and biexciton states having the energies ϵ_i and $\epsilon_{ij}=\epsilon_i-\epsilon_j$. The dampings are $\Gamma_{ij}=(\Gamma_i+\Gamma_j)/2$, and for $i\neq j$ they represent the phenomenological coherence decay rate of the ij transition while for $i=j$ they describe the population decay of the state i.

The explicit set of quantum numbers characterizing the states here abstractly denoted by the index i was not yet specified. The eigenstates of even a single electron-hole pair inside a rigid spherical potential well are not explicitly known. Nevertheless, there are some simple plausible approximations often in use due to Efros and Efros.[1] The cases of strong and intermediate confinements were properly discussed in the literature and present no ambiguities. In what follows we are interested here only in the case of large quantum dots, having a radius R much bigger than the exciton Bohr radius a_B in the bulk semiconductor. Under these circumstances it is argued on physical[1] as well as on mathematical grounds[12] that the lowest-lying states of an electron-hole pair may be well

described by a product of the wave function of the ground-state relative motion ϕ in the bulk with that of the confined center-of-mass motion $\psi_{l,m,n}$

$$\Psi_e(\mathbf{x}_e,\mathbf{x}_h)=\phi(\mathbf{x})\psi_{l,m,n}(\mathbf{X});\quad (e\equiv\{lmn\})\ . \tag{3.2}$$

Here $\mathbf{x}_e,\mathbf{x}_h$ are the coordinates of the electron and hole, respectively, while $\mathbf{x}$ and $\mathbf{X}$ are their relative center-of-mass coordinates, respectively. The ground-state wave function of the relative motion is given by

$$\phi(\mathbf{x})=\frac{1}{\sqrt{\pi a_B^3}}\exp\left[-\frac{|\mathbf{x}|}{a_B}\right]\ , \tag{3.3}$$

and that of the center-of-mass motion by

$$\psi_{l,m,k}(\mathbf{X})=\phi_{l,n}(r)Y_{lm}(\theta,\phi)\quad (r\equiv|\mathbf{X}|) \tag{3.4}$$

($l=0,1,2,\ldots$; $m=0,\pm1,\pm2,\ldots,\pm l$; $n=1,2,3,\ldots$) with the well-known spherical functions $Y_{lm}(\theta,\phi)$.

We give here only the s-wave eigenfunctions and eigenenergies we need for our further applications,

$$\phi_{0,n}(r)=\frac{1}{\sqrt{2\pi}}\frac{\sin(n\pi r/R)}{r}\ . \tag{3.5}$$

Within this approximation, the energy of the electron-hole pair state is given by the bulk exciton ground-state energy shifted through the "quantization" of the center-of-mass kinetic energy,

$$\epsilon_{00n}=E_g-E_R+\frac{\hbar^2}{2(m_e+m_h)}\left[\frac{n\pi}{R}\right]^2\ , \tag{3.6}$$

where E_g is the band gap and E_R is the bulk exciton binding energy.

At its turn, the matrix element of the polarization operator between the vacuum and the one pair state with quantum number $e\equiv\{lmn\}$ is given by

$$\begin{aligned}P_{0e}&=\frac{p_{cv}}{\sqrt{\pi a_B^3}}\int d\mathbf{x}\psi_{l,m,k}(\mathbf{x})\\&=\delta_{l,0}\delta_{m,0}(-1)^{n+1}\frac{p_{cv}}{\pi}\left[\frac{2}{\lambda}\right]^{3/2}\frac{1}{n}\ .\end{aligned} \tag{3.7}$$

Here p_{cv} is the Bloch part of the interband matrix element and the smallness parameter $\lambda\equiv a_B/R$ of the weak confinement was introduced. At first glance an "enhancement" with $\lambda^{-3/2}$ of the oscillator strength occurs. As we shall see later, this actually has no consequences.

A simple extension of these results to many-pair states is to assume that the electron-hole pairs are ideal bosons with the Hamiltonian within the second quantization formalism given by

$$H^0=\sum_e\epsilon_e b_e^\dagger b_e \tag{3.8}$$

and the polarization operator given by

$$P^0=\lambda^{-3/2}\sum_e g_e^d(b_e^\dagger+b_e) \tag{3.9}$$

with

$$g_e^d=\delta_{l,0}\delta_{m,0}p_{cv}\frac{2\sqrt{2}}{\pi}\frac{(-1)^{n+1}}{n}\ . \tag{3.10}$$

If, as usual, one completes this picture with the assumption that all the decay parameters are equal,

$$\Gamma_i^0=\gamma\ ,$$

then one has a very simple model, which, however, has a vanishing third-order susceptibility.[7] Even more, it is well known, that such a model has no optical nonlinearities at all.[19,20]

Any deviation from this naive exciton-boson picture may give rise to a nonvanishing third-order susceptibility. For example, the introduction of the molecular bound state (true biexciton) gives rise to the typical biexcitonic nonlinearities. The corresponding polarization matrix elements have no volumic enhancement factors and therefore their discussion is simple. They also are not expected to give rise to strong volume-dependent effects. In what follows we shall be concerned in more detail with the properties of the slightly improved bosonic model in which exchange interactions between the excitons as well as exchange polarizations are taken into account. We shall admit also that the decay parameters Γ_i are not necessarily all identical.

If one takes into account that the excitons are composite objects, then the energy of the state with two excitons differs from the sum of the energies of the two excitons, due to the direct and exchange Coulomb interaction of the constituents. For large-sphere radii the exchange contribution dominates. This effect may be considered through an additional piece in the Hamiltonian

$$\delta H=\tfrac{1}{2}\lambda^3\sum_{e,e'}V^x_{e,e'}b_e^\dagger b_{e'}^\dagger b_{e'}b_e\ . \tag{3.11}$$

At the same time an additional exchange piece in the polarization appears,

$$\delta P=\lambda^{3/2}\tfrac{1}{2}\sum_{e,e'e''}g^x_{e,e',e''}b_e^\dagger b_{e'}b_{e''}+\text{H.c.} \tag{3.12}$$

The explicit expressions of the exchange interaction energies and exchange polarizations may be found in Ref. 13. Here we just give their expressions for the s states,

$$V^x_{n,n'}=E_R\frac{52/3}{1+\delta_{n,n'}}\int_0^1 dr\left[\frac{\sin(n\pi r)\sin(n'\pi r)}{r}\right]^2\ ,$$

$$g^x_{n,n',n''}=-7\sqrt{2}\int_0^1\frac{dr}{r}\sin(n\pi r)\sin(n'\pi r)\sin(n''\pi r)\ . \tag{3.13}$$

It is clear that the smallness of λ makes the δH and δP asymptotically small. The question is then how this smallness gets compensated through the volumic enhancement of the bosonic polarization P^0 [Eq. (3.10)]?

An explicit algebra shows that the inclusion of δH, together with taking into account that the decay parameters are not identical, gives rise to a nonlinear susceptibility

$$\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_1^{\rm sym}=\frac{1}{8\pi a_B^3}\sum_{e,e'}(g_e^d g_{e'}^d)^2[V_{e,e'}+i\lambda^{-3}(\Gamma_{0,e}-\Gamma_{(e,e'),e'})]A_{e,e'}\ , \tag{3.14}$$

where all the known radius dependencies were turned into explicit powers of λ except for the radius dependence of the energies ϵ_e in the expression of $A_{e,e'}$,

$$A_{e,e'}\equiv\frac{1}{(\epsilon_e-\hbar\omega_T-i\Gamma_{0e})(\epsilon_e+V_{e,e'}-\hbar\omega_T-i\Gamma_{(e,e'),e})}\{F_{e,e'}+G_{e,e'}\}\ ,$$

$$F_{e,e'}=\frac{2\Gamma_{e'0}/\Gamma_{e'e'}}{\Gamma_{e',0}^2+(\epsilon_{e'}-\hbar\omega_P)^2}+\left[\frac{1}{\Gamma_{e'0}-i(\epsilon_{e'}-\hbar\omega_P)}+\frac{1}{\Gamma_{e'0}+i(\epsilon_{e'}-\hbar\omega_T)}\right]\frac{1}{\Gamma_{e'e'}-i(\hbar\omega_T-\hbar\omega_P)}$$
$$+\frac{1}{\Gamma_{e'0}-i(\epsilon_{e'}-\hbar\omega_P)}\left[\frac{1}{\Gamma_{ee'}+i(\epsilon_e+\epsilon_{e'}+V_{e,e'})}+\frac{1}{\Gamma_{ee'}+i((\epsilon_e+\epsilon_{e'}+V_{e,e'})-\hbar\omega_T+\hbar\omega_P)}\right]\ , \tag{3.15}$$

$$G_{e,e'}=\frac{1}{\epsilon_e+\epsilon_{e'}+V_{e,e'}-\hbar\omega_T-\hbar\omega_P-i\Gamma_{(e,e'),e'}}$$
$$\times\left[\frac{1}{\epsilon_e-\hbar\omega_T-i\Gamma_{0e}}+\frac{1}{\epsilon_e-\hbar\omega_P-i\Gamma_{0e}}-\frac{1}{\epsilon_{e'}-\hbar\omega_T-i\Gamma_{0e'}}-\frac{1}{\epsilon_{e'}-\hbar\omega_P-i\Gamma_{0e'}}\right]\ .$$

Still open, however, is the question of the radius dependence of the decay parameters Γ. From Eq. (3.14) it is obvious that either the difference of the one-exciton and two-exciton polarization decay rates vanishes at least as fast as the inverse volume of the dot,

$$\Gamma_{0,e}-\Gamma_{(e,e'),e'}\propto\lambda^3\ ,$$

or the susceptibility is not properly defined, because obviously it will be extensive. Since our model is not a pure Hamiltonian one, such difficulties are not unexpected. Therefore we are compelled to admit for the consistency of the model that

$$\Gamma_{0,e}-\Gamma_{(e,e'),e'}=\lambda^3\gamma_{e,e'}\ , \tag{3.16}$$

with $\gamma_{e,e'}$ remaining finite when $\lambda\to 0$. Then,

$$\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_1^{\rm sym}=\frac{1}{8\pi a_B^3}\sum_{e,e'}(g_e^d g_{e'}^d)^2[V_{e,e'}+i\gamma_{e,e'}]A_{e,e'}\ . \tag{3.17}$$

We remark that, even without the explicit exciton-exciton interaction energy $V_{e,e'}$, one would obtain a nonvanishing third-order susceptibility due to the term $\gamma_{e,e'}$, which in turn is also an implicit consequence of the exciton-exciton interaction.

The inclusion of δP, in turn, gives rise to another nonlinearity. Since, however, δP is already of the order $\lambda^{3/2}$, the inclusion of a single such correction in spite of the enhanced P^0 already gives an intensive contribution, and the inclusion of a second power of δP is superfluous, giving rise only to a small correction, vanishing for $\lambda\to 0$. Omitting this correction, one can write then the second piece of the susceptibility as

$$\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_2^{\rm sym}=\frac{1}{4\pi a_B^3}\sum_{e,e',e''}g_e^d g_{e'}^d g_{e''}^d g_{e,e',e''}^x B(e,e',e'')\ , \tag{3.18}$$

where

$$B(e,e',e'')=C_{(e,e'),e''}+C_{(e,e'),e''} \tag{3.19}$$

and

$$C_{(e,e'),e''}\equiv\frac{1}{\Gamma_{(e,e')0}+i(\epsilon_e+\epsilon_{e'}+V_{e,e'}-\hbar\omega_P-\hbar\omega_T)}\left[\frac{1}{\Gamma_{e0}+i(\epsilon_e-\hbar\omega_T)}-\frac{1}{\Gamma_{(e,e')e''}+i(\epsilon_e+\epsilon_{e'}+V_{e,e'}-\epsilon_{e''}-\hbar\omega_T)}\right]$$
$$\times\left[\frac{1}{\Gamma_{e''0}+i(\epsilon_{e''}-\hbar\omega_P)}+\frac{1}{\Gamma_{e''0}+i(\epsilon_{e''}-\hbar\omega_T)}\right]-\frac{1}{\Gamma_{(e,e')e}+i(\epsilon_{e'}+V_{ee'}-\hbar\omega_T)}$$
$$\times\left[\frac{1}{\Gamma_{e0}-i(\epsilon_e-\hbar\omega_P)}\left[\frac{1}{\Gamma_{ee''}-i(\epsilon_3-\epsilon_{e''})}+\frac{1}{\Gamma_{ee''}-i(\epsilon_e-\epsilon_{e''}+\hbar\omega_T-\hbar\omega_P)}\right]\right.$$
$$\left.+\frac{1}{\Gamma_{e''0}+i(\epsilon_{e''}-\hbar\omega_P)}\frac{1}{\Gamma_{ee''}-i(\epsilon_e-\epsilon_{e''})}+\frac{1}{\Gamma_{e''0}+i(\epsilon_{e''}-\hbar\omega_T)}\frac{1}{\Gamma_{ee''}-i(\epsilon_e-\epsilon_{e''}+\hbar\omega_T-\hbar\omega_P)}\right]\ . \tag{3.20}$$

Both pieces of the third-order susceptibility, Eqs. (3.17) and (3.18), are smooth functions of the dot radius. The enhancement factors appearing in the unperturbed polarization were completely compensated. Whether an "explosion" of the third-order susceptibility with the growth of the radius still occurs can be decided only upon the analysis of the radius dependence of the series in the two equations, (3.17) and (3.18).

The nervous point of the theory is, however, the fact that the nonlinearity may be completely dependent on the knowledge of a very small correction to the decay parameters, vanishing in the bulk. We shall illustrate this point later.

IV. ON THE INFINITE RADIUS LIMIT AND THE RADIATIVE RECOMBINATION IN BIG QUANTUM DOTS

After the introduction of the explicit expressions of the relevant matrix elements, the structure of the series defining $\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_1^{\rm sym}$ and $\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_2^{\rm sym}$ is given by

$$\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_1^{\rm sym}=-\frac{p_{cv}^4}{(a_B E_R)^3}\frac{52}{3\pi^3}\int_0^1\frac{dr}{r^2}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}[\sin(n_1\pi r)\sin(n_2\pi r)]^2 A\left[\frac{n_1}{R},\frac{n_2}{R};\omega_P,\omega_T\right], \tag{4.1}$$

$$\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)_2^{\rm sym}=-\frac{p_{cv}^4}{(A_B E_R)^3}\frac{28}{\pi^4}\int_0^1\frac{dr}{r}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}(-1)^{n_1+n_2+n_3}\sin(n_1\pi r)\sin(n_2\pi r)\sin(n_2\pi r)$$
$$\times B\left[\frac{n_1}{R},\frac{n_2}{R},\frac{n_3}{R};\omega_P,\omega_T\right]. \tag{4.2}$$

We took here $\gamma_{n_1 n_2}=0$, and for the simplicity of the discussion we ignored the energy corrections of the order λ^3 due to the exciton-exciton interaction. The functions A and B in these series consist of products of energy denominators (with the energies measured in units of E_R). They are asymptotically decreasing for high n's at fixed R. [The quantized exciton energies are given by Eq. (3.6).] At fixed n's, however, they are tending to some definite finite functions of ω_P and ω_T as R goes to infinity.

On the other hand, the series with constant A and B are well-known convergent and explicitly summable series. Therefore it is easy to find the asymptotic expression of the susceptibility for $R\to\infty$,

$$\lim_{R\to\infty}\tilde{\chi}_3(\omega_P,-\omega_P,\omega_T)^{\rm sym}=\frac{p_{cv}^4}{(A_B E_R)^3}[-3.816A(0,0;\omega_P,\omega_T)+0.3708B(0,0,0;\omega_P,\omega_T)]. \tag{4.3}$$

Therefore, the unbounded enhancement of the third-order susceptibility with the increasing radius of the sphere (due to the volumic factors in the matrix elements) does not take place. Nevertheless, as we shall see, numerical computations show that the maxima of this limiting susceptibility are very high in comparison to their values at $R/a_B=10$ and the limiting behavior is achieved slowly only above $R/a_B=100$.

Leaving aside the uncertainty contained in the unknown radius dependence of the damping parameters, one may ask whether the asymptotic expression Eq. (4.3) can be taken into earnest? Indeed, a correct treatment of very large microcrystals must take into account the existence of the dissociated pair states, as well as the finiteness of the wavelength of the electromagnetic field. This very last aspect we shall illustrate in the example of the direct recombination of an exciton in the microcrystal.

In the bulk the direct recombination of an exciton without simultaneous phonon emission is forbidden by the conservation of energy and momentum (with the exception of certain momenta, where the exciton-photon mixing occurs) and therefore it occurs mainly through surface or impurity states. In a quantum dot, however, a direct radiative recombination is also allowed. Our dipole interaction Hamiltonian Eq. (2.1) admits from the beginning that the wavelength of the photon is negligible in comparison to the radius of the dot and therefore is not suitable for the discussion of the radiative decay in the limit of radii that are bigger than the wavelength of the emitted radiation. A correct treatment must take into account the local nature of the electromagnetic interaction and the finite wavelength of the photon. Therefore one should consider the interaction of the electrons and holes in the quantum dot with the radiation field according to the Hamiltonian

$$\tilde{H}_{\rm em}=p_{cv}\int d\mathbf{x}\tilde{\psi}_e(\mathbf{x})\tilde{\psi}_h(\mathbf{x})\tilde{E}^{(+)}(\mathbf{x})+\text{H.c.}, \tag{4.4}$$

where the second quantized wave functions for the electrons and holes $\tilde{\psi}_{e,h}(\mathbf{x})$ as well as the creation part of the electric-field operator

$$\tilde{E}^{(+)}(\mathbf{x})=\sum_{\mathbf{k}}\left[\frac{\hbar\omega_{\mathbf{k}}}{2V}\right]^{1/2}a_{\mathbf{k}}^{\dagger}e^{i\mathbf{kr}} \tag{4.5}$$

were introduced. (The volume V here is the formal quantization volume of the photons and has nothing to do with the volume of the quantum dot.) The classical counterpart of this Hamiltonian for $k\to 0$ coincides with Eq. (3.1).

By applying the golden rule of quantum mechanics one may calculate the lifetime of the one-pair state e, due to direct radiative recombination in the dot according to

$$\Gamma_e=\frac{2\pi}{\hbar}\sum_{\mathbf{k}}|\langle 0|\tilde{H}_{\rm em}|e\rangle|^2\delta(\epsilon_e-\hbar\omega_{\mathbf{k}}). \tag{4.6}$$

We shall jump over the straightforward calculations and give only the explicit result

$$\Gamma_e = \frac{32\pi^2 p_{cv}^2}{\hbar a_B^3} \kappa_{n,l}^2 \frac{(kR)^3}{[\kappa_{n,l}^2 - (kR)^2]^2} j_l(kR)^2 \tag{4.7}$$

where the explicit weak confinement quantum numbers l,m,n of the state e were introduced, j_l are Bessel functions of the first kind, $\kappa_{n,l}$ are their zeros, and $k \equiv \epsilon_{n,l}/\hbar c$.

For $R \to \infty$ the argument kR goes to infinity and, for any finite l and n, Γ_e vanishes faster (but not monotonously) as any power of $1/R$. This is in perfect agreement with the before-mentioned result for unconfined excitons, which of course also may be obtained from Eqs. (4.4) and (4.6) with plane waves for the center-of-mass motion of the exciton.

On the other hand, if the photon wavelength is still much bigger than the radius of the sphere, i.e., $kR \ll 1$, then one finds

$$\Gamma_e \simeq \delta_{l,0} \frac{32\pi^2 p_{cv}^2}{\hbar a_B^3} \frac{(kR)^3}{(n\pi)^2} .$$

One may not, however, conclude that the decay rate is enhanced with the radius,[9] since kR was already assumed to be very small.

This also shows how difficult the consideration of the volume dependence of the decay parameters is even within the simplest possible mechanism for the simplest lifetime.

V. NUMERICAL RESULTS AND DISCUSSION

In this section we shall give some numerical evaluations of the third-order susceptibility. The susceptibilities are all normalized to

$$10^5 (p_{cv}^4)(a_B E_R)^3 ,$$

and are therefore dimensionless. Instead of the true photon energies, we use $w = (\hbar\omega - E_x)/E_R$, where $E_x = E_g - E_R$ is the energy of the bulk exciton. The dot radius, as usual, is taken in units of the exciton Bohr radius a_B.

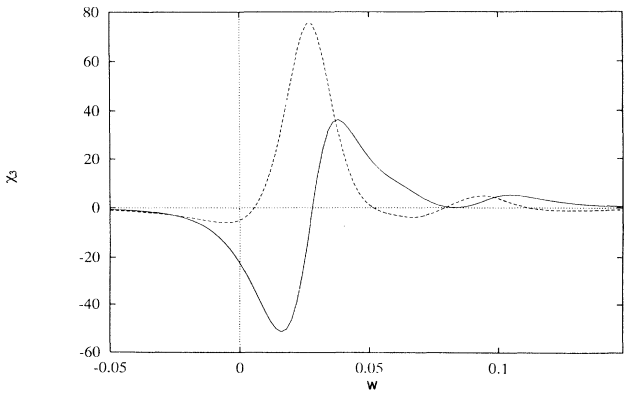

FIG. 1. The imaginary (full curve) and real (dotted curve) parts of $\tilde{\chi}_3(w,w,-w)^{\rm sym}$ 10^{-5} $(a_b E_R)^3/p_{cv}^4$ as a function of $w \equiv (\hbar\omega - E_x)/E_R$ at $R/a_B = 10$.

Except for the last figure, where a fit to experiment was attempted, we always use a common width parameter $\Gamma = 0.03 E_R$ and a hole-electron mass ratio $m_h/m_e = 4$.

The typical behavior of the single-beam third-order susceptibility $\tilde{\chi}_3(\omega,\omega,-\omega)^{\rm sym}$ in the exciton region within the weak confinement model of large quantum dots is illustrated in Fig. 1. The numerical curves (for the real and imaginary parts) are obtained for a dot of radius $R = 10a_B$. The simultaneous dependence on the frequency and the radius of the dot is shown in the three-dimensional Figs. 2(a) and 2(b). One may see a slight shift to the origin (E_x) and an enhancement with the increasing radius. This enhancement achieves (for $R \gg 100a_B$) its asymptotic value of about six (not represented in the figure) compared to the susceptibility at $R = 10a_B$. The contribution of the exchange part of the susceptibility Eq. (3.18) was found to be negligible. On the contrary, the energy corrections of order λ^3 in the denominators of the direct susceptibility Eq. (3.17) were found to be important for the frequency dependence at moderate radii $R \simeq 10a_B$.

The pump-test third-order susceptibility $\tilde{\chi}_3(\omega_P, -\omega_P, \omega_T)^{\rm sym}$ as a function of the test frequency for a fixed pump frequency situated slightly below (respectively, slightly above) the origin (E_x) is given in Figs. 3(a) and 3(b). Attention should be paid to the change of scale. Again, one may see the enhancement effect with increasing radius in the three-dimensional representation (simultaneous test frequency and radius dependence at fixed pump frequency $w_P = 0.01$) of Figs. 4(a) and 4(b). The asymptotic enhancement factor is found to be about

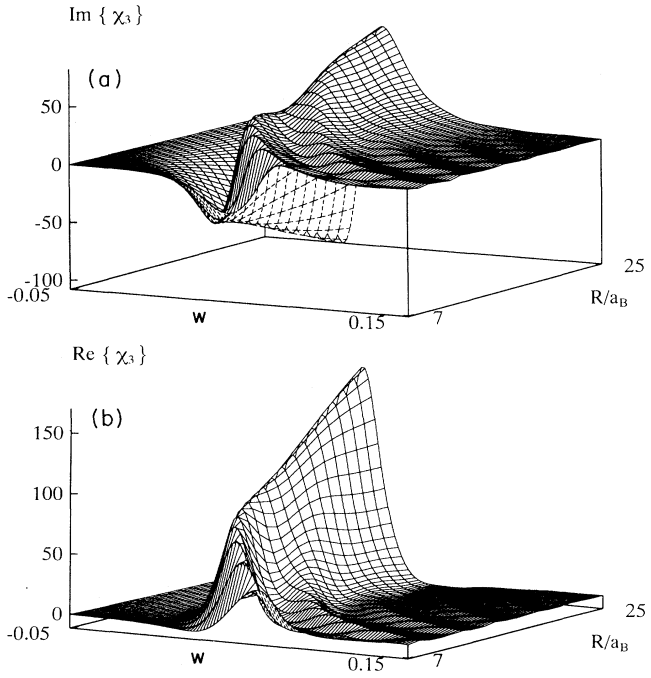

FIG. 2. The (a) imaginary and (b) real parts of $\tilde{\chi}_3(w,w,-w)^{\rm sym}$ 10^{-5} $(a_B E_R)^3/p_{cv}^4$ as a function of $w \equiv (\hbar\omega - E_x)/E_R$ and R/a_B.

eight.

The simultaneous pump- and test-frequency dependence at fixed $R=10a_B$ is given in Figs. 5(a) and 5(b).

The enhancement of the third-order susceptibilities with increasing dot radius is due to the accumulation of the poles at the bulk exciton energy and, in contradistinction to an enhancement through a volumic factor, is limited to an overall factor that is less than an order of magnitude between $R=10a_B$ and $R=\infty$. Of course, the comments of the previous section regarding the validity of this theory for very big radii have to be kept in mind.

On the other hand, consideration of a very small difference between the width parameters according to Eq. (3.16) leads to essential quantitative changes. As we already mentioned, the breakdown of certain relations between the decay parameters acts as a new source of nonlinearity. For example, even in the absence of exciton-exciton exchange interactions, one may obtain with a suitable parameter $\gamma_{e,e'}=V_{e,e'}$ of Eq. (3.16) the same third-order susceptibility, but with the real and imaginary parts interchanged. This also means that for $\gamma_{e,e'}\gg V_{e,e'}$, the shape of the susceptibility curves of Fig. 1 is completely changed (minima are replaced with maxima). This is perhaps an extreme case, but already with a parameter $\gamma_{e,e'}=0.5V_{100,100}$, which at $R=15a_B$ corresponds to an uncertainty in the width parameters of less

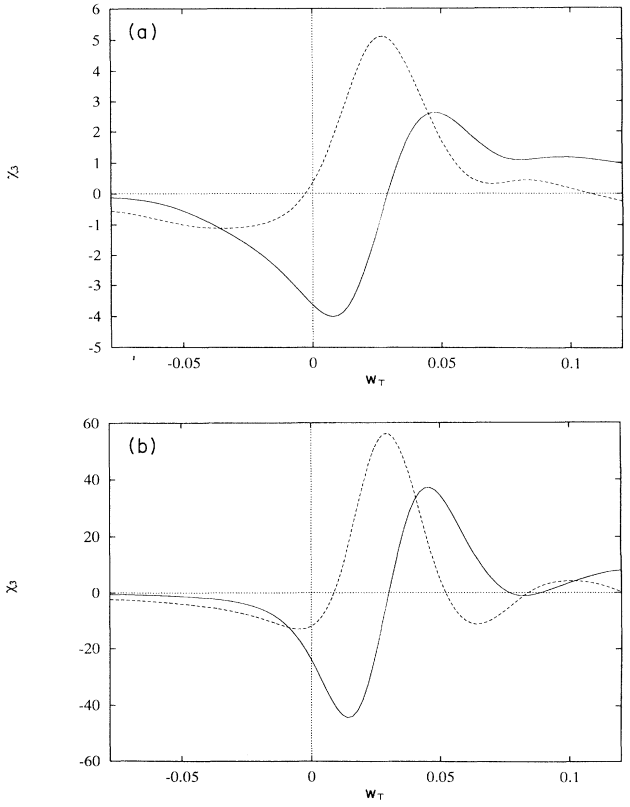

FIG. 3. The (a) imaginary (full curve) and (b) real (dotted curve) parts of $\tilde{\chi}_3(w_P,w_T,-w_P)^{\rm sym}\ 10^{-5}\ (a_BE_R)^3/p_{cv}^4$ as a function of $w_T\equiv(\hbar\omega_T-E_x)/E_R$ at $R/a_B=10$ for the pump frequency $w_P=-0.05,+0.01$, respectively.

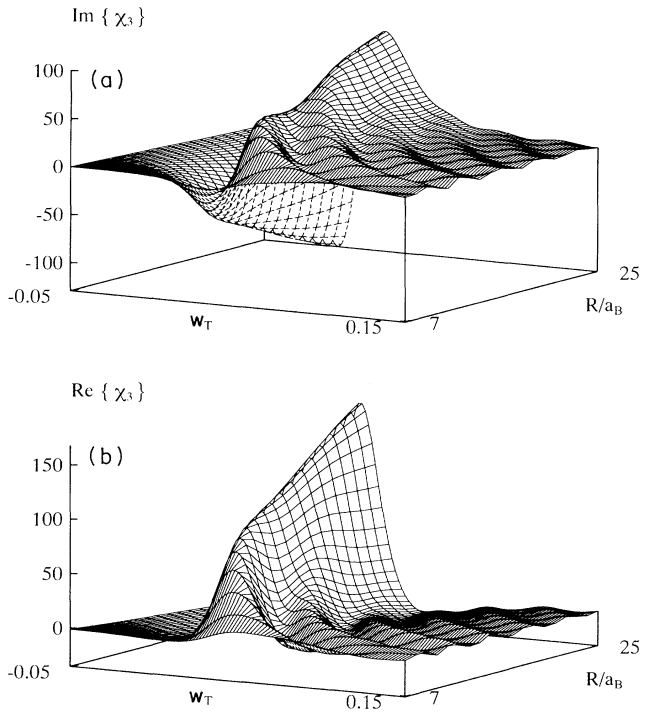

FIG. 4. The (a) imaginary and (b) real parts of $\tilde{\chi}_3(w_P,w_T,-w_P)^{\rm sym}\ 10^{-5}\ (a_BE_R)^3/p_{cv}^4$ as a function of $w_T\equiv(\hbar\omega_T-E_x)/E_R$ and R/a_B at fixed $w_P=+0.01$.

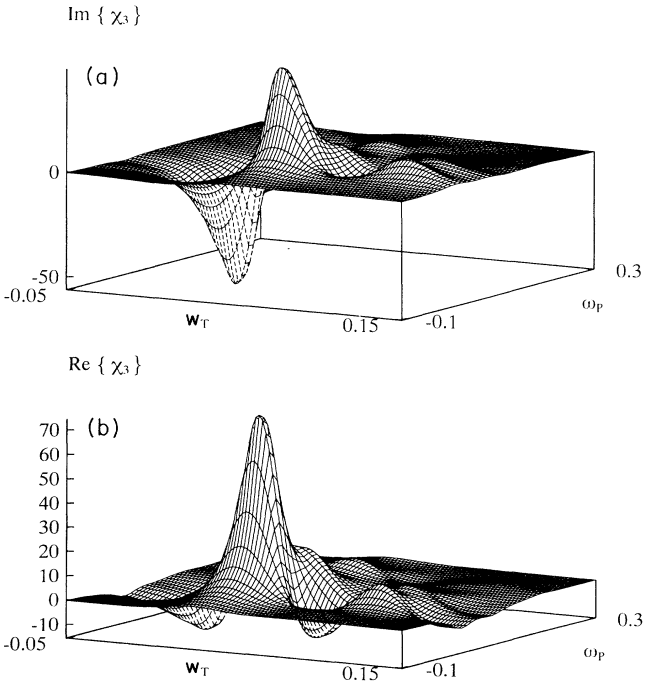

FIG. 5. The (a) imaginary and (b) real parts of $\tilde{\chi}_3(w_P,w_T,-w_P)^{\rm sym}\ 10^{-5}\ (a_BE_R)^3/p_{cv}^4$ as a function of $w_T\equiv(\hbar\omega_T-E_x)/E_R$ and $w_P\equiv(\hbar\omega_P-E_x)/E_R$ at fixed $R/a_B=10$.

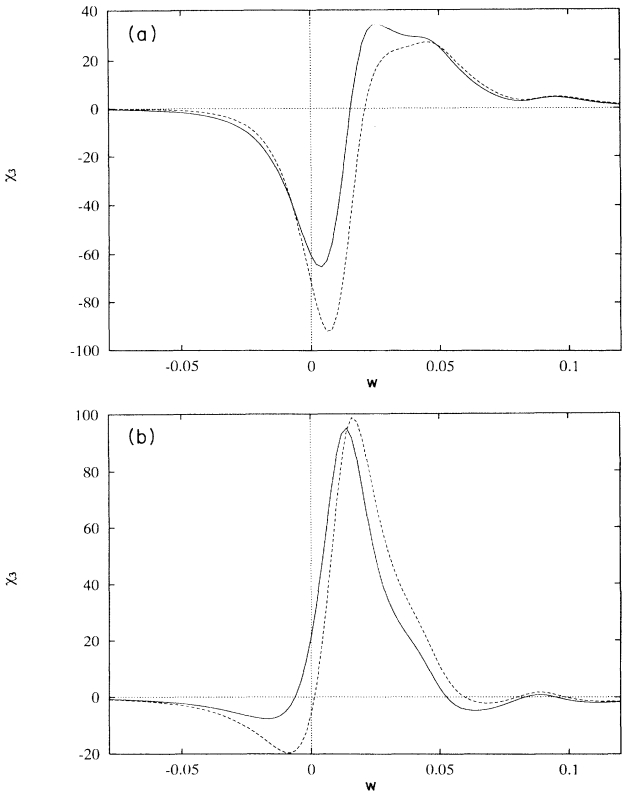

FIG. 6. The (a) imaginary and (b) real parts of $\tilde{\chi}_3(w,w,-w)^{\rm sym}$ 10^{-5} $(a_B E_R)^3/p_{cv}^4$ as a function of $w \equiv (\hbar\omega - E_x)/E_R$ at $R/a_B = 15$: with $\gamma_{e,e'} = 0$ (full curves) and $\gamma_{e,e'} = 0.5 V_{100,100}$ (dashed curves).

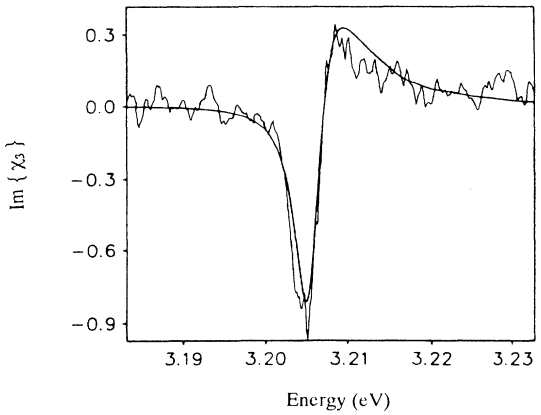

FIG. 7. Experimentally measured Im $\tilde{\chi}_3(w_P, w_T, -w_P)^{\rm sym}$ (arbitrary units) in CuCl and theoretical fits: with unique $\Gamma = 4$ meV (dashed curve) and with $\Gamma_{e0} = 4.5$ meV, $\Gamma_{be} = 5$ meV, $\Gamma_{b0} = 3.5$, $\Gamma_{ee'} = 2$ meV (full curve).

than 10% (bearing in mind that $\delta\Gamma = \lambda^3\gamma$!), one modifies significantly the values of the susceptibility as it can be seen in Figs. 6(a) and 6(b). These results illustrate our point about the instability of the susceptibility theory of big quantum dots against small variations of the width parameters and therefore its weak predictive character.

Nevertheless, it is instructive to fit the recently measured picosecond differential absorption data on CuCl quantum dots ($R = 70$ Å $\simeq 10 a_B$) in a glass matrix[6] ($\hbar\omega_P = 3.2053$ eV) with our theoretical formulas. A best fit with a unique width parameter of $\Gamma = 4$ meV is represented with a dashed curve in Fig. 7. The experimental curve is the oscillating one. A much better fit, however, can be achieved with slightly different width parameter $\Gamma_{e0} = 4.5$ meV, $\Gamma_{be} = 5$ meV, $\Gamma_{b0} = 3.5$, and $\Gamma_{ee'} = 2$ meV, given by the smooth continuous curve.

We may conclude that the weak confinement theory of the third-order susceptibility of the microcrystals is compatible with the experimental data, but due to its inherent sensitivity to small volume-dependent variations of the width parameters it has no strong predictive character. Small variations of the relaxation times that are vanishing in the bulk limit act as sources of new independent nonlinearities of the same magnitude as those due to exciton exchange effects.

ACKNOWLEDGMENTS

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