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Theory of the linear and nonlinear optical properties of semiconductor microcrystallites

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We analyze theoretically the optical properties of ideal semiconductor crystallites so small that they show quantum confinement in all three dimensions [quantum dots (QD's)]. In the limit of a QD much smaller than the bulk exciton size, the linear spectrum will be a series of lines, and we consider the phonon broadening of these lines. The lowest interband transition will saturate like a two-level system, without exchange and Coulomb screening. Depending on the broadening, the absorption and the changes in absorption and refractive index resulting from saturation can become very large, and the local-field effects can become so strong as to give optical bistability without external feedback. The small QD limit is more readily achieved with narrow-band-gap semiconductors.

I. INTRODUCTION

In recent years, advantage has been taken of the ability of modern crystal-growth techniques to fabricate artificial semiconductor nanostructures. It is now readily possible to make structures that show quantum size effects, at least in one direction, and that consequently exhibit novel physical properties not encountered in natural materials. The most widely fabricated and utilized of these nanostructures in optics are quantum wells, i.e., ultrathin alternating semiconductor layers of different composition. Part of the reason for the interest in quantum wells in nonlinear optics is the strong nonlinear response in the vicinity of quasi-two-dimensional exciton resonances (for recent reviews, see Refs. 1 and 2). In addition, it is found that these quasi-two-dimensional excitons remain well resolved even at room temperature, a peculiarity that results in unusual transient behavior under ultrafast excitation.[3–5]

The comparison of quantum wells with conventional bulk semiconductor material indicates that the confinement of electronic envelope wave functions over dimensions of the order of the carrier de Broglie wavelengths indeed provides a novel means to engineer optical nonlinearities. It is thus natural to examine if further carrier confinement in lower-dimensionality semiconductor structures, i.e., one-dimensional quantum wires or zero-dimensional quantum dots (QD's), could induce new and interesting properties. Such nonlinear phenomena are of some practical interest because of the continuing need for better nonlinear optical materials in, for example, applications to optical switching and signal processing. Presently, intensive work is done on the fabrication of such structures in a number of laboratories. The techniques that are explored include electron beam lithography,[6] colloidal particle interrupted growth in solvents,[7,8] enhanced interdiffusion,[9] particle growth in glasses,[10,11] and patterned epitaxial growth.[12]

Some basic linear optical properties of QD's are already understood theoretically. The interband absorption spectrum should change from continuous bands to a set of discrete lines[13] as the size of the crystallite is decreased. The main purpose of this article is to understand what will happen to the nonlinear optical properties associated with interband absorption in quantum dots. We will concern ourselves primarily with the absorption (or, more strictly, the imaginary part of the dielectric constant) inside a single quantum dot. We will not consider any possible optical interaction between quantum dots; such phenomena can be treated in a subsequent macroscopic optical theory. The actual nonlinear absorption and refraction phenomena in QD's turn out to be relatively simple, as we will describe below. As we will discuss, the only surviving mechanism for nonlinear absorption near the lowest resonance (neglecting multiphoton absorption) is state filling. This contrasts strongly with both three- and quasi-two-dimensional semiconductors where screening, exchange, and the related band-gap renormalization are also important. A more difficult problem, however, is understanding some other aspects of the linear absorption not previously considered, especially the broadening of the absorption lines. Without a knowledge of the broadening, we can make no useful estimate of the size of the nonlinear absorption, for example, since this depends on the width of the linear absorption line. At present, broadening is in practice usually dominated by inhomogeneities in the size and shape of the microcrystallites in samples containing many such QD's. More fundamentally, however, it is determined by other mechanisms, predominantly phonon broadening, that cannot be eliminated by better fabrication. It is these mechanisms that set the limit to the properties of QD's, and we consider them in this paper.

In the course of considering these linear and nonlinear properties, we find also that we have to define more precisely what we mean by a semiconductor QD, at least for the purposes of this paper. We cannot simply define it to include all structures, no matter how small, made of constituent materials that are semiconducting in the bulk. The properties of molecules or "clusters" are so different from those of crystalline structures that we cannot hope to encompass them all within one simple theory. This is true both for their chemical properties and the effects of vibrations. Hence we will consider useful limits on the size of the structures for the validity of the physical properties involved.

The present article is organized as follows. First, in Sec. II, we consider the useful limits of our theoretical approach, and we examine the changes in both the electronic level structure and coupling to lattice vibrations that result from increasing confinement. Then in Sec. III, we discuss the saturation of optical absorption of the discrete transitions in the QD's. In Sec. IV we briefly discuss local field effects that will further alter the externally perceived optical properties compared to bulk material. We draw our conclusions in Sec. V.

II. LINEAR OPTICAL PROPERTIES

A. Electronic structure

As we make a semiconductor "crystal" smaller and smaller, the physical properties change in many ways. In a large crystal, the overall shape and size of the crystal make little or no difference to its internal properties. As the crystal becomes smaller, however, the effects of the surface become increasingly important. The most extreme consequence is that as the fraction of atoms at the surface becomes larger, the arrangement of the nuclei changes in order to relax the energy of the system as a whole, i.e., a transition from crystalline to molecular (cluster) behavior takes place.

Semiconductor microcrystallites in vacuum will undergo a transition from the bulk structure to more closed-packed molecular arrangements even for quite small surface atoms/bulk atoms ratios so that they minimize the number of broken bonds (which are costly in energy). Recent estimates for Si show that the crossover to the bulk structure takes place if the number of atoms is $\sim 10^3$.[14,15] If the particles are embedded in a host material, the critical cluster size for crystalline behavior can be much smaller because of the saturation of surface bonds by host atoms. Consequently, we cannot put a simple limit on the structure size for crystalline behavior as it will depend on the crystal environment. In what follows, we shall consider QD larger than this critical size only. Such particles are small crystalline fragments, i.e., they are "chemically" identical to the corresponding bulk semiconductors.

Even if we make the crystallites sufficiently large that the nuclei still retain substantially the same relative positions as in the bulk crystal, the electronic states may be substantially different. Depending on the QD size, the quasiparticle ("electrons" and "holes") spectrum is considerably altered by the quantum confinement of the extended electronic states. For QD with a spatial extension of several lattice constants, as a first approximation we can use the effective mass approximation to describe the size quantization of electrons and holes, in much the same way as in quantum wells.[16] Similar but more sophisticated techniques have been used to study, for example, the properties of small metal particles such as Na in the shell model for jellium, which due to the delocalization of the electrons do not exhibit a pronounced dependence on size of their chemical structure.[17,18] Again, as in quantum wells, we will be able to model the principal consequences of confinement with the simplifying assumption of infinite potential barriers for the electron and hole at the boundaries of the QD. Thus, in the simplest, high-symmetry situations, the electron and hole eigenstates can be just the particle in a sphere or box states. It is therefore likely that there is a range of sizes (e.g., between a 25-Å cube and a 250-Å cube) for which the effects of the quantum confinement on the extended electronic states may be large, yet the structure may still be crystalline in all directions, and this is a simple working definition of a QD.

Of course, the shape of the particle can also now influence the energy-level structure. In a large bulk crystal, the surface is such a small perturbation on the bulk properties that the surface shape does not in practice alter the symmetry properties of the wave functions. As is well known from quantum wells, however, one also has to account for a possible reduction of the symmetry in small, confined systems, or, to put it another way, the shape of the surface influences the symmetry of the states. A spherical QD has a higher symmetry than any crystal so that, for example, the heavy and light hole states of GaAs would remain degenerate under such spherical quantum confinement. This would not, however, hold for a platelet QD, in which case the hole states would be split, so that one would have to deal with two kinds of holes with different confinement energies, optical selection rules, etc., just as in quantum wells. (Similar conclusions have been arrived at by Brus.[19]) These shape-induced band-structure effects shall not concern us further here, although they do not represent a fundamental problem, and our discussion could be extended to cover them. In what follows, we will limit ourselves to the simplest model, a two-band semiconductor with spin degeneracy only, and will consider spherical or cubic QD's. There is of course no requirement that the QD should have a regular shape in order to show quantum confinement and a discrete energy-level spectrum, and the main conclusions of our study of the nonlinear optical properties will also be valid regardless of the precise external shape.

Another effect is the simple electrostatic phenomenon of image forces that will occur for charged particles inside a medium of one dielectric constant that is in turn embedded in a host medium of different dielectric constant. Such effects influence the Coulomb interaction between the size-quantized electrons and holes.[19] This depends strongly on the ratio of the dielectric constants of the host and QD materials and, again, on the shape of the QD. It is intuitively clear that in a highly symmetric (i.e., spherical or cubic) QD these effects are small, because most of the electromagnetic interaction between carriers takes place through the QD material. In a platelet, however, the situation is similar to that in quantum wells or semiconductor films,[20] and there is a stronger enhancement of

Coulomb effects if the background has a smaller dielectric constant than the QD (as is often the case). In what follows, we will simply neglect image force effects. In the case of strong confinement, they may not be large enough effects to distort the wave functions significantly because Coulomb effects are then relatively weak anyway, as will be discussed below. Of course, embedding the QD in a medium of different dielectric constant can still have profound consequences for the optical properties as seen from outside the QD because of local-field effects, and we will return to this point below.

With our simplifying assumptions and conditions, it is simple to calculate the single-particle energy levels of the system. The quantum confinement will split the bulk conduction (c) and valence (v) bands into a series of discrete energy levels (energy shells in spherical QD), the degeneracy and separation of which depend on the QD shape. These levels can be characterized by spin and sets of discrete momenta k. For example, for a sphere with radius R and

$$\nu=c,v,\ \ m_c=m_e,\ \ m_v=-m_h\ , \tag{1}$$

one obtains[13]

$$\Psi_{\nu nlm}(\mathbf{r})=Y_{lm}(\theta,\phi)\frac{1}{R}\left[\frac{2}{r}\right]^{1/2}\frac{J_{l+1/2}(k_{nl}r)}{J_{l+3/2}(k_{nl}R)}U_\nu(\mathbf{r})\ , \tag{2}$$

$$E_{\nu nl}=\pm\frac{E_g}{2}+\frac{\hbar^2k_{nl}^2}{2m_\nu}\ , \tag{3}$$

where $-l\le m\le l$; $l=0,1,2,\ldots$; $n=1,2,3,\ldots$; and

$$J_{l+1/2}(k_{nl}R)=0\ , \tag{4}$$

whereas for a cube with length L

$$\Psi_{\nu nlm}(\mathbf{r})=\left[\frac{2}{L}\right]^{3/2}\sin\left[\frac{n\pi}{L}x\right]\sin\left[\frac{l\pi}{L}y\right]\times\sin\left[\frac{m\pi}{L}z\right]U_\nu(\mathbf{r})\ , \tag{5}$$

$$E_{\nu nlm}=\pm\frac{E_g}{2}+\frac{\hbar^2\pi^2}{2m_\nu L^2}(n^2+l^2+m^2)\ , \tag{6}$$

where $n,l,m=1,2,3,\ldots$. Here, J_μ are the Bessel functions and Y_{lm} the normalized spherical functions. $U_\nu(\mathbf{r})$ are the cell periodic parts of the bulk Bloch functions at the band edge, which we presume to be unchanged, as explained above. Equations (2)—(6) simply follow from the requirement that the wave functions vanish at the corresponding QD surfaces, which may not be true in reality, particularly for the high-lying states where the wave function may penetrate significantly into the barriers. High-lying states may also be influenced by nonparabolicity effects often encountered in narrow-gap semiconductors.

Just as in quantum wells, the confinement in QD leads to a blue shift of the electron and hole states. The optical transitions, which probe the nature of the electron-hole pair states, will also become discrete. These two phenomena make the optical properties of QD's very different from the bulk. What makes the QD attractive for optics is the fact that this quantization is accompanied by the concentration of bulk oscillator strength into single spectral lines and small volumes, so that an enhanced linear and nonlinear optical response is to be expected, and we will discuss these phenomena below.

B. Linear optical susceptibility

Due to the presence of the surface, the optical susceptibility χ of a QD is a nonlocal function in real space, i.e., $\chi=\chi(\mathbf{R},\mathbf{R}')\neq\chi(\mathbf{R}-\mathbf{R}')$. For example, a uniform field will produce a polarization that varies with absolute position inside the quantum dot because of the confinement of the wave functions. However, since the photon wavelength is much larger than the QD size, this nonlocality is not normally important, and we may replace the nonlocal χ by its "QD-averaged" value $(1/V)\int d^3\mathbf{R}\int d^3\mathbf{R}'\chi(\mathbf{R},\mathbf{R}')$, where V is the QD volume. For the same reason, spatial variations in the electric field inside the QD are not very important; a suitable average field can be used. This is important when considering local-field effects in QD's of low symmetry. Only certain shapes, such as spheres, show uniform internal fields when immersed in originally uniform fields in media of different dielectric constant; the nonuniform internal field in other shapes, such as cubes or platelets, is of little consequence for the QD case because of this averaging. This averaging could become invalid in the case of very sharp and/or strong resonances where the real part of the dielectric function could become very large in the vicinity of the resonance, and hence the wavelength could become shorter than the QD size. We will not consider this here, and the numerical examples that we will give will not result in such large dielectric constants. Whether this will be important depends on the broadening of the lines; very narrow lines could result in very large dielectric constants. We will discuss local-field effects further below in Sec. IV.

If for the moment we neglect the Coulomb attraction between electrons and holes, the calculation of χ becomes trivial. The spatial average over the QD volume leads simply to overlap integrals of the conduction and valence "band" wave functions. These integrals can be evaluated exactly, and they yield the well-known selection rule that optical transitions can only take place between states having the same quantum numbers. This it true regardless of the shape of the QD (provided that the internal field is uniform), but to be strictly correct it does rely on the assumption of infinitely high barriers so that the electron and hole eigenfunctions are identical; since electrons and holes penetrate into the barriers by different amounts in reality, the wave functions are not strictly identical and finite transition probabilities exist on the "forbidden" transitions except where these are symmetry forbidden. For the states (2) $[V=(4\pi R^3/3]$ we find with $E_e=E_c$ and $E_h=-E_v$,

$$\mathrm{Im}\chi=\frac{C}{V}\sum_{n,l}(2l+1)\delta(E-E_{enl}-E_{hnl})\ , \tag{7}$$

whereas for the states (5) ($V=L^3$),

$$\mathrm{Im}\chi=\frac{C}{V}\sum_{n,l,m}\delta(E-E_{enlm}-E_{hnlm})\,, \tag{8}$$

where

$$C=\frac{2\pi e^2\hbar^2\,|p_{cv}|^2}{m_0^2E^2}\,. \tag{9}$$

Here, E is the photon energy and p_{cv} the bulk optical matrix element. In what follows, we treat C as a constant, as the variations in E will be small compared to E_e+E_h. We have already summed over spin in (9). Equations (7) and (8) do not yet include local-field corrections which will be discussed later. Equation (8) is also the form of the generic expression for an arbitrary shape and size of QD (including a macroscopic crystal) if we regard n, l, and m as the general quantum numbers required to describe the states, and subject to neglect of electron-hole interaction. Equation (7) is then a special case where many of the states are degenerate in energy.

The absorption spectra (7) and (8) consist of a series of discrete lines, which shift to higher frequencies as the QD size decreases. It is interesting to compare this QD absorption to that of a bulk exciton. In the bulk, with electron-hole interaction included, the absorption becomes

$$\mathrm{Im}\chi=C\sum_{p}|U_p(0)|^2\delta(E-E_p)\,, \tag{10}$$

where p indexes the excitonic states and $|U_p(0)|^2$ is the probability of finding the electron and hole in the same (unit) volume in the given excitonic state. The spectral weight of the QD lines is proportional to V^{-1}, whereas the spectral weight of the exciton lines is proportional to $|U_p(0)|^2$. For the lowest (e.g., $1S$) exciton state, $|U_p(0)|^2\sim a_0^{-3}$ (a_0 is the Bohr radius). Hence the spectral weight of the QD transitions is a factor of $\sim a_0^3/V$ larger than that of the bulk exciton. For the moment we have come to this conclusion neglecting the electron-hole interaction in the QD, but as we will discuss below, in some circumstances this may not be very important anyway. The general conclusion from this discussion of spectral weights is that they are proportional to the reciprocal of the confinement volume, regardless of whether the confinement results from the Coulomb interaction or from externally imposed confinement. [This conclusion also holds for quantum well excitons, where the confinement in one direction is external (resulting from the barriers) and in the other two is Coulomb induced.] Consequently, by making the QD smaller than the bulk exciton we may make resonances with larger spectral weight than that of the bulk exciton, and we may hope to engineer correspondingly larger optical nonlinearities just as in quantum wells.

Now we will consider the effects of the electron-hole Coulomb interaction, and we will consequently make another restriction on the QD's that is important for optics. We will consider only QD's in which the QD is significantly smaller than the bulk exciton. In this case the confinement resulting from the QD dominates over the mutual relative Coulomb confinement that gives rise to the bulk exciton. (The bulk exciton is of course a "quantum-confined" state of relative electron-hole motion resulting from the Coulomb potential of electron and hole rather than any fixed external potential.) Then the eigen wave functions of the electrons and holes are negligibly influenced by the Coulomb attraction between them, and formulas (7) and (8) are again valid. We can formalize this qualitative argument. For QD much smaller than the bulk exciton Bohr radius, the residual Coulomb interaction between the electrons and holes can be easily included by noting that the confinement energy scales like L^{-2} whereas the Coulomb energy scales like L^{-1} (L is the linear dimension of the QD). If $L\ll a_0$, this allows us to treat the electron-hole correlation in perturbation theory, and it becomes an arbitrarily small perturbation for an arbitrarily small QD. In general, the inclusion of the Coulomb interaction leads to a small renormalization of the oscillator strengths and to small red shifts of the various transitions (see below). Obviously, as one decreases the size of a crystallite from $L\gg a_0$ to $L\ll a_0$, the lowest bulk exciton transition changes continuously into the lowest QD transition. Simultaneously, oscillatory structures associated with the higher QD states appear.

The necessary criteria for QD's with the restrictions required by our theory are likely to be satisfied by the III-V compounds, which posses small bulk band gaps E_g and hence small electron and hole effective masses, m_e and m_h. Excitons in these compounds are genuine Wannier excitons, i.e., they are strongly delocalized and almost hydrogenic. It is thus easy to achieve a QD size L much smaller then the bulk exciton Bohr radius a_0, which can be as large as several hundred Å, without having to make the QD so small that it is no longer a crystal. Under this condition, both the electrons and the holes are readily size quantized, the electron confinement energy $\sim\hbar^2/(2m_eL^2)$ being larger than the hole confinement energy $\sim\hbar^2/(2m_hL^2)$, since usually $m_e\ll m_h$. We will give calculations for two representative III-V materials, GaAs and InSb, below.

There have already been measurements of the optical properties of very small semiconductor structures.[8,10,11] In particular, the overall blue shift of the absorption spectrum has been clearly identified. However, these investigations have concentrated so far on CuCl, CuBr, and some II-VI compounds that do not possess strongly delocalized excitons. Consequently, the limit $L\ll a_0$ has not yet been reached and different forms of size quantization have been observed, such as size-quantized excitons and size-quantized electrons only. Also, the strong increase in oscillator strength was partly spoiled by a large inhomogeneous broadening resulting from inhomogeneities in the size and shape of the structures.

One further phenomenon worth mentioning briefly here in connection with linear optical properties is the effect of static electric fields on the spectra. Recent studies of the excitonic electroabsorption in quantum wells have shown new effects qualitatively different from those in bulk semiconductors.[21,22] These effects have been successfully explained as a quantum-confined Stark effect. Similar effects are expected in QD. In particular, a simple model introduced by us (quantum-confined Franz-Keldysh effect)[23] applies to QD in the limit $L\ll a_0$, in which the Coulomb interaction is negligible. A homogeneous electric field will give rise to new transitions, and the envelope of Imχ will rapidly approach the bulk Franz-Keldysh behavior[24,25] when the potential drop across the QD becomes larger than the confinement energy. Details of these electric field effects will be given elsewhere.

C. Phonon broadening of optical spectra

The discussion so far has concentrated only on the weights and positions of the optical transitions. We will now discuss the broadening mechanisms.

In systems containing a large number of semiconductor microcrystallites several mechanisms may contribute to the broadening of optical spectra. Fluctuations of the crystallite size *and* shape may lead to an inhomogeneous broadening, when considering the properties of multiple QD's, similar to the inhomogeneous broadening in quantum wells due to fluctuations in the layer thickness.[26,27] This type of broadening can be controlled by improved fabrication, at least in principle, and it shall not concern us further here; we will consider only those processes that are intrinsic to the QD and that cannot be avoided by any improvement in manufacture. In contrast to the case of a single quantum well, where fluctuations within a single layer cause broadening when sampled with a macroscopic optical beam, there is no such broadening anyway in the case of a single QD. We shall also neglect the natural linewidth, even though it will increase with decreasing QD size, due to the enhancement of the radiative transition probability under quantum confinement. This is well justified for the QD sizes under consideration. What remains to be discussed is the broadening due to the coupling to lattice vibrations. We will show that it is qualitatively different from that in the bulk.

The lattice dynamical properties of small QD's are different from those of bulk crystals. With decreasing QD size, surface modes will appear and ultimately one will recover a discrete vibrational spectrum, similar to that of molecules. Propagating phonon modes will strictly only exist if the QD is embedded in a host material with an almost identical lattice structure. Since we limit ourselves to QD with at least $\sim 10^3$ atoms, the number of degrees of freedom is however already huge, and we will *model* the relevant vibrational modes by the corresponding (propagating) bulk modes, i.e., we will neglect any size quantization of the phonons. Starting from the bulk, the first significant changes in the broadening of optical transitions occur because the electrons and holes become localized, and not because the phonons become localized. The discrete nature of the localized vibrational modes would not be resolvable in optical spectra except for extremely small QD's because the energy separation between modes would be small on the scale of the electronic energy levels; this follows from the small electron mass/ion mass ratio since confinement energy is inversely proportional to mass.

One immediate consequence of the confinement of the electronic states is the disappearance of the temperature-dependent broadening mechanism that dominates in room-temperature quantum wells.[2,3] In this quantum well mechanism, the exciton once created is rapidly ionized by absorbing an optical phonon to create free electrons and holes. This shortening of the exciton lifetime results in a simple lifetime broadening of the exciton line. This mechanism disappears in the QD because there will not normally be higher electron and/or hole states of the right energy to act as final states for the phonon absorption process. Only when the separation between the quantized electronic states coincides with (multiples of) the optical phonon energy will this mechanism be possible. In compensation, however, other mechanisms become stronger as we make the QD smaller, in particular, the coupling to short-wavelength phonons. This increased coupling will increase the strength of those processes in which phonons are absorbed or emitted as part of the absorption process itself. These processes give rise to phonon sidebands. Furthermore, the phonon sidebands may become sharper because in a QD there is no motional reduction of the phonon sidebands in contrast to bulk materials.

Phonon sidebands exist for both optical and acoustic phonons. In the case of optical phonons, they result in "replicas" of the zero-phonon absorption transition spaced by one optical phonon energy. This in itself might not be too injurious to the nonlinear optical properties, which are interesting in the vicinity of any narrow resonance, as long as the optical absorption strength was not distributed among too many such sidebands. The case of acoustic phonon sidebands is similar in principle, but there is a quasicontinuum of possible phonon energies from essentially zero up, and hence all the phonon sidebands tend to overlap to give a line broadening and possibly a significant line shift. This line broadening mechanism will be the significant one in our case, although we will consider all phonon sidebands below.

In what follows, we will consider the lowest electron-hole pair state only. We shall refer to it as an exciton, even though its spatial extent is determined by the quantum confinement, and not by the Coulomb interaction. Including terms of order L^{-1}, the exciton has an energy

$$E_x = E_e + E_h - U \ , \tag{11}$$

where E_e and E_h are the electron and hole ground-state energies and

$$\begin{aligned} U &= \int d^3r \int d^3r' \, |\phi(\mathbf{r})|^2 \frac{e^2}{\epsilon_0 |\mathbf{r}-\mathbf{r}'|} |\phi(\mathbf{r}')|^2 \\ &= O\left[e^2/\epsilon_0 L \right] \end{aligned} \tag{12}$$

is the Coulomb integral, $\phi(\mathbf{r})$ being the ground-state envelope function. If the electron and hole confinement energies are much larger than both the optical phonon energy and the Debye energy, we may safely neglect the mixing of different states by the phonons. The problems then reduces to the familiar problem of a localized state coupled to lattice vibrations,[28,29] and the Hamiltonian can be written

$$\begin{aligned} H = {} & \sum_{\lambda} E_x c_\lambda^\dagger c_\lambda + \sum_{n,\mathbf{q}} \hbar\omega_{n\mathbf{q}} (b_{n\mathbf{q}}^\dagger b_{n\mathbf{q}} + \tfrac{1}{2}) \\ & + \sum_{\lambda,n,\mathbf{q}} c_\lambda^\dagger c_\lambda (M_{n\mathbf{q}} b_{n\mathbf{q}} + \text{H.c.}) \ , \end{aligned} \tag{13}$$

where

$$M_{\mathrm{nq}}=(M^{c}_{\mathrm{nq}}-M^{v}_{\mathrm{nq}})\int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}}\,|\phi(\mathbf{r})|^2 \;. \tag{14}$$

Here, λ denotes the four degenerate exciton states (three triplet and one singlet) and n the various phonon modes. M^{c}_{nq} (M^{v}_{nq}) is the conduction (valence) -electron—phonon matrix element in the bulk.

In the bulk, the broadening of Wannier exciton lines is mainly determined by the polar coupling of the electron and hole to optical phonons.[30] The nonpolar coupling of the hole to optical phonons and the piezoelectric and deformation potential coupling of both the electron and the hole to acoustic phonons are usually not very important. This is because most materials are only weakly piezoelectric and the large spatial extent of Wannier excitons averages out short-range potential fluctuations.

The situation in QD is completely different. Due to the *local* charge neutrality of the QD exciton there is no polar coupling of the exciton to optical phonons (for infinite barriers). The matrix element (14) is identical to zero; the "polaron clouds" of the electron and hole exactly cancel each other. This decreasing polar coupling of the exciton to optical phonons is however accompanied by an increasing coupling to short-wavelength phonons, due to the decrease of the spatial extent of the exciton with decreasing crystallite size. This tendency towards increased coupling is immediately apparent from the integral in (14), which is essentially a Fourier transform of $|\phi(\mathbf{r})|^2$; as $|\phi(\mathbf{r})|^2$ becomes more concentrated in real space, as by quantum confinement, the integral becomes larger for large q. (For extended states, this same integral reduces to momentum conservation). The actual volume scaling of the coupling to short-wavelength phonons depends also on the $\mathbf{q}$ dependence of $M^{c}_{\mathrm{nq}}-M^{v}_{\mathrm{nq}}$. In the simplest case of a short-range coupling $M_0=M^{c}_0-M^{v}_0$ to Einstein phonons with frequency ω_0, the dimensionless coupling strength $S=\sum_{\mathbf{q}}|M_{0\mathbf{q}}/(\hbar\omega_0)|^2$ (see below) varies like $\int d^3r\,|\phi(\mathbf{r})|^4\sim 1/V$ for a QD and $\sim 1/a_0^3$ for a bulk exciton. Therefore, it is enhanced by a factor a_0^3/V under quantum confinement. Any real situation, such as coupling to acoustic phonons, will be more complicated than this, but the net result will be an increased coupling to short-wavelength phonons as the QD becomes smaller.

The Hamiltonian (13) ("independent boson model") can be diagonalized exactly. The problem is equivalent to that of displaced harmonic oscillators. Correspondingly, the imaginary part of the optical susceptibility is determined by the overlap of the unperturbed and displaced oscillator states. The result has the well-known form

$$\mathrm{Im}\chi=\frac{C}{2\pi V\hbar}\int_{-\infty}^{+\infty}dt\, e^{i\hbar^{-1}(E-E_x)t-F(t)} \;, \tag{15}$$

where

$$\begin{aligned}F(t)=&-\frac{it}{\hbar}\sum_{n,\mathbf{q}}\frac{|M_{\mathrm{nq}}|^2}{\hbar\omega_{\mathrm{nq}}}\\&+\sum_{n,\mathbf{q}}\frac{|M_{\mathrm{nq}}|^2}{|\hbar\omega_{\mathrm{nq}}|^2}\{(g_{\mathrm{nq}}+1)[1-\exp(-i\omega_{\mathrm{nq}}t)]\\&\qquad+g_{\mathrm{nq}}[1-\exp(i\omega_{\mathrm{nq}}t)]\}\end{aligned} \tag{16}$$

and

$$g_{\mathrm{nq}}=[\exp(\hbar\omega_{\mathrm{nq}}/k_BT)-1]^{-1} \;. \tag{17}$$

The derivation and a detailed discussion of (15) and (16) can be found in Ref. 31.

It is useful to split $F(t)$ in a part $F_0(t)$ due to the nonpolar coupling to optical phonons (the polar coupling being zero as discussed above) and a part $F_{ac}(t)$ due to the coupling to acoustic phonons. Within the Einstein model, optical phonons with frequency ω_0 give rise to a "line shape" (i.e., a set of phonon sidebands or satellites) of the form[28]

$$\begin{aligned}\mathrm{Im}\chi=\frac{C}{V}e^{-S(2g_0+1)}\sum_{l=-\infty}^{+\infty}&\left[\frac{g_0+1}{g_0}\right]^{l/2}\\&\times I_l\{2S[g_0(g_0+1)]^{1/2}\}\\&\times\delta(E-E_x+S\hbar\omega_0-l\hbar\omega_0) \;,\end{aligned} \tag{18}$$

where $S=\sum_{\mathbf{q}}|M_{0\mathbf{q}}/(\hbar\omega_0)|^2$ is the Huang-Rhys parameter and I_l are the Bessel functions of the second kind. Equation (18) is a series of δ functions, spaced ω_0 apart. The coefficients of the delta functions correspond to the probability that l phonons are created ($l\geq 0$) or destroyed ($l<0$) during the optical transition. At zero temperature ($l\geq 0$) this probability follows a Poisson distribution $S^le^{-S}/l!$ and S can be identified with the average number of phonons emitted. For large $S\gg 1$ the Poisson distribution becomes a Gaussian, centered at $l=S$. The important III-V compounds such as GaAs are however weak coupling materials ($S\lesssim 0.1$ for QD larger than 50 Å) and hence most of the spectral weight (a fraction e^{-S}) will be in the zero-phonon line which is situated at $E_x-S\hbar\omega_0$, where $S\hbar\omega_0$ is the lattice relaxation energy.

The general behavior of $\mathrm{Im}\chi$, including now the acoustic phonons, can be obtained by convolving (18) with the Fourier transform of $e^{-F_{ac}(t)}$. This leads to a shift and a broadening of all optical phonon satellites because of the acoustic phonons. The individual spectral weights of the optical phonon sidebands do not however change. In weakly piezoelectric crystals and at zero temperature, the piezoelectric coupling changes the δ functions in (18) into infrared power-law singularities. This is because the average number of piezoelectric phonons created during the optical transition diverges. At low temperatures, each singularity will be smeared over a width $\sim\Theta k_BT$, where $\Theta=\Theta_c-\Theta_v$ is the dimensionless piezoelectric coupling constant.[29] Again, this coupling constant is usually small ($\Theta\lesssim 0.1$). For weak exciton-phonon coupling materials, we may thus conclude that the low-temperature exciton absorption spectrum in QD is dominated by the zero-(optical) phonon line. Its low-energy tail will be more or less exponential, whereas its central part will be an asymmetric Lorentzian whose width increases with temperature. The same conclusion holds for the emission spectrum which is just the mirror image of the absorption spectrum about the zero-phonon line. Also, Stokes's shift between emission and absorption due to phonons will be small.

With increasing temperature the relative weight of the zero- (optical) phonon line decreases and the spectrum broadens until the sidebands are completely smeared. However, in the case of GaAs, even at room temperature the majority of the spectral weight will still be in the zero-optical phonon line. We estimate that, for a 50-Å GaAs QD, the room-temperature exciton linewidth due to phonons will not be very different from that in the bulk; much the same can be said for the polaron shift. The polar coupling to optical phonons and the lifetime broadening by optical phonon ionization will be essentially absent, but there will now be the enhanced coupling of the exciton to short-wavelength phonons under quantum confinement as discussed above. We may thus reasonably hope to continue the process already noted for quantum wells[2] where the quantum confinement increases the strength of the exciton resonance without substantially increasing the phonon broadening. At low temperatures, the increased coupling to short-wavelength phonons will increase the linewidth compared to the bulk, but relatively narrow linewidths are predicted by our estimates. Hence we can conclude that over a useful range of sizes in weak phonon coupling materials such as III-V's, down to quite small QD the intrinsic phonon broadening will not preclude narrow lines for the discrete QD transitions.

In all QD studied so far, the exciton absorption linewidth was mainly determined by large fluctuations in the QD size, and not by the coupling to phonons. This holds both for the colloidal suspensions of semiconductors[7,8] and for the small semiconductor particles crystallized in glass matrices.[10,11] Optical emission was mainly from defect states and thus very broad and red shifted, due to the strong coupling of these states to lattice vibrations. Fast relaxation into such states, which are due to surface imperfections, will also give rise to lifetime broadening at low temperatures.

D. Illustrative examples

Although the precise values of the broadening are uncertain, we will give illustrative calculations of the linear susceptibility near a transition in small QD's. This will show explicitly the large absorption and refractive index changes and the distortion of absorption lines for strong resonances (as seen in absorption coefficient), and will provide example numbers for the nonlinear properties discussed below.

We give two examples, one for GaAs and one for InSb. In both cases we calculate only the lowest transition, using (8) to calculate the area of the δ function. For $|p_{cv}|^2$ we perform the usual averaging over polarization directions (yielding a factor of $\frac{1}{3}$), so that $|p_{cv}|^2 \rightarrow m_0 P^2$. We use published values for the matrix elements P^2,[32] neglecting any k dependence. This may not be a very good approximation because of the strong confinement we will use, but it will give a quantitative feel for the magnitude of the effects.

We assume that the absorption line (as seen in the imaginary part of the dielectric constant ϵ_2) is Lorentzian and that all the absorption is in the zero- (optical) phonon line as discussed above. The effects of all the other transitions are lumped together into background dielectric constants ϵ_∞, which are taken to be 12 and 16, respectively, for GaAs and InSb. In the vicinity of the resonance the dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$ may therefore be written as

$$\epsilon = \epsilon_\infty + \beta(\delta + i)/(1+\delta^2) , \tag{19}$$

where δ is the normalized detuning

$$\delta = (\Omega_x - \omega)/\Gamma_x ,$$

with $\hbar\omega$ being the photon energy E, $\hbar\Omega_x$ being the lowest transition energy E_x, and $\hbar\Gamma_x$ being the broadening. $\beta = 4\pi C/\hbar\Gamma_x V$ is chosen to give the Lorentzian for ϵ_2 the same area as that of the δ function from (8).

The GaAs QD is a 56-Å diameter sphere, whereas the InSb QD is 260 Å in diameter. The resulting quantum shifts of the first transition are difficult to estimate accurately. In the case of GaAs, the shift will be comparable to the widths of the relevant conduction and valence bands, and the first quantum dot transition may include a significant fraction of the oscillator strength of these bands. In the case of InSb the shift is comparable to the band-gap energy. We have used estimated approximate values for the lowest transition energies of ~2.1 eV and 0.43 eV for the GaAs and InSb spheres respectively. For the GaAs QD, we have chosen a linewidth of 0.5 meV. This is larger than the homogeneous linewidth (0.2 meV) measured for the GaAs bulk exciton at low temperature,[33] and is considerably larger than our estimate of the theoretical limit of QD phonon broadening at low temperature. For the InSb QD, bulk exciton linewidths are difficult to estimate because of the extremely low exciton binding energy. The band edge itself is known to be extremely abrupt, falling three decades in ~3 meV at low temperature.[34] The size of the InSb QD here is so large that the broadening from increased coupling to short-wavelength phonons is very small. We use a value of 0.1 meV for illustration. In both cases therefore we have chosen linewidths larger than the bulk and our low-temperature QD estimates, though still small compared to those likely to be encountered using present QD fabrication techniques, at least for multiple dots. The resulting calculations are shown in Fig. 1 (GaAs) and Fig. 2 (InSb). Refractive index n and absorption coefficient α are deduced from the complex dielectric constant ϵ in the usual manner, using $n^2 - \kappa^2 = \epsilon_1$, $2n\kappa = \epsilon_2$, and $\alpha = 2\omega\kappa/c$.

These calculations show several interesting features. First, the absolute strength of the resonance is indeed large compared to typical absorption and refraction behavior in the bulk materials. Second, the absorption strength is now so large that the refractive index changes significantly in the vicinity of the resonance, and hence the absorption coefficient is now no longer a symmetrical line. For the same reason, for the linewidths in these calculations, ϵ_1 also goes negative. Increasing the linewidth or the size of the QD would progressively eliminate both of these phenomena. It is also interesting to note the contrast between the two materials. Because of the factor of E^2 in the denominator of (9), the narrow gap QD can be a

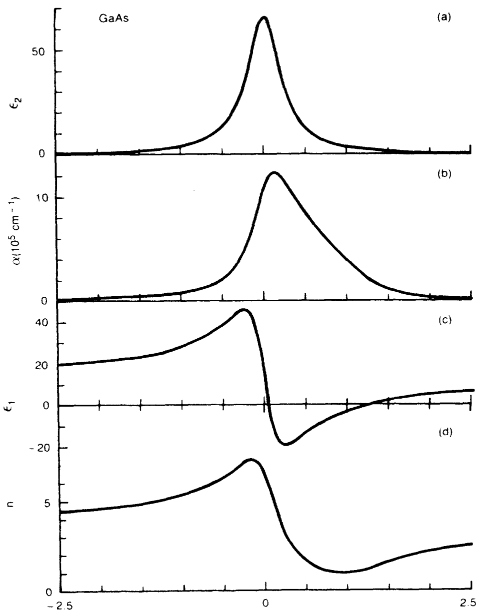

FIG. 1. Linear optical properties near the first quantum dot transition (estimated to be at ~2.1 eV) as seen inside a 56-Å GaAs sphere, assuming a broadening of 0.5 meV, and a background dielectric constant $\epsilon_\infty = 12$. (a) Imaginary part, ϵ_2, of the dielectric constant; (b) absorption coefficient, α; (c) real part, ϵ_1, of the dielectric constant; (d) refractive index, n.

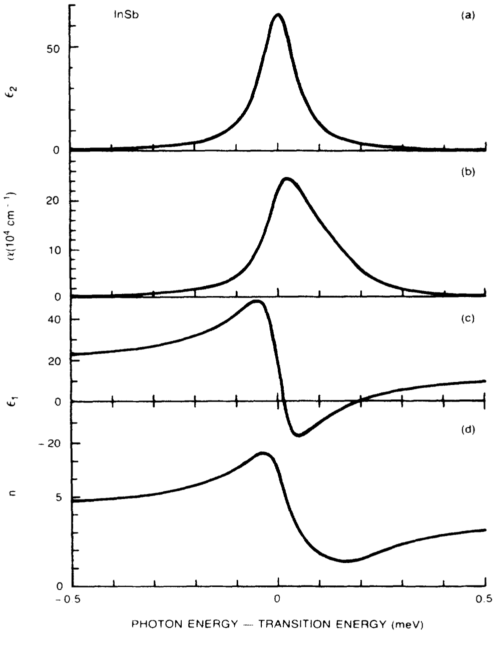

FIG. 2. As Fig. 1 but for an InSb sphere 260 Å in diameter, with transition energy of 0.43 eV, 0.1 meV linewidth, and background dielectric constant $\epsilon_\infty = 16$.

much larger volume for comparable strengths of the resonance as seen in the dielectric constants and refractive index; the absorption coefficient contains an implicit factor E (i.e., ω) that makes it relatively smaller for lower photon energies. Further decreasing the QD size in the narrow band-gap InSb case will increase the area under the resonance, but this is partly offset in the dielectric constants by the increased confinement energy which makes the factor E^2 in (9) larger again. In physically small quantum dots (e.g., < 50 Å), made using III-V direct narrow band-gap materials, the band-gap energy of the material from which the dot is formed will have relatively little influence on the transition energy because the k value is so high that the behavior very near to zone center is no longer relevant.

III. NONLINEAR ABSORPTION AND REFRACTION

When electron-hole pairs are created in a semiconductor by interband optical absorption, they influence the absorption spectrum. Most obviously, they fill states, preventing further absorption into these states by Pauli exclusion and hence saturating the absorption. The pairs usually also modify the nature of the electronic states because of Coulomb or exchange interactions. In bulk semiconductors, both of these interactions strongly modify the exciton absorption spectrum.[35,36] In quantum wells, the Coulomb interaction has relatively little effect on the excitons, although exchange is still significant.[4,5] This is because of the reduced dimensionality[5] and shows up as unusual transient behavior[3,4] and as a blue shift of excitons at low temperatures.[37,38] Below, we argue that in QD's only the state filling is important for absorption saturation of the lowest transition, just as in two-level systems.

Screening of the Coulomb interaction by charged particles requires that the screening particles undergo transitions, usually intraband, corresponding to a slight rearrangement in real space. In a QD, the allowed states are separated by large energies so that such transitions are difficult and screening is strongly inhibited. For the same reason, it is also difficult to polarize the exciton. Coulomb effects on the exciton wave function are thus suppressed by the quantum confinement, in much the same way as the effects of polar optical phonons on the excitons. If there are electrons and holes in levels in the QD, there will however be Coulomb interaction between the resulting net charge density and the net charge density of any created electron-hole pair. This will in principle influence the energy of the created pair. This effect is minimal however for much the same reasons that the effects of polar optical phonons are reduced. Allowed transitions in the QD spectrum correspond to the creation of electrons and holes in states of the same quantum numbers with substantially identical wave functions and hence substantially zero net charge density. In the ideal case of perfect confinement, the wave functions are exactly equal in the effective mass envelope approximation. This insensitivity of the transition energies to charge density is independent of whether the existing particles are equal numbers of electrons and holes or not, and regardless of whether or not existing electrons and holes are identically distributed between the allowed quantum states.

In general, it is possible to have two electrons or holes in any given energy level, because the individual electron and hole states are spin degenerate. This means however that there is no exchange interaction between the excited particles in a given energy level, because they have different spins. Hence there are identically no exchange effects if we only create electrons and holes in a given conduction level and a given hole level, respectively. This will be the case for absorption on the lowest QD transition. There will be exchange interactions with electrons and holes in other levels in the QD, but in the case of saturation of the lowest QD transition in an otherwise unexcited QD, there will be no populations in these other levels. Only if the temperature becomes very high will any other levels become occupied.

Because exchange and Coulomb effects are rigorously negligible, the absorption saturation of the lowest transition in the QD can be treated like a pair of two-level systems, one for each spin. Hence the absorption saturates as

$$\epsilon=\epsilon_\infty+\frac{\beta(\delta+i)}{1+\delta^2+I/I_s}\ , \tag{20}$$

where we define the "intensity" $I=E_0^2$ with E_0 being the peak amplitude of the oscillating electric field inside the QD. The saturation intensity is $I_s=\hbar/(\beta\tau V)$, where τ is the recombination time. We have not attempted to specify a value for τ since this lifetime will be very dependent on fabrication. It should be noted, however, that this lifetime has no relation to the broadening calculated above. The fundamental phonon broadening discussed above is not a lifetime broadening. Lifetime broadening from recombination will only become important if the lifetime becomes very short (e.g., <1 ps for 1 meV linewidth). It is also important to note that the intensities defined here are squared field amplitudes and do not exactly represent the true intensity, i.e., the rate of energy flow across a unit area in a unit time. The problem with the true intensity is that it involves the energy velocity, and this varies greatly in the vicinity of a strong resonance.[39] The squared field amplitudes are rigorously correct regardless of energy velocity dispersion, and are a suitable form for the discussion of local fields below. The saturation in terms of the external true intensity outside of and far from the QD is straightforward because there the dispersion is negligible.

When the optical polarization is such that transitions are allowed for both spins, complete saturation of this absorption will occur when there is one excited electron-hole pair per QD (two pairs is the maximum possible, and this corresponds to inversion). From this we may deduce the absorbed energy density required to saturate the transition, namely, one photon energy per QD.

The magnitude of the change in absorption per absorbed photon per unit volume is not significantly different in the QD from that of quantum well or bulk excitons for a given linewidth. Although the absorption in the QD is larger, the volume in which one photon must be absorbed for saturation is correspondingly smaller. The real advantage of the QD is perhaps that the absolute changes in absorption and consequently in the refractive index can be much larger before the transition saturates. This is particularly important for nonlinear refractive effects, where in bulk and quantum well material the readily saturable excitonic nonlinear absorption often completely saturates before enough index change or absorption change takes place to make a given device switch. Furthermore, this theory predicts that relatively complete saturation of absorption should be possible in the QD, because there are no competing mechanisms such as bandgap renormalization that inhibit deep absorption saturation in bulk and quantum well materials.

IV. LOCAL-FIELD EFFECTS

When fabricated, the QD's will be most likely embedded in a matrix or deposited on a substrate; thus they will be surrounded by a medium of different (and usually smaller) dielectric constant. In this case in addition to the electronic confinement discussed in the previous sections local-field effects due to the dielectric confinement will strongly influence the optical properties of the QD. Even in the case where the surrounding medium has a similar background dielectric constant, the dielectric constant in the QD can be very different in the vicinity of a resonance, and local-field effects cannot be neglected. The consequences of such local-field effects with semiconductor microcrystallites have been briefly discussed by some of us before,[40] with intrinsic optical bistability being a possible consequence. Similar intrinsic bistability resulting from local-field effects in small particles has also recently been discussed by Leung.[41] In this section we discuss such effects specifically in the context of small QD's.

The field inside a particle small compared to the wavelength is different from the field in the surrounding medium.[42,43] In an irregularly shaped particle the field can be highly nonuniform and is concentrated in the regions of large curvature. This is of course the well-known mechanism utilized in "lightning rods." The concentration of the field inside the particle can produce major changes in the optical response; it is responsible for the unusual properties of metal island films,[44] as well as for surface enhanced Raman scattering[45] and for the large nonlinearities of metal and semiconductor doped glasses.[46,47] In the most general case there is no simple analytical form to describe the distribution of the field inside the particle. However for some simple geometrical shapes, such as ellipsoids or spheres, the field inside the particle is uniform and proportional to the field outside. It is then possible to define a local-field factor f, such that $E_{\text{in}}=fE_{\text{out}}$. The local-field factor depends on the shape of the particle and on the dielectric constant of the particle $\epsilon=\epsilon_1+i\epsilon_2$ relative to that of the surrounding medium. For simplicity we assume that the particles are in vacuum. However if the medium surrounding the particle is not the vacuum, then all the formulas still apply provided that the dielectric constant is normalized to that of this surrounding matrix. In the case of the simple shapes for which the field in the particle is uniform, it turns out that the shape dependence can be characterized by a single parameter, the depolarization factor A.[43] Then $f=[1+A(\epsilon-1)]^{-1}$ and the intensity inside the particle is $I_{\text{in}}=FI_{\text{out}}$ with

$$F=|f|^2=\frac{A^{-2}}{(\epsilon_1-1+A^{-1})^2+\epsilon_2^2}\ . \tag{21}$$

In general the real part of the dielectric constant is larger than 1, so that $F<1$ and the field intensity inside the particle is smaller than outside. However the field intensity inside the particle can become very large in a region of anomalous dispersion for large negative ϵ_1 and small ϵ_2.

We now consider the dispersion of local-field and intensity factors due to the particular dielectric constant of the QD as discussed in the preceding sections. At first, we will neglect the saturation processes to get a better physical insight into the mechanisms. For the two-level-system-like behavior as in (19), the spectral dependence of F can be expressed in a universal form as a function of the two reduced parameters, a characteristic detuning $\delta_0=-\beta/[2(\epsilon_\infty-1+A^{-1})]$ that measures the ratio of the resonant to the nonresonant oscillator strengths (note that with our convention δ_0 is negative) and F_∞, the asymptotic value of F far from resonance, i.e., $F=F_\infty=1/[A(\epsilon_\infty-1+A^{-1})]^2$. Hence we obtain

$$F=F_\infty\frac{1+\delta^2}{1+(\delta-2\delta_0)^2}\ . \tag{22}$$

This line shape is the well-known Fano-interference profile;[48] it is plotted in Fig. 3 and deserves several comments. Far from resonance F approaches $F_\infty<1$. The field inside the particle is smaller than outside and the apparent dielectric constant is reduced. In a small range around the resonance very large changes occur. F presents two extrema $F_\pm$ for $\delta_\pm=\delta_0\pm(1+\delta_0^2)^{1/2}$ symmetrically spaced around δ_0, the detuning for which the asymptote is crossed. The magnitude of the two extrema are related by $F_+F_-=F_\infty^2$. Thus for small negative values of δ around δ_- the field is concentrated inside the particle, whereas in the vicinity of δ_+ the field is expelled from the particle. If the resonant contribution is large compared to the constant background then the minimum of F occurs almost at resonance $\delta_+\sim 0$ and $F_+\sim 0$, whereas the maximum occurs at $\delta_-\sim 2\delta_0$ and $F_-\rightarrow\infty$. In this case all the extremely steep variations of F occur in a very small range of frequencies close to the resonance; on one side the field is very strongly concentrated in the particle and on the other side the field hardly penetrates into the particle.

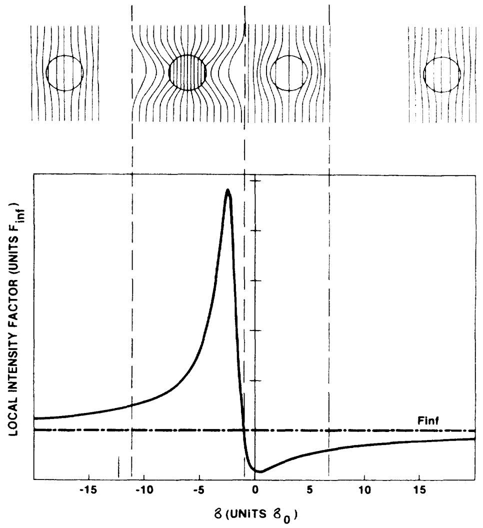

FIG. 3. Dispersion of the local intensity factor for a dielectric constant given by (19). In the reduced units this lineshape is universal and corresponds to the Fano-interference profile.

It is very clear from this discussion that the local-field effects will enhance any sensitivity of the dielectric constant to the applied field. In particular, because of saturation effects the dielectric constant inside the QD depends on the intensity, and hence any change in the intensity incident on the QD will modify the local-field factor; this in turn will change the intensity in the particle, which will change the dielectric constant and so on. This establishes an intrinsic feedback mechanism that, depending on the value of the detuning, can be positive or negative. Hence regions of intrinsic optical bistability can occur,[49,50] involving a single QD and of course requiring no external feedback.

To describe this mechanism correctly, we need to use a self-consistent description of local-field effects and saturation. When an intensity I_{out} is applied to a saturable QD, the dielectric constant inside the QD including local-field effects is given using (20) by

$$\epsilon=\epsilon_\infty+\beta(\delta+i)/[1+\delta^2+FJ]\ , \tag{23}$$

where $J=I_{\text{out}}/I_s$ is the incident (field-amplitude-squared) intensity normalized to the saturation intensity. Because in (23) the real and imaginary parts of ϵ are related by $\epsilon_1=\epsilon_\infty+\epsilon_2\delta$, an analytical solution of this equation can be found in the form of the cubic relation

$$\epsilon_2^3-\beta\frac{1+\delta/\delta_0}{1+\delta^2}\epsilon_2^2+\left[\frac{\beta^2}{4\delta_0^2(1+\delta^2)}+\frac{A^{-2}J+\beta^2\delta/\delta_0}{(1+\delta^2)^2}\right]\epsilon_2-\frac{\beta^3}{4\delta_0^2(1+\delta^2)^2}=0\ . \tag{24a}$$

This equation can be cast into a slightly different form that gives a better insight into the underlying physics. Remembering that for $J=0$, $\epsilon_{20}=\beta/(1+\delta^2)$ and that the saturation intensity for a detuning δ is $I_s(\delta)=(1+\delta^2)I_s$, we can rewrite (24a) as

$$\frac{\epsilon_{20}-\epsilon_2}{\epsilon_2}=\frac{FI_{\text{out}}}{I_s(\delta)}\ , \tag{24b}$$

which expresses the fact that at a given frequency the relative change of the imaginary part of the dielectric con-

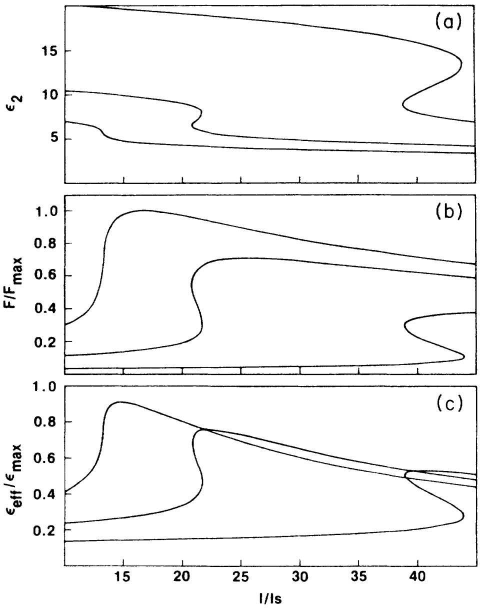

FIG. 4. Plots of the imaginary part of the dielectric constant (a), of the local intensity factor (b), and of the imaginary part of the effective dielectric constant (c) for a 56-Å-diameter GaAs sphere as a function of the light intensity normalized to the saturation intensity. The detunings are $\delta=-1.5$, -2.25, and -2.75. Other parameters are as in Fig. 1.

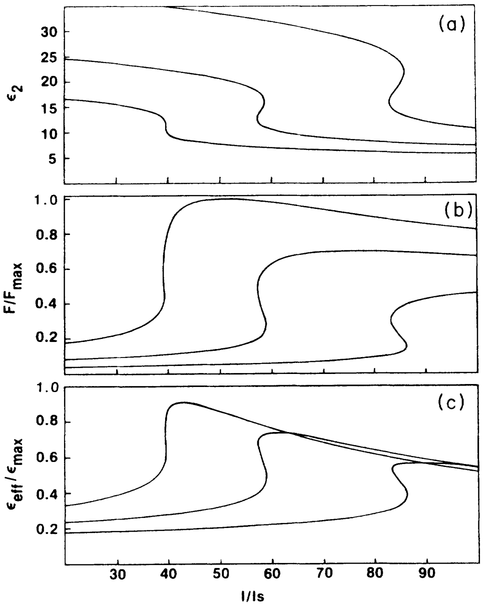

FIG. 5. Same plots as in Fig. 4 but for a 260-Å-diameter InSb sphere. The detunings are $\delta=-1$, -1.4, and -1.8. Other parameters are as in Fig. 2.

stant is simply the effective intensity inside the QD normalized to the saturation intensity at this frequency.

To illustrate this discussion we have solved (24a) using parameters for GaAs and InSb QD as discussed in the preceding sections. We assume that the QD have a spherical shape, i.e., $A=\frac{1}{3}$. In Fig. 4 we present the variations of ϵ_2 and F as functions of the intensity for a 56-Å-diameter GaAs sphere at three detunings -1.5, -2.25, and -2.75. In Fig. 5 the corresponding quantities for a 260-Å-diameter InSb sphere are plotted for the three detunings -1, -1.4, -1.8. Two types of behavior can occur. For small negative detunings the positive feedback is strong enough to produce an intrinsic bistability of the QD. The corresponding curves exhibit the characteristic "*S*" shape showing that the dielectric response is a multivalued function of the intensity in a certain range. Near the bistable region, the local-field factor is rather small and although the effective dielectric constant also exhibits the bistable behavior, the step at the switching transition is compressed as compared to that of ϵ_2. It is also interesting to note that the orientation of the "*S*" in the ϵ_2 curve is opposed to that of the two other ones because of the influence of the real part of ϵ. For larger negative detunings the feedback is just strong enough to produce a kink in the curve of ϵ_2. This implies the possibility of strong modulation of the absorption for a narrow range of intensities, hence offering differential gain.

The mechanism we have described should be observable in a single QD. In the case of QD's arranged in a matrix, the sensitivity of δ_0 to the shape factor A and to the size through β can be utilized for wavelength selective excitation of some particular subsets of QD's. This can add flexibility in storage or switching applications. If the QD's are located sufficiently close to one another that "macroscopic" electromagnetic interactions become important, collective effects should appear. They can be described by conventional electromagnetic theory and will cause renormalization of the parameters in (23) as discussed for example in Ref. 45. Most of the conclusions of this section will remain valid in this case.

V. CONCLUSIONS

We have examined theoretically the linear and nonlinear optical properties of a semiconductor microcrystallite or QD. We conclude first that there is a useful range of sizes of QD's for which (i) the electronic states are still like those of a crystalline semiconductor and can be usefully described by the effective mass approximation using envelope functions to describe the effects of confinement, (ii) the confinement dominates over the Coulomb interaction of electron and hole so that the allowed optical transitions are essentially between single-particle eigenstates, and (iii) the increased coupling to short-wavelength phonons that is inherent in such small structures is not so strong that the broadening of the absorption lines from this unavoidable mechanism will be much larger than that which exists anyway in the bulk material. In this "small-QD" limit, which will occur for QD's much smaller than the bulk exciton size, the linear absorption spectrum will be rigorously a series of lines. This limit can probably be attained in GaAs and other, narrower-gap semiconductors. It will be more difficult to attain in wider-gap materials because the bulk exciton is so small; the necessary very small crystallite might be even more difficult to fabricate, and it might have to contain so few atoms that it might not behave like a crystalline semiconductor. It becomes easier to achieve this limit for narrower band-gap materials because larger crystallite sizes can be used.

In the small QD limit, the absorption saturation of the lowest interband transition will take on a very simple form, corresponding to the saturation of a two-level system. There will be no band-gap renormalization. Hence the saturation may be relatively complete. The absorbed energy density for a given change of absorption will not be better than bulk or quantum well systems with similar broadenings, but the QD has the substantial advantage that the available change in absorption and/or index could be very large. When the effects of local fields are considered, it is found that these could have substantial consequences for the nonlinear properties. Under relatively extreme conditions, bistability may be possible due to the feedback of the changes in dielectric constant from absorption saturation on the local field factor. This serves to demonstrate that local field effects can be very important in describing the QD optical properties.

All of the discussion in this paper concerns the optical properties of a perfect QD, because this sets the limit on what we may hope to achieve. Whether such a QD can be made remains to be seen, and this is the subject of much research. This discussion shows however that, in principle, it is possible to make artificial materials with very desirable optical properties, and hopefully this will stimulate further research in this area.

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