Far-infrared response of spherical quantum dots: Dielectric effects and the generalized Kohn's theorem

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The influence of the dielectric environment on the far-infrared (FIR) absorption spectra of two-electron spherical quantum dots is theoretically studied. Effective mass and envelope function approaches with realistic steplike confining potentials are used. Special attention is paid to absorptions that are induced by the electron-electron interaction. High confining barriers make the FIR absorption coefficients almost independent of the quantum dot dielectric environment. Low barrier heights and strong dielectric mismatches preserve the strong fundamental (Kohn) mode but yield the cancellation of excited absorptions, thus monitoring dielectrically induced phase transitions from volume to surface states.

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I. INTRODUCTION

A direct consequence of the generalized Kohn's theorem is that we cannot expect many-body effects on far-infrared (FIR) absorptions in a quantum dot (QD) confined by a parabolic potential, as long as the interparticle interaction depends on the relative distance between carriers only.[1] Motivated by the experimental results obtained by Sikorski and Merkt,[2] several authors[3–5] demonstrated that the insensitivity of the FIR absorption spectra to Coulomb interaction comes from the separability of the center-of-mass motion from the relative motion in the many-body Hamiltonian when parabolic confining potentials are involved. Then, since the dipole operator couples exclusively to the center-of-mass Hamiltonian, the FIR radiation promotes only center-of-mass excitations, yielding a FIR spectrum similar to that of a single carrier in the QD.

However, deviations from the generalized Kohn's theorem have been reported in parabolic QDs. For instance, intersubband mixing[6] and spin-orbit coupling[7] do not allow the separation of the center-of-mass motion, thus yielding a FIR absorption spectrum that may reveal many-body effects. These effects become significant for the valence band but are negligible for the conduction band excitations of few-electron QDs.[1]

A larger influence of the electron-electron interaction on the FIR absorption spectra arises in QDs whose confining potential deviates from the parabolic shape (see, e.g., Ref. 8). In most cases, the spatial confining potential in QDs originates from the band offset between neighbor materials. Thus, although parabolic potentials may be appropriate to describe the low-lying states of large QDs, they are not suitable to account for confinement in small nanocrystals, such as the nearly spherical nanocrystallites synthesized by wet chemistry methods or in the case of multishell QDs, for example. One should employ steplike confining potentials instead. If we do so, the center-of-mass and relative motions cannot decouple and, as a consequence, the electron-electron interaction may affect the FIR absorption spectra so that even new Coulomb-induced transitions may arise.[9]

The extent to which many-body effects are reflected in the FIR absorption spectrum depends on the relevance of these effects in the system dynamics, which in turn is governed by the ratio between the kinetic energy T and the Coulomb repulsion energy V. The simplest model one can adopt for the description of QDs confined by steplike potentials is the full confinement of the carriers in the dot by means of infinitely high barriers located at the QD border. In this case, the so-called confinement level a_0^*/R (a_0^* and R standing for the effective Bohr and the QD radii, respectively) determines the relevance of the electron-electron interaction effects in the FIR absorption spectrum of spherical QDs.[10]

However, the assumption of infinitely high barriers is often too restrictive to accurately describe the QD physics. Indeed, several studies[11–13] have shown that the relaxation of such a strong condition (by employing finite barrier confining potentials) considerably improves the agreement between theoretical predictions and experimental observations. We will show later that the height of the confining barrier by itself does not alter the many-body contribution to the FIR absorption spectra. However, we will also show that the barrier height can yield dramatic changes when combined with another type of confinement that also affects the coupling between the center-of-mass and relative motions, i.e., the dielectric confinement. As stated above, a necessary condition for the generalized Kohn's theorem to remain valid is that the electron-electron interaction is dependent only on the relative distance between the electrons. This holds when the dielectric response of the medium is homogeneous, but definitely not when the dielectric constant of the QD material is different from that of the surrounding medium. In such a case, image charges arise at the interface between the two media, modifying the Coulomb interaction potential due to the interaction between each electron and the image charges induced by the others (polarization of the Coulomb interaction; see, e.g., Refs. 14 and 15). The modified potential cannot be expressed exclusively in terms of interelectron distances and so the polarization of the Coulomb interaction itself breaks the generalized Kohn's theorem.

In addition to the polarization of the Coulomb interaction (a many-particle effect), dielectric confinement also presents a single-particle contribution, the so-called self-polarization potential, which accounts for the interaction of the electrons with their own induced charges. This potential presents a

profile revealing a slight destabilization in the medium with a higher dielectric constant (the QD material in the present work) and a deep, narrow attractive well close to the interface in the other medium[15,16] (which we will consider to be air or a vacuum). Under conditions of large dielectric mismatch, the image charges can have a considerable effect on the QD energy spectrum and the electronic density distribution in the QD. Thus, it has recently been reported[16,17] that, under specific conditions, the electronic density can undergo a transition from volume states (i.e., states confined in the QD volume) to surface states, the latter being localized mainly in the self-polarization potential well. Interestingly, the relevance of many-body effects in these surface states is mostly governed by polarization effects. Indeed, when the QD is embedded in a high dielectric constant matrix, the electrons in the surface state behave as almost independent particles, whereas an enhanced angular correlation leads to the formation of a Wigner-like molecule when the surrounding medium is air or a vacuum.[16] Therefore, important changes in the FIR absorption spectra can be expected when dielectrically induced surface states are formed.

In this paper we show how both the relaxation of the infinite barrier condition and the presence of dielectric mismatches influence the low-energy region of the FIR absorption spectrum of a two-electron spherical QD. We concentrate on the absorption coefficients corresponding to a certain type of transitions which are induced by the electron-electron interaction. We will show that, in the presence of high confining barriers, the different contributions of image charges (single- and two-particle effects) almost cancel each other out. In the absence of dielectric mismatch effects, the relaxation of the infinite barrier condition has almost no effect on the FIR spectra. Therefore, in both situations, the confinement level a_0^*/R characterizes the many-body contribution to the FIR absorption spectra. But decreasing the confining barrier height in conditions of strong dielectric mismatch can yield a sudden change in the FIR absorption spectrum. This change can be associated with a previously reported dielectrically induced phase transition from volume to surface states,[16] which could therefore be monitored by means of FIR spectroscopy measurements.

II. THEORETICAL OUTLINE

We work within the effective mass and envelope function approximations, and we consider only the conduction band states. Within the dipole approximation, the absorption coefficient associated to a transition from the ground $|0\rangle$ to an excited state $|n\rangle$ can be calculated as

$$\Gamma = |\langle n|\mathbf{r}|0\rangle|^2. \tag{1}$$

Since, according to a theorem by Wigner,[18] the ground state symmetry of a two-electron spherical QD in the absence of external fields is ^1S_g, the selection rules allow transitions only to excited states with symmetry ^1P_u.[19] Thus, only these transitions can be active in the absorption spectra. To account for the low-lying states of both symmetries, first we solve the one-particle effective-mass Schrödinger equation, in atomic units,

$$\mathcal{H}(\mathbf{r}) = -\frac{1}{2}\nabla\left(\frac{1}{m^*(r)}\nabla\right) + V(r) + V_s(r), \tag{2}$$

considering a position-dependent electron effective mass[20] $m^*(r)$ and a steplike confining potential $V(r)$, and including the self-polarization potential $V_s(r)$, which is previously computed following the procedure given in Ref. 21. The radial parts of the exact single-particle eigenfunctions are determined numerically on a grid extending far beyond the dot radius R. Products of these basis functions are then used to construct configuration-interaction (CI) expansions of the symmetry- and spin-adapted two-electron configurations. The two-electron Hamiltonian containing Coulomb interaction and polarization terms[15] is then diagonalized in the CI basis set. As a result, we get two-particle wave functions and energies. We use as many single-particle basis functions and as long a CI expansion as are needed to achieve convergence and the required accuracy.[22] Due to the degeneracy of the three $n\,^1P_u$ wave functions exclusively differing in the quantum number associated with the z projection of the total angular momentum (M_z), the eigenstates (and, therefore, the absorption coefficients) are only computed for a given value of M_z. The use of the Wigner-Eckart theorem[23] then yields the total absorption coefficient

$$\Gamma_n = \sum_{M_z=-1,0,1} |\langle nM_z|\mathbf{r}|0\rangle|^2, \tag{3}$$

which is proportional to the absorption intensity.

III. RESULTS AND DISCUSSION

We concentrate on the absorption coefficients involving the ground state and the four ^1P_u lowest-lying states. The first and most intense transition Γ_1 corresponds to the excitation from the ground state to the $1\,^1P_u$ state. This transition is the only one that is allowed when the confinement potential is harmonic. We are interested, though, in transitions induced by center-of-mass and relative motion coupling, and more particularly in those induced by the electron-electron interaction. Therefore, we will pay attention to the absorptions Γ_2 ($1\,^1S_g \rightarrow 2\,^1P_u$), Γ_3 ($1\,^1S_g \rightarrow 3\,^1P_u$), and Γ_4 ($1\,^1S_g \rightarrow 4\,^1P_u$), arising next in the spectrum, which are forbidden in the case of parabolic potentials. Their strengths relative to Γ_1 are represented in Fig. 1, as a function of the confinement level a_0^*/R for two different confining barrier heights, namely, $V_0 \rightarrow \infty$ and $V_0 = 0.5$ eV. In this first series of calculations dielectric effects are ignored. The dielectric constant for the QD surroundings is then chosen to be the same as that of the QD.

When the electrons are in the strong confinement regime (i.e., when a_0^*/R is large), the Coulomb repulsion becomes negligible, and the kinetic energy dominates the system dynamics. In these conditions, the electrons behave as independent particles in the QD and the absorptions induced by the Coulomb interaction then become negligible. This behavior is observed in Fig. 1 for Γ_2 and Γ_3, which tend asymptotically to zero as we increase a_0^*/R. Thus we can say that these transitions are induced by the Coulomb interaction. In contrast, the relative coefficient of Γ_4 remains almost constant in

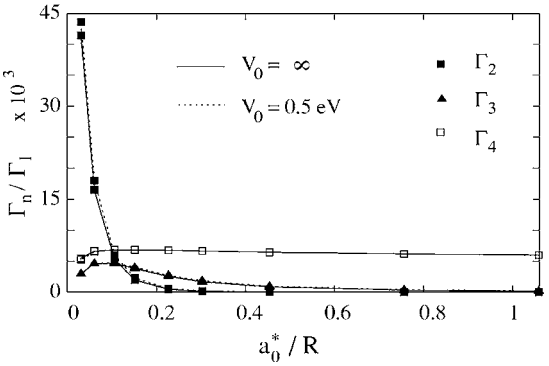

FIG. 1. Absorption coefficients Γ_2 (solid squares), Γ_3 (solid triangles), and Γ_4 (open squares) relative to Γ_1 vs the electron confinement level a_0^*/R, in the absence of dielectric mismatch, for two different barrier heights $V_0=\infty$ (solid lines) and 0.5 eV (dotted lines). Lines are only guides for the eye.

all the confinement range, denoting that it is basically a single-particle effect (arising from the center-of-mass and relative motion coupling).

As we move toward the other limit, i.e., the weak confinement regime, the relative coefficients of Γ_2 and Γ_3 become significant, following the increasing relevance of the Coulomb repulsion. In particular, Γ_2 increases exponentially, becoming extremely enhanced for small a_0^*/R values. In this limit of weak confinement, the Coulomb interactions exert a decisive influence on the system dynamics, yielding a strong correlation between the electrons that may eventually give rise to Wigner phases in the QD volume. As we show next, the peculiar enhancement of Γ_2 is related to the presence of Wigner-like states in the QD, similar to those predicted by Ugajin[9] in the case of two-dimensional (2D) square well QDs. To monitor these states, in Fig. 2 we have represented the radial pair density $P(r_1,r_2)=2\int|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2 r_1^2 r_2^2 \sin\theta_1 \sin\theta_2\, d\phi_1 d\phi_2 d\theta_1 d\theta_2$ for the ground state ^1S_g [Fig. 2(a)] and the three ^1P_u lowest-lying states [Figs. 2(b)–2(d)], which are involved in the absorptions Γ_1, Γ_2, and Γ_3, respectively. Figure 2, which corresponds to an extremely weak confinement regime $a_0^*/R=0.03$, reveals that the strong absorption coefficient Γ_2 is associated with a large redistribution of the electronic density in the transition [see Figs. 2(a) and 2(c)], which is not the case of the other transitions. Indeed, the excited state involved in this transition [Fig. 2(c)] presents a singular electronic distribution characterized by a radial Wigner-like localization of the electronic density, where the electrons avoid each other by localizing their electronic density in different radial positions.

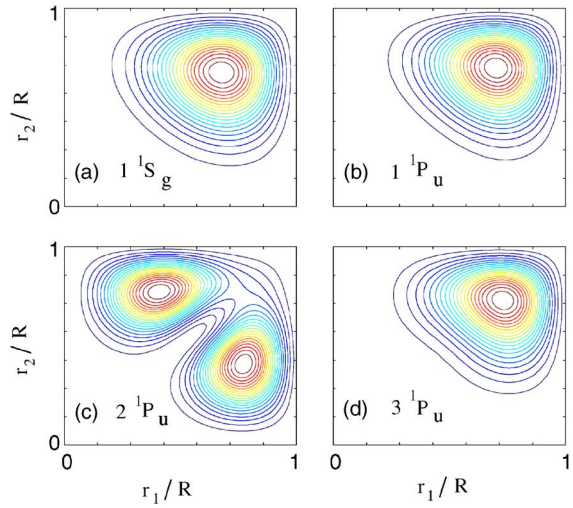

FIG. 2. (Color online) Radial pair densities $P(r_1,r_2)$ of the two-electron ^1S_g ground and three ^1P_u lowest-lying states for $a_0^*=0.03$, $V_0=\infty$, in the absence of dielectric mismatch between the QD and the surrounding medium.

Figure 1 also reveals that in the absence of dielectric mismatch it is the confinement level a_0^*/R that determines the relative strength of the FIR absorptions independently of the confining barrier height, as shown by the comparison of the results obtained with $V_0\to\infty$ (full lines in Fig. 1) and $V_0=0.5$ eV (dotted lines in Fig. 1), which almost coincide. We will show later that, in the presence of large dielectric mismatch between the QD and its environment, this is no longer necessarily true.

To approach the study of the dielectric effects on the FIR absorption spectrum, we will consider first the case of a QD confined by impenetrable barriers and immersed in air or a vacuum ($m^*=\varepsilon=1$). The choice of such a QD environment is made in order to maximize the polarization charges.[15] Once the external medium is fixed, the amount of image charge that arises at the QD border depends exclusively on the QD dielectric response; the larger the QD dielectric constant is, the larger the amount of induced charge will be in our case. However, increasing the QD dielectric constant also enhances the screening of the direct electron-electron interaction (bare Coulomb interaction). Therefore, one must be careful when studying changes in the FIR absorptions as an exclusive function of the dielectric mismatch (i.e., the QD dielectric constant) because the total absorption coefficients will depend on both the direct Coulomb and polarization contributions. Thus, to isolate the dielectric mismatch effect, in Fig. 3 we have analyzed the absorption coefficients Γ_2 and Γ_3 (corresponding to transitions induced by the electron-electron interaction) relative to Γ_1 as a function of the QD dielectric constant ε_{QD}, but simultaneously changing the electron effective mass in order to keep the confinement level a_0^*/R (and thus the bare Coulomb contribution) constant. These calculations are presented in Fig. 3 for $a_0^*/R=0.06$, with $R=7$ nm. In addition, the data series corresponding to the absence of dielectric mismatch have been included for the sake of comparison (series labeled as *B*). Since dielectric discontinuity gives rise to two different contributions, namely, a many-particle effect coming from the polarization of the electron-electron interaction and a single-particle one coming from the self-polarization, and we are mostly interested in many-particle effects, in Fig. 3 we also present a set of calculations including the dielectric contribution corresponding exclusively to the polarization of the electron-electron interaction (*S*0 series in Fig. 3). We should remark that this calculation does not correspond to any real case, in the sense that this contribution cannot be disentangled from the self-polarization one. However, it will provide a deep insight into the analysis of many-body effects on the absorption coefficients.

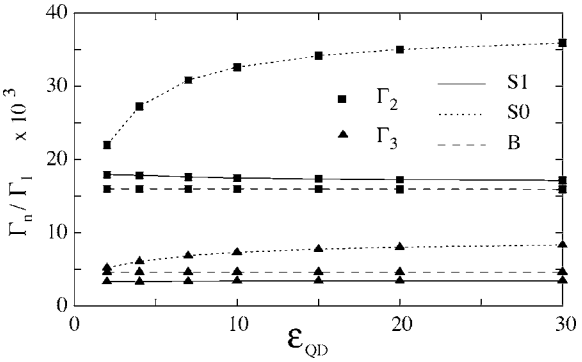

FIG. 3. Coulomb-induced absorption coefficients Γ_2 (squares) and Γ_3 (triangles) relative to Γ_1 as a function of the QD dielectric constant ε_{QD}, for an $R=7$ nm, $V_0=\infty$ two-electron spherical QD in air or a vacuum. The $S1$ series include full dielectric effects; the $S0$ series exclude the self-polarization contribution. The B series correspond to the case of dielectric matching between the QD and the surroundings. All calculations have been performed for a fixed value of $a_0^*/R=0.06$. Lines are only guides for the eye.

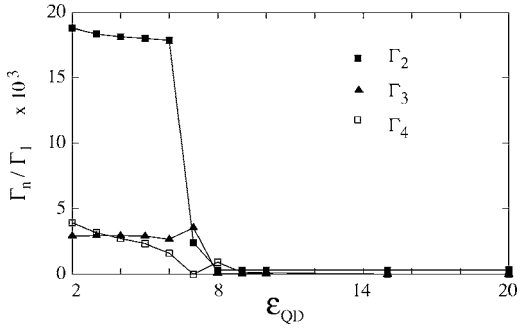

FIG. 4. Absorption coefficients Γ_2 (solid squares), Γ_3 (solid triangles), and Γ_4 (open squares) relative to Γ_1 as a function of the QD dielectric constant ε_{QD}, for an $R=7$ nm, $V_0=1.5$ eV two-electron spherical QD in air or a vacuum. All calculations have been performed for a fixed value of $a_0^*/R=0.06$. Lines are only guides for the eye.

As we stated above, the presence of polarization charges modifies the electron-electron interaction potential in such a way that it can no longer be expressed as an exclusive function of interelectron distances. This fact enhances the coupling between the center-of-mass and relative motions, so that we could expect a larger influence of many-body effects on the FIR absorption coefficients when the polarization of the electron-electron interaction is taken into account. This is reflected in Fig. 3 ($S0$ data series), where both Γ_2 and Γ_3 are enhanced with respect to the case of a QD that is dielectrically matched to the environment.

However, when the self-polarization contribution is also taken into account (the $S1$ series in Fig. 3), the influence of the dielectric effects almost cancels out. This surprising result could be explained by considering the particular profile of the self-polarization potential within the QD volume, which becomes more and more destabilizing as we move away from the QD center.[16,24] This one-particle potential is superimposed on the spatial confining potential, resulting in a profile that deviates from the parabolic shape to a lesser extent than the steplike one. Therefore, self-polarization tends to diminish the center-of-mass and relative motion coupling, in contrast to the enhancement produced by the Coulomb polarization potential. Thus, both effects somehow compensate, and the influence of many-body effects on the FIR absorption coefficients remains almost unaltered. Interestingly, the sum of one- and two-particle dielectric contributions becomes almost independent of the QD dielectric constant, so that, although the resulting Γ_2 and Γ_3 are slightly different from their counterparts in the absence of dielectric mismatch, the relative absorption coefficients are still determined by the confinement level a_0^*/R.

The issue of considering finite confining barriers and, simultaneously, strong dielectric mismatches is rather more involved, because in this case the leakage of the electronic density into the barrier region can completely change the physics in the QD. Indeed, when the confining barrier is small enough (or the dielectric mismatch large enough) a transition from volume states to surface states may occur.[16,17,25] The driving force is the narrow, deep well of the self-polarization potential, which is able to trap the electronic density in a thin spherical crown in the external medium, close to the QD border. Many-particle interactions take on special relevance in these surface states. Thus, the electronic density undergoes a strong radial localization in a nonscreening external medium ($\varepsilon=1$), yielding a large enhancement of the angular electron correlation. Consequently, the electrons exhibit a strong tendency to avoid each other, and localize their electronic density in diametrically opposite positions within the spherical crown, i.e., forming an angular Wigner-like molecule.[16] The different localization of the electronic density, together with the enhancement of many-body interactions, leads us to expect important changes in the FIR absorption spectrum when these surface states are formed.

The results presented in Fig. 4 correspond to the same calculations as in Fig. 3, but in this case the infinite height confining barrier has been replaced by one with a finite 1.5 eV height. When the QD dielectric constant is low ($\varepsilon_{QD}<7$ in Fig. 4), the self-polarization potential well is not deep enough to overcome the destabilizing barrier of the spatial confining potential, and the electronic density remains within the QD volume. In such a situation, the FIR absorption coefficients are similar to those corresponding to high confining barriers (see Fig. 4). However, as ε_{QD} increases (thus increasing the dielectric mismatch), the self-polarization potential well becomes deeper and eventually capable of promoting the electronic density from the QD volume to the surface once ε_{QD} is larger than a given threshold ($\varepsilon_{QD}\approx 7$ in our case). As shown in Fig. 4, this transition goes in parallel with a cancellation of the relative coefficients of Γ_2, Γ_3, and Γ_4, thus yielding a FIR absorption spectrum rather different from the case of QD-environment dielectric matching.[26]

The results obtained for $\varepsilon_{QD}>7$ are, however, apparently contradictory. Indeed, the correlation effects in these surface states are strongly enhanced, so we could expect larger absorption coefficients for the transitions induced by the Coulomb interaction. Yet Fig. 4 shows that, actually, these coefficients are suppressed. We can rationalize the above results

by describing the two strongly interacting electrons in the surface state by a model of two electrons forced to move in a spherical surface. In the limit of strong interaction the two electrons form a Wigner molecule similar to a rigid rotor with one electron sited at the very opposite position from the other one in the spherical surface. Within this model, the two-electron system presents only rotational states having a null dipolar moment. Thus, the FIR radiation yields a null absorption coefficient for any dipole transition. Obviously, this is not exactly our case, since the transition Γ_1 is still active in the FIR absorption spectrum. This happens because actually the rigid rotor approximation is a model that is too simplified to accurately describe the angular Wigner-type molecule formed. Indeed, the real system presents a vibrational mode involving oscillations of the relative angle between the electrons, which is fixed in the rigid rotor model. Therefore, the nonforbidden absorption Γ_1 can be associated with the (only) allowed transition from the ground vibrational state of this relative angle oscillation mode. The larger the Wigner character of the electronic system is, the lower the intensity and the larger the absorption energy of this transition will be.[27]

IV. CONCLUSIONS

We have studied the sensitivity of the FIR absorption spectrum of two-electron spherical quantum dots with steplike confining potentials to the barrier height and the dielectric mismatch between the dot and its environment, focusing on absorptions induced by the Coulomb interaction. Despite the large effect that the two different (single- and two-particle) dielectric contributions exert in isolation, their interplay does not yield significant effects in the FIR absorption coefficients when high confining barriers are involved. Accordingly, the many-body contribution to the FIR absorption spectrum is governed by the QD confinement level a_0^*/R. But, in the presence of low confining barriers, the dielectric mismatch can induce a transition from volume to surface states, yielding dramatic changes in the FIR absorption spectra. Among others, Coulomb-induced absorptions cancel out despite the enhanced electron-electron repulsion within the surface state, and the spectrum resembles that of a parabolic quantum dot, with only one active absorption peak. Our findings provide theoretical evidence that FIR absorption measurements can be suitable for monitoring surface states. This result encourages experimental work directed toward confirming the predicted formation of dielectrically induced surface states in quantum dots under low-barrier and high-dielectric-mismatch conditions.

ACKNOWLEDGMENTS

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[19] We employ the standard $^{2S+1}L_{g/u}$ spectroscopic notation for the eigenstates of the spherical many-electron QD, where S and L stand for the spin and spatial angular momentum quantum numbers, and g (u) for the inversion symmetry [gerade (ungerade)]. Eventually, we supply the notation with a quantum number $n = 1,2,3,\ldots$ ($n^{2S+1}L_{g/u}$) which labels the nth state of a given symmetry.
[20] In general, the electron effective mass of the QD and its surrounding medium are different. Then, m^* is position dependent. In particular, when the QD has spherical shape m^* depends only on the radial coordinate r.
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are expected to be the largest. We employ a single-particle basis set involving the four lowest-lying states of each angular momentum $l=0$, 1, 2, 3, 4, 5, and 6 symmetry. This yields 70 (96) CI configurations for ^1S_g (^1P_u).

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[26] We outline next the behavior of Γ_1, in order to complete the information about the predicted FIR spectra. Concerning Fig. 1, we can say that Γ_1 has a moderate steady increase as we move toward the strong confinement regime. Thus, $\Gamma_1(a_0^*/R=1.06)$ is about 30% larger than $\Gamma_1(a_0^*/R=0.06)$. As for the influence of ε_{QD} on Γ_1 in the presence of an infinite spatial potential barrier height (corresponding to Fig. 3), it is completely negligible, while it is moderate for $V_0=1.5$ eV (Fig. 4), where $\Gamma_1(\varepsilon_{QD}=2)$ is about 40% of $\Gamma_1(\varepsilon_{QD}=70)$.

[27] For completeness, we have also studied the case in which the surface states are formed as a consequence of the QD dielectric discontinuity with a high dielectric constant surrounding medium, obtaining that, again, only the fundamental absorption Γ_1 survives. However, in this case the Coulomb repulsion is not enhanced, but almost totally screened due to polarization charges (Ref. 16). In consequence, the electrons in the surface states behave almost as independent particles, yielding an absorption spectrum similar to that of a single electron in the same dot. Thinking anew of the spherical surface model for this single electron in the surface crown, we notice that the system presents only rotational modes and that the absorption Γ_1 must correspond to the only allowed transition from the ground rotational state.