Dark excitons due to direct Coulomb interactions in silicon quantum dots

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Electron-hole exchange interactions can lead to spin-forbidden ''dark'' excitons in direct-gap quantum dots. Here, we explore an alternative mechanism for creating optically forbidden excitons. In a large spherical quantum dot made of a diamond-structure semiconductor, the symmetry of the valence band maximum ~VBM! is t_2. The symmetry of the conduction band minimum ~CBM! in direct-gap material is a_1, but for indirect-gap systems the symmetry could be ~depending on size! a_1, e, or t_2

inverse micelles synthesis,[16] and thermal vaporization.[17] The most popular experiments that probe QD's are optical measurements,[10,11,17] in which an electron-hole pair ~an exciton! is generated in the QD by the incoming photons. The physics of the experiment is dominated by the electron and hole energy levels, the electron-hole Coulomb interaction, and the response or screening of the rest of the electrons in the valence band.

The classical theoretical approach to the problem is the effective mass approximation ~EMA!, which predicts that the shift in the single-particle energy gap scales as $1/R^2$ with the radius R of a quantum dot. The EMA and a size-independent screening assumption predict that the Coulomb energy scales as $1/R$ in the limit $R \rightarrow 0$. However, recent microscopic calculations,[7,8,18–22] show that the single-particle energy gap dependence on R is less strong. This is due mainly to band mixing and nonparabolicity effects. In addition, the Coulomb binding energies are expected to increase faster than $1/R$ because the dielectric screening becomes less efficient than in the bulk.[23–25]

In the past, the calculation of energy levels of QD's was also performed using EMA,[26] empirical tight binding,[7,18–20] empirical pseudopotential methods,[1,3,22] and local density approximation.[8,24] The symmetry of the band-edge wave functions has been discussed in detail by Ren[7,9] and Delley *et al.*[8]

where n_m is the dimension of the subspace of the representation m, g is the total number of operations Q in the symmetry group, $\chi_Q^{(m)}$ is the character corresponding to the operation Q in the representation m, and $\hat{O}_Q$ is an operator that applies the transformation Q of the group to the wave function $c(\mathbf{r})$. Then we calculate the matrix element

$$p\sim c, m! = \ ^{\wedge} c| P^{(m)}$$

$$J_{he,h'e'} = e^2 \sum_{s_1,s_2} \int \int c^*_{h'}(\mathbf{r}_1, s_1)\, c^*_{e}(\mathbf{r}_2, s_2)\, c$$

be described by a single screening function $\overline{e}(|\mathbf{r}_1-\mathbf{r}_2|,R)$. Third, we choose an analytical approximation for $\overline{e}(|\mathbf{r}_1-\mathbf{r}_2|,R)$ which is described in Ref. 31.

Our foregoing argument suggests that the exchange interaction must also be screened. In the past, it was believed that

ingly, any approximation for the screening function $\epsilon(r,R)$ for a dot should converge to the form given by Resta for all values of r when the dot size R goes to infinity. Figure 2 shows that our screening function has this property. In Fig. 2, we have also plotted the distance dependent screening function used by Ögüt *et al.*[24] In that work, it is assumed that $\bar{\epsilon}(r,R)=\epsilon^{dot}(r)$. This assumption gives a screening function that depends only on the interparticle distance r ~independent of the size of the dot!. Figure 2 shows that in the approximation used by Ögüt *et al.* $\bar{\epsilon}(r)$ is only equal to the bulk value when the interparticle distance r is infinity. For all other r, the screening function used by Ögüt *et al.* is significantly different. It thus does not describe bulk screening correctly.

D. Comparison of the present method with other approaches

The present method differs form the classical EMA treatment of free-standing QD's ~Refs. 2 and 26! in several ways: ~1! The present method provides the microscopic structure of the wave functions, not just the envelope structure. ~2! It does not require the wave function to vanish at the boundaries of the QD. ~3! The numerical solution of Eq. ~1! allows us to include unlimited multiband couplings. ~4! The method describes the true physical symmetries of the dot ~recall that even the most perfect Si QD does not have spherical symmetry, as assumed in the EMA, but rather T_d symmetry!.

As to comparison of the present method and tight binding, we note that both methods can give equivalent results if the tight-binding basis is large enough. However ~1!, the description of the wave function is variationally much more direct and flexible in the plane-wave pseudopotential method; and ~2! while the position-dependent wave functions are in general not accessible to a tight-binding model ~only the expansion coefficients are!

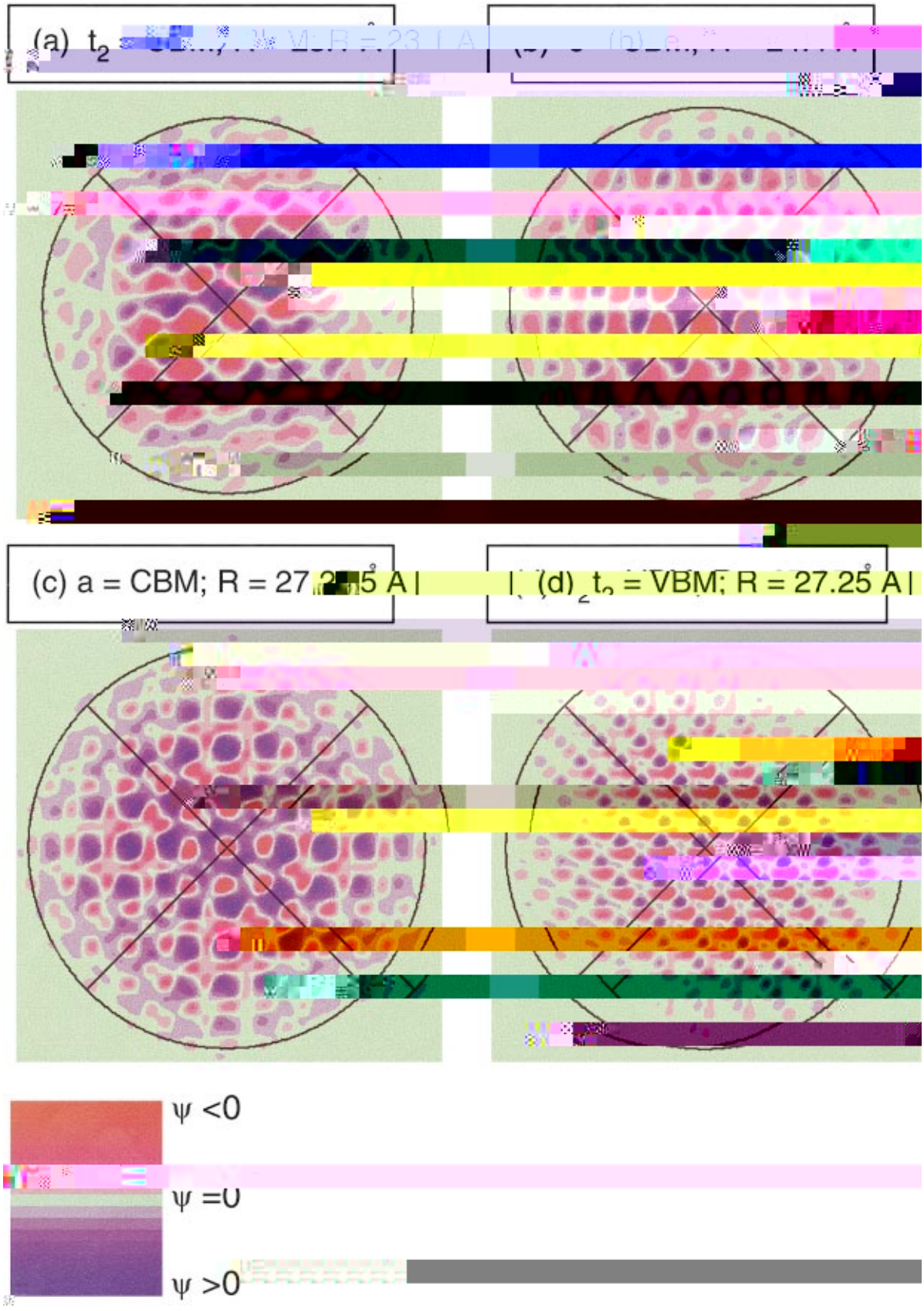

FIG. 3. ~Color! Calculated wave functions, depicted along the

Figure 4 shows the calculated single-particle energies compared with the empirical tight-binding results of Delerue *et al.*[37] and Ren.[7] This figure shows a very good agreement with the calculation of Delerue *et al.*[37] The agreement with the calculation of Ren is not as good. The difference between the calculations of Ren and those of Delerue *et al.*[37] is that the former uses a smaller set of adjustable matrix elements in the empirical tight-binding Hamiltonian.

Also shown in Fig. 4 are the recent experimental data of van Buuren *et al.*,[17] which fall well below all calculated and measured values ~see Fig. 5 below!. Since the quantities measured in this experiment are very different from standard measurements,[10,11] we will review them, so as to establish if there is a relationship with calculated quantities. van Buuren *et al.*[17] measured the shift in the energy of the conduction-band minimum from the dot to the bulk, i.e.,

$$\Delta\alpha_{CBM} = \alpha_{CBM}^{dot} - \alpha_{CBM}^{bulk}, \tag{18}$$

and the valence-band shift

$$\Delta\alpha_{VBM} = \alpha_{VBM}^{dot} - \alpha_{VBM}^{bulk}. \tag{19}$$

The band gap of the dot was thus

$$\alpha_g(dot) = \alpha_g(bulk) + \Delta\alpha_{CBM} - \Delta\alpha_{VBM}. \tag{20}$$

To obtain $\Delta\alpha_{CBM}$, van Buuren *et al.* measured the difference between $2p \rightarrow$CBM core-level absorption in the dot and in the bulk:

$$\Delta\alpha_{CBM} = \Delta E^{dot}(\mathrm{Si}_{2p} \rightarrow \mathrm{CBM}) - \Delta E^{bulk}(\mathrm{Si}_{2p} \rightarrow \mathrm{CBM}), \tag{21}$$

whereas to obtain $\Delta\alpha_{VBM}$, they combined VBM photoemission with Si$2p$ photoemission, i.e.,

$$\Delta\alpha_{VBM} = [\Delta E^{dot}(\mathrm{VBM} \rightarrow \mathrm{vac}) - \Delta E^{dot}(\mathrm{Si}_{2p} \rightarrow \mathrm{vac})] - [\Delta E^{bulk}(\mathrm{VBM} \rightarrow \mathrm{vac}) - \Delta E^{dot}(\mathrm{Si}_{2p} \rightarrow \mathrm{vac})]. \tag{22}$$

In Eq. (21), $\Delta E^{dot}(\mathrm{Si}_{2p} \rightarrow \mathrm{CBM})$ is the energy difference between a dot with an electron in the CBM and a hole in its $2p$ core level and a dot in the ground state. In Eq. (22), $\Delta E^{dot}(\mathrm{VBM} \rightarrow \mathrm{vac})$ is the ionization energy of the dot VBM, and $\Delta E^{dot}(\mathrm{Si}_{2p} \rightarrow \mathrm{vac})$ is the ionization energy of the dot $2p$ core level.

It was already noted by van Buuren *et al.*[17] that the *measured* single-particle gap $\alpha_{,\Delta}$

obtained using the configuration-interaction method described in Sec. II B. The detailed structure of the exciton multiplet will be described in the next section. In Fig. 5, full symbols correspond to experimental results and open symbols correspond to theoretical predictions. We see an excellent agreement between our results and the recent photoluminescence ~PL! data of Wolkin *et al.*[10] on oxygen-free samples. We also show the *absorption* data of Furukawa *et al.*,[11] used in the past to compare with theory.[24] The absorption-determined gas is much higher than the PL-determined gap for the following reason. For indirect-gap bulk semiconductors absorption does not give reliable values for the *lowest* gap ~because of the small intensity!; 1 Tf 79

the ordering of the energy levels and they introduce energy correction on the order of 1 meV only.

Because the lowest energy exciton has A_1 symmetry, the exciton is dark, which results from both the exchange interaction and the direct Coulomb contribution of the Coulomb interaction. Therefore, an exciton in the ground state has to flip the spin and also has to change the orbital symmetry in order to recombine in a dipolar transition. That means that the exciton transition is forbidden both by spin and orbital symmetry. However, spin-orbit coupling, which is not included in the present calculation, can partially mix singlet and triplet states.

Another example of dark exciton is shown in Figs. 7 and 8 for a much smaller dot. The QD has 211 Si atoms with additional 140 H atoms on its surface. The effective radius of the Si dot is $R = 10.03$ Å. The symmetry of the VBM for this dot is t_1, whereas the CBM is t_2 ~see Table II!. In the absence of e-h interaction @Fig. 7~a!#, this $t_1 \times t_2$ exciton is

allowed state ~i.e., $^1T_2$), and emits from the lowest-energy triplet ~e.g., $^3A_1$

els of different symmetry could be mixed. A comparison between optical experiments and our theoretical results seems to show that the Franck-Condon shifts are small. Accordingly, we suspect that additional splittings or mixings due to lattice distortion should be small compared to the Coulomb or exchange splittings.

IV. SIZE DEPENDENCE OF THE SINGLE-PARTICLE

$$\Delta\overline{J}_C(R) = b/R^g. \qquad (32)$$

The form of Eq. (32) is also used to obtain the fits $\overline{K}_C(R)$, and $\Delta\overline{K}_C(R)$ of Eqs. (29) and (30). Table III gives the values of the exponent g obtained from the fittings.

The first observation is that the exponent obtained for the size scaling of the direct-screened Coulomb energy J_C ; $R^{-1.49}$ is larger than the one obtained in simplified models that use a size-independent screening constant and the EMA: J ; R^{-1}. Note from Eq. (9) that the scaling of J depends on the wave function structure and on the scaling of $\overline{e}(r,R)$. In our calculation, the wave function is not constrained to be zero at the surface of the dot, which is the usual boundary condition for the envelope wave function in free-standing QD's. This leads to a *reduced*[48] electron-hole binding energy, so the unscreened Coulomb energy scales as $J(\textit{unscreened})$; $R^{-0.82}$. On the other hand, our $\overline{e}(r,R)$ depends on the dot size being smaller than the R

infinite potential barrier approximation were used. Thus, nonparabolicity of the bulk band reduces n.

V. CONCLUSIONS

We have found that Coulomb interactions are very important in determining the symmetry of excitons in quantum dots made of a bulk indirect-gap material. In particular, ~1! direct Coulomb interactions are able to split the energies of excitons that have degenerate single-particle energies. ~2! When the symmetry of the CBM is t_2, the direct Coulomb interaction lowers the energy of a dark exciton below the optically active ones. ~3! Exchange corrections raise the energy of singlet states; because exchange splittings are different for each exciton symmetry, the ordering of symmetries is altered by the exchange interaction. In general, the exchange splitting is smaller for T singlets than for E or A_1, which lowers their energies below the other singlets. But, the T_2 singlet remains at higher energy than the T_1. ~4! When the symmetry of the CBM is not t_2, the lower energy excitons have T_2 symmetry. Thus, when the CBM symmetry is not t_2, the lowest exciton is spin-forbidden only. ~5! The hole wave function of the lowest-energy exciton belongs to the t_2 symmetry even in some cases in which the symmetry of the VBM is t_1. This is due to the fact that, for small dots, the electron-hole direct Coulomb attraction is significantly larger when the hole is t_2 than when it is t_1. ~6! We find that our dark-bright excitonic splitting agrees very well with the experimental optical data of Calcott *et al.*[41] and thermal data Kovalev *et al.*[42] The agreement is not as good with the thermal data of Calcott *et al.*[41] and Brongersma *et al.*[43] Finally, ~7! in contradiction with simple textbook arguments, we have found that the relevance of the Coulomb direct interaction, exchange interaction, and correlation effects increase as compared to the single-particle energy splittings for smaller dots. This effect is a consequence of a realistic description of the dot potential and the interparticle screening.

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good to describe the surface region ~i.e., when the distance from one particle to the surface of the dot is on the order of r_e!. Nevertheless, the wave functions are strongly localized in the interior of the dots and, therefore, any correction introduced at the surface must be small.

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