Structure- and spin-dependent excitation energies and lifetimes of Si and Ge nanocrystals from *ab initio* calculations

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We calculate spin-dependent excitation energies of Ge and Si nanocrystals by means of a Δ-self-consistent-field method that considers the excitation of an electron-hole pair and thus includes the electron-hole Coulomb interaction. The method is based on local-density and local-spin-density calculations and yet reproduces the respective time-dependent local-density approximation results well. In addition, lattice contributions to the luminescence Stokes shift and the radiative lifetimes of the electron-hole pairs are calculated. All quantities are discussed in terms of their confinement dependence as well as with respect to the different behavior of Ge and Si crystallites. A detailed comparison to experimental work and to other theoretical results is presented.

I. INTRODUCTION

The physics of semiconductor nanocrystals (NC's) is an active field of research in terms of both applied and pure science. Most of the envisaged applications are based on the novel optical properties of the NC's as compared to their bulk counterparts. This holds, in particular, for silicon and germanium nanocrystals for which intense photoluminescence (PL) has been detected in the visible and infrared spectral region.[1–3] However, a complete understanding of the origin and the mechanism of this phenomenon has not yet been achieved.

The empty and occupied states contributing to the PL can be either states which are more or less extended throughout the whole nanocrystals but confined by their barriers,[2–4] or else they can be surface or interface states or be influenced by defects.[2–4] The efficient luminescence from quantum-confined states[5] remains one of the most interesting issues. In fact, one has fabricated small NC's with optical properties which have been assigned to the recombination of confined excitons.[3] However, the PL properties depend strongly on the preparation conditions, e.g., on possible oxidation.[3,6] Moreover, the emission energies and transition strengths depend on the spin state of the confined excitons.[7–11]

In order to understand the physics of PL, the emission energies, the optical transition probabilities, and the characteristic radiative lifetimes have to be studied in detail together with their dependences on the NC size, the atomic geometry, and the material of the nanocrystal. The theoretical activities have focused on the size dependence of the excitation energies of Si nanocrystals using either semiempirical techniques,[12] empirical pseudopotentials,[13] Quantum Monte Carlo,[14] or *ab initio* methods.[15] The central issue of the studies was the inclusion of many-body effects in order to account for the interaction of the excited electrons and holes with the other electrons, and for the direct electron-hole interaction. For that purpose, many-body perturbation theory techniques,[12,16] time-dependent density-functional theory,[17,19] and delta-self-consistent-field (ΔSCF) methods[18,19–21] have been applied. However, all these calculations have been performed for a fixed atomic geometry. Structural relaxation after excitation of the NC's which gives

rise to the Stokes shift between absorption and luminescence spectra[22] has been targeted theoretically only very recently.[25] To our knowledge, the spin influence on the exciton energies has been studied in only one case.[11]

Many experimental and theoretical results are available for Si nanocrystals and porous silicon. However, care has to be taken when the comparison of different results is made. Most theoretical models assume structures saturated by hydrogen atoms,[11,17,21] whereas many experimental results are obtained in environments which introduce oxygen to the surface of the crystallites. This is the case for NC's embedded in SiO_2 or for samples which are exposed to air before the measurements. It has been demonstrated for both Si[2] and Ge[3] that the oxygen has a strong influence on the luminescence properties. A number of recent investigations shows that the creation of oxygen defects or oxygen-related surface states can alter the optical properties completely.[23,24,26] It is, therefore, important to compare our calculated values with experiments where oxygen does not play a dominant role. For most experiments, however, this cannot be assured *a priori*.

In the present paper we investigate the influence of structural relaxation in the presence of electron-hole-pair excitations as well as the spin influence on the exciton energies of Si and Ge NC's. Stokes shifts and spin-splitting energies are extracted. The average strength of the optical transitions of a NC with given diameter is characterized by the corresponding radiative lifetime. The paper is organized as follows. After a description of the numerical ingredients of the calculations in Sec. II, results are presented in Sec. III for the excitation energies, the Stokes shift, the exchange splitting between the singlet and the triplet excitons, and, finally, the radiative lifetimes. Throughout the paper, pertinent experimental results are discussed in relation to our results, as are the theoretical results obtained by means of other methods.

II. MODEL AND COMPUTATIONAL METHODS

The calculations are based on density-functional theory (DFT) in local-density approximation (LDA) and local-spin-density approximation (LSDA). We employ the Vienna *ab initio* simulation package (VASP) (Ref. 27) and the projector augmented-wave method (PAW).[28] The supercell

approach is taken in order to use the plane-wave expansion of the eigenfunctions. The electron-electron interaction is described within the parametrization of Perdew and Zunger.[29] Nonlinear core corrections are taken into account.[30] Applied to bulk materials, the method yields cubic lattice constants of 5.647 Å for Ge and 5.404 Å for Si and DFT-LDA gaps of 0.00 eV and 0.47 eV at the theoretical lattice constants.

The optical properties are calculated within the independent-particle approximation. The PAW method[31] allows the generation of all-electron wave functions and, hence, transition matrix elements. This approach is applicable to bulk material[32] and NC's.[21]

Excitation energies are calculated by means of the ΔSCF method combined with occupation constraints. Within this method the lowest excitation energies are described by differences of total energies E. For instance, the quasiparticle gap E_g^{QP} without account of the direct interaction of electron and hole can be described by the difference of ionization energy (energy to remove an electron from the N-electron system) and electron affinity (energy gain when an electron is added to the N-electron system),[19,33]

$$E_g^{QP} = E(N+1) + E(N-1) - 2E(N). \qquad (1)$$

This approach is exact for exact DFT. Within the local approximation the exchange-correlation functional is an analytic function of the local electron density. It is known that in this case in the bulk limit Eq. (1) simply yields the difference of the Kohn-Sham eigenvalues of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital.[34,35] If the total energies are described within DFT-LDA, quasiparticle corrections are included in Eq. (1) only for systems with spatial confinement. The size limit of the diameter of Si nanocrystals is about 2.5 nm.[33]

An approach similar to Eq. (1) is possible for the lowest exciton pair energies E_g^{ex} which account not only for the reaction of the system in the presence of an extra electron ($N+1$) or a hole (missing electron) ($N-1$), the so-called quasiparticle or self-energy effects, but also for the attractive Coulomb interaction of the excited electron and hole screened by the remaining electrons. For confined systems with free-exciton radii larger than the nanocrystal diameter, one finds[21]

$$E_g^{ex} = E(N, e+h) - E(N). \qquad (2)$$

The calculation of the total energy $E(N, e+h)$ of the N-electron system with an excited electron-hole pair is possible by using the occupation constraint that the highest occupied single-particle state of the ground-state system contains a hole.

There is another advantage of the occupation constraint. It allows the minimization of the total energy $E(N, e+h)$ with respect to the atomic coordinates in the presence of an electron-hole pair. In the new geometry of the excited state one obtains new total energies $E^*(N, e+h)$ and $E^*(N)$. The pair excitation energy

$$E_g^{ex*} = E^*(N, e+h) - E^*(N) \qquad (3)$$

characterizes the lowest emission energy which is relevant in a luminescence experiment. By contrast, the energy E_g^{ex} describes the onset of the optical absorption. Consequently, the energy difference $E_g^{ex} - E_g^{ex*}$ can be identified with the Stokes shift between the absorption and emission edges of nanocrystals with a given diameter or, more precisely, the same number of atoms.

We construct approximately spherical NC's by starting from one atom and adding its nearest neighbors, thereby assuming the tetrahedral coordination of the respective cubic bulk material. Successively adding the nearest neighbors of the surface atoms shell by shell we obtain NC's of 5, 17, 41, 83, 147, 239, and 363 atoms. The outer bonds are saturated by H atoms. We use the supercell method with simple-cubic cells, the size of which corresponds to 216, 512, or 1000 atoms of bulk material, depending on the size of the respective NC. For instance, for Ge we use edge lengths of 1.7, 2.3, and 2.8 nm.

Keeping the T_d symmetry of the starting configuration, LDA ionic relaxation is carried out for all atoms for both the ground state of the NC's and the state with one excited electron-hole pair. For the smallest crystallites of quasimolecular size, electronic excitation can result in symmetry changes, up to the point of fragmentation.[36] However, as we are primarily interested in the behavior of crystallites of intermediate size, the relaxation using the symmetry constraint is expected to yield reliable results. For the ground state, the T_d restraint is natural because the fully occupied "valence" states have the symmetry of the crystallite. The fully relaxed structure is used for the calculations of the excitation energies and of the optical properties. The details of the relaxation pattern as well as the influence of relaxation and NC shape on the electronic structure and the optical properties have been discussed elsewhere.[37]

For bulk semiconductors, the optical excitation usually creates singlet excitons due to the spin selection rule. Triplet excitons are hardly ever discussed. However, in strongly confined Si systems there are many observations of triplet excitons due to the electron-hole exchange interaction.[7–9,38] Since the corresponding optical transitions are spin-forbidden they have been termed "dark" excitons in contrast to the "bright" spin-allowed singlet excitons.[11] Usually the triplet excitons are slightly lower in energy. The corresponding difference in the excitation energies E_g^{ex}(dark) $- E_g^{ex}$(bright) defines the spin or exchange splitting of the exciton energies. To calculate this splitting in the framework of the ΔSCF method and DFT, we include the spin polarization within the LSDA. In the spin-polarized case the correlation energy for arbitrary polarization is determined by using the same interpolation between the nonpolarized and the fully polarized case as for the exchange energy. This is the so-called standard interpolation.[39] The total energies E_g^{ex}(dark) and E_g^{ex}(bright) are computed fixing the total spin (or, more strictly speaking, the z component of the total spin) of the excited electron system of the nanocrystal. The geometries are taken from the LDA calculations.
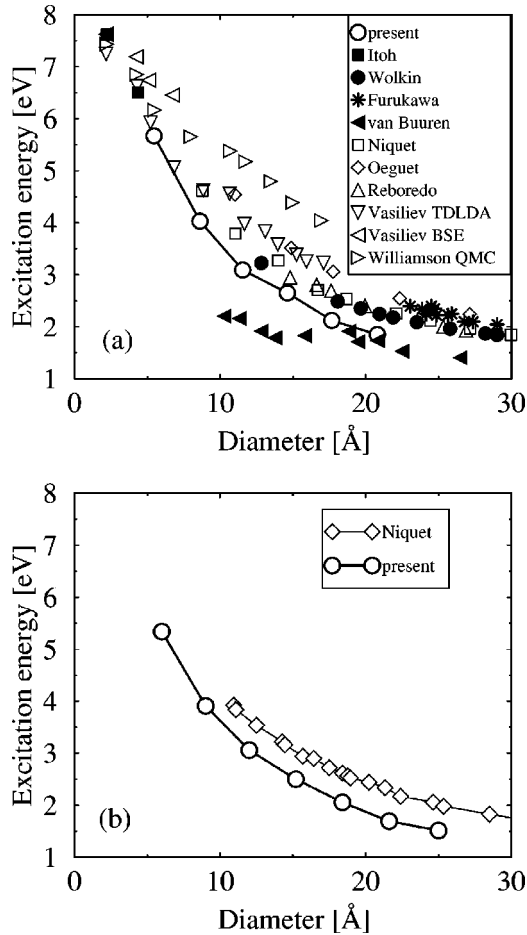
FIG. 1. Lowest electron-hole-pair excitation energies of Si (a) and Ge (b) nanocrystals. The empty symbols are theoretical results, while the filled symbols indicate experimental values. (a) Besides the present results we show the results of absorption measurements of Itoh *et al.* (Ref. 61) and Furukawa *et al.* (Ref. 41), PL of Wolkin *et al.* (Ref. 2), and the combined photoemission and core-level absorption spectra of van Buuren *et al.* (Ref. 43). Theoretical results are *ab initio* of Ögüt *et al.* (Ref. 19), empirical-pseudopotential of Reboredo *et al.* (Ref. 11), time-dependent density-functional theory and Bethe-Salpeter-equation results of Vasiliev *et al.* (Ref. 17) and quantum Monte Carlo of Williamson *et al.* (Ref. 14). (b) The present results are compared to those of Niquet *et al.* (Ref. 58).

III. RESULTS

A. Excitation energies

In Fig. 1 we present the pair-excitation energies E_g^{ex} calculated for the ground-state geometries according to Eq. (2) along with other theoretical and with experimental results. For both Si and Ge the calculated pair excitation energies show the well-known approximate $1/d$ (d-diameter) dependence.[21,40] Our results agree well with other calculations that also simultaneously account for quasiparticle effects on electron and hole and the Coulomb attraction of electron and hole. For small crystallite sizes ($\lesssim 1$ nm) our results for Si nanocrystals in Fig. 1(a) agree well with the pair excitation energies obtained within the time-dependent local-density approximation (TDLDA).[17] In the intermediate range of crystallite diameters of 1–2 nm the ΔSCF energies

lie below the TDLDA results. It seems that the vertex corrections, i.e., the direct Coulomb attraction of electrons and holes, are underestimated in the XC kernel of the TDLDA. For larger nanocrystals (>2 nm) there is an indication that both the TDLDA and the ΔSCF approach yield excitation energies which are too small because the crystallites are already too large. As mentioned before, in the bulk limit both theories do not give correct excitation energies. The excitation energies resulting from a solution of the Bethe-Salpeter equation[17] are somewhat larger and, hence, probably indicate a weaker effective electron-hole attraction. The energies obtained by the other ΔSCF method in Eq. (1) and reduced by a screened Coulomb energy[19] are also slightly larger. The estimated excitonic shifts, e.g., the 0.3 eV for a Si nanocrystal with $d=2.24$ nm,[19] are obviously underestimated. Our values agree better with those based on empirical pseudopotentials and Coulomb integrals.[11] The fact that the tiny underestimates of our ΔSCF excitation energies with respect to the values of Reboredo *et al.*[11] increase with increasing diameter may be discussed as an indication that our approach breaks down and, in the bulk limit, gives the Kohn-Sham gaps. Recent Quantum Monte Carlo results[14] differ distinctively from all the other results in the intermediate size range.

The comparison with experimental data is difficult, despite the huge amount of excitation energies measured in photoluminescence and absorption experiments. The majority of these data sets does not describe quantized electronic states localized in the interior of the nanocrystals. Many data sets are related to defect states or interface states localized in the interface region between crystallite material and matrix material. However, the PL peak positions measured by Wolkin *et al.*[2] are certainly due to confinement effects. Moreover, they have been shown to change strongly after exposure to oxygen[2] which indicates that the results reproduced in Fig. 1(a) are due to largely oxygen-free samples.

Similar conclusions hold for the absorption data of Furakawa and Miyasato.[41] The agreement of our calculated pair energies and the experimental data, in particular with the PL values,[2] is good. The difference of the largest nanocrystals considered may indicate that the validity of the ΔSCF method becomes questionable for the larger radii.[42] On the other hand, the gap energies inferred from the measurements of van Buuren *et al.*[43] fall below the other calculated and measured values. This may be essentially a consequence of the large core-exciton binding energies occurring in the x-ray absorption of the underlying combined experiments.[11]

In contrast to luminescence from silicon nanocrystals, there are, to the best of our knowledge, no experimental results for Ge which can be clearly attributed to the recombination of quantum-confined excitons. The results of Takeoka *et al.*[38] do not show the expected size dependence for luminescence from quantum-confined systems. For that reason, our excitation energies for Ge nanocrystals shown in Fig. 1(b) are considered a prediction. They are compared to the tight-binding result of Niquet *et al.* which does not, however, include Coulomb and self-energy effects.[44] Consequently, our excitation energies are about 0.6 eV smaller, quite independently of the NC diameter.
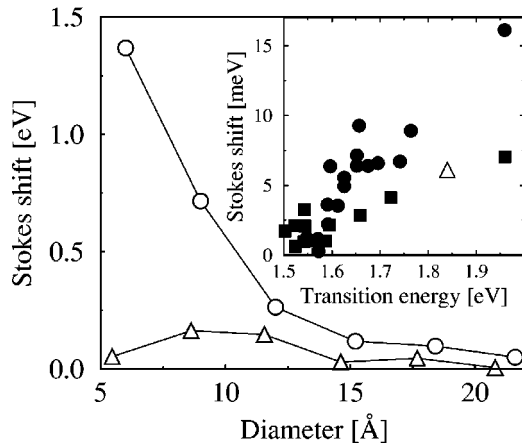
FIG. 2. Structural contribution (see text) of the luminescence Stokes shift for Si (triangles) and Ge (circles). The inset shows shifts measured for resonant excitation vs excitation energy for H-terminated porous Si (filled squares) and surface-oxidized Si NC's (filled circles) (Ref. 22), along with the calculated value for the largest NC (triangle).

B. Stokes shift

The PL peak energies are redshifted with respect to the lowest absorption energies. This shift is influenced by two main contributions. First of all, after thermalization of electrons and holes the linewidth of the PL spectra determines the shifts as discussed in Refs. 45 and 46. This is an effect of the size distribution of the crystallites. The recombination probability of the electron-hole pairs is inversely proportional to the transition energy. Consequently, after nonresonant high-energy excitation the larger nanocrystals of a size distribution contribute more to the PL signal. In an absorption experiment, on the other hand, more or less all nanocrystals contribute. Second, there is the structural contribution which is described by the difference in the energies of Eq. (2) and Eq. (3). Finally we mention that another contribution to the Stokes shift due to the splitting between the singlet and the triplet exciton has been discussed.[22]

The contribution due to the structural relaxation encompasses two different effects. There is the volumelike structural relaxation which is consistent with the assumption of T_d symmetry. This part of the effect is similar to the breathing mode in defect physics. Second, there is the effect which is due to a possible symmetry break after the excitation, as recently discussed by Puzder et al.[25] Of course, both effects are not independent. The fixed-symmetry structural contribution to the Stokes shift represents the lower limit of the Stokes shifts. Additional non-symmetry-conserving relaxations further lower the total energies. As the size of the crystallites increases, the crystallite will be increasingly better described as having a bulklike interior and a surface governed by surface phenomena.

Moreover, the hydrogenated crystallites have always been thought of as a model for both free crystallites (which they really are) as well as for crystallites embedded in a matrix with a very large gap. In the latter case, there will be some symmetry stabilization, depending on the interface region. In dependence of this, the value of the real Stokes shift will lie between the free-symmetry and the symmetry-restrained results.

The difference between the energies of the ground-state and the excited-state geometry, i.e., the structural contribution to the Stokes shift, is shown in Fig. 2. No attempt has been made to model the contribution related to the size distribution of the NC's. The contribution plotted in Fig. 2 is, therefore, only directly measurable in resonance experiments, in which only NC's with a definite size are excited.

In order to go beyond the symmetry-constraint calculations we did tests which indicated the following: For the 83-atom Si crystallite, the T_d Stokes shift is particularly small with 0.03 eV. This might be a consequence of the model of the particular crystallite. For a detailed discussion of the model please see Ref. 37. A relaxation of the same crystallite but without the symmetry constraint yielded a pair excitation energy of 2.1 eV, making the Stokes shift about 0.4 eV. Hence this crystallite has not yet reached the size regime where the symmetry-keeping volume contribution is dominant.

However, the fact that the Stokes shift of our largest crystallite agrees fairly well with experiment seems to be an indication that in this size regime (about 2.5 nm diameter) the symmetry break is already supplanted by the fixed-symmetry contribution as the main cause of the structural part of the Stokes shift.

Over the whole range of sizes, the fixed-symmetry structural Stokes shift is much larger for Ge than for Si. While for Ge even for the diameter of 2 nm the shift is appreciable, for the corresponding Si crystallite it has the small value of 5 meV. The differences between Ge and Si are a consequence of the different symmetries of the electron-hole pairs in Ge and Si crystallites due to the different physical character of the contributing single-particle states, especially to the LUMO states due to the different bulk band structures. Moreover, the bonding in Ge nanocrystals is weaker than that in Si. Consequently, the geometrical changes due to the electron-hole pair tend to be larger and can induce larger changes in the excitation energies. Thus it is no surprise that the structural contributions to the Stokes shift are different in the two materials.

Unfortunately, direct comparison with experimental Stokes shifts is difficult because measured values contain all the discussed effects—in particular that due to the size distribution of the NC's. Nonresonantly measured Stokes shifts can be as large as 1 eV for Si nanocrystals in a SiO_2 matrix.[47] For a resonant excitation of Si NC's, much smaller Stokes shifts of the order of a few millielectron volt and up to 50 meV are observed.[22] The inset of Fig. 2 with Stokes shifts as a function of the excitation energies demonstrates that our calculated Stokes shifts for the largest NC's are close to values measured resonantly for H-terminated porous Si. The shifts for surface-oxidized Si NC's are only slightly larger than the calculated value for the nanocrystals corresponding to this transition energy.

C. Exchange splitting between singlet and triplet excitons

Spin-polarized calculations have been carried out to calculate the exchange splitting between singlet and triplet ex-
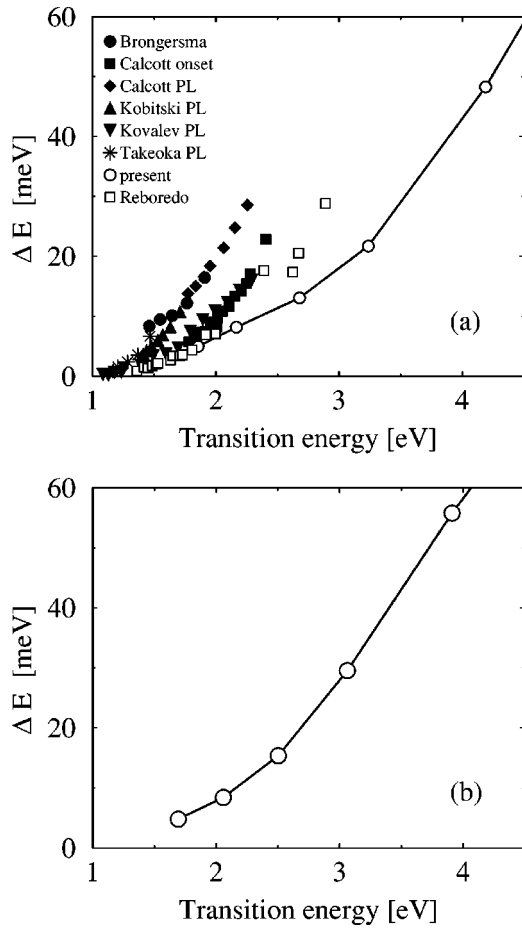
FIG. 3. Spin-exchange splitting between singlet and triplet excitons: (a) silicon, (b) germanium. Besides calculated values (circles) we show results of empirical-pseudopotential calculations of Reboredo *et al.* (Ref. 11), the absorption measurements of Calcott *et al.* (Ref. 7) and the PL data of Calcott *et al.* (Ref. 7), Brongersma *et al.* (Ref. 8), Kobitski *et al.* (Ref. 9), Kovalev *et al.* (Ref. 10) and Takeoka *et al.* (Ref. 38) for oxidized Si NC's or porous Si.

FIG. 4. (a) Radiative lifetimes for Si (a) and Ge (b) nanocrystals vs diameter. Beside the present results (circles) we show the calculated values of Lippens *et al.* (Ref. 51), Takagahara *et al.* (Ref. 52), and Hill *et al.* (Ref. 54) as well as tight-binding results of Niquet *et al.* (Ref. 58). Experimental results are shown of Wilcoxon *et al.* (Ref. 56), Xie *et al.* (taken from Ref. 56), Littau *et al.* (Ref. 55), Wilson *et al.* (Ref. 62) and Kanemitsu *et al.* (Ref. 63).

citons within the present ΔSCF method as the difference $E_g^{\mathrm{ex}}(\mathrm{dark})$-$E_g^{\mathrm{ex}}(\mathrm{bright})$. The LDA-relaxed ground-state geometries have been used. The results are shown in Fig. 3 in dependence on the singlet pair-excitation energy. There is an approximately quadratic relationship between spin-exchange splitting and pair excitation energy. Because of the approximate $1/d$ size dependence of the excitation energy, a much stronger dependence of the splittings on the nanocrystal size is predicted. The splittings for Ge are similar, perhaps slightly larger.

The calculated splittings are compared in Fig. 3(a) with experimental data[7–10] and calculated values of other authors[11] for Si nanostructures. For smaller transition energies, i.e., larger sizes, the agreement among the calculated data is good. With increasing transition energies, however, a tendency is observed that the ΔSCF values underestimate the spin-exchange splitting. In principle, this is also true for the comparison with the experimental data. However, this comparison is questionable for two different reasons. First, all the experimental samples involve oxygen. However, unlike for
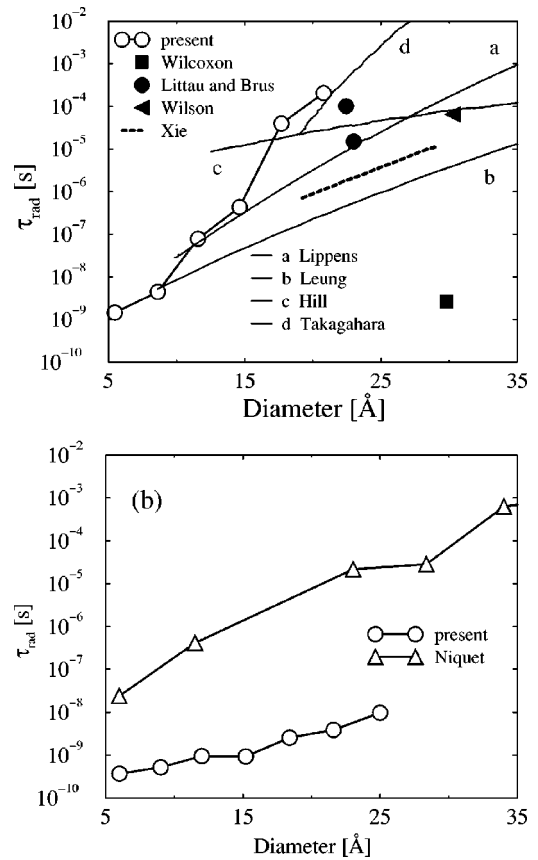
the PL energies,[2] so far it seems not clear how the splitting is influenced by the oxygen. Probably, in all the experiments the exciton energies are partially related to defect states or interface states. Second, the DFT-LSDA (Ref. 39) used here is not able to describe pure multiplets. This is a general problem.[48] A rigorous description of multiplets requires symmetry-adapted exchange-correlation functionals, which are not available.[49] In the spin-polarized approach one can only fix the projection M_S of the total spin S but not the total spin itself. One describes actually a high-spin state with $S = 1$, $M_S = \pm 1$ (which is a triplet state) and a low-spin state with $M_S = 0$ (which is probably a mixture of spin states). Consequently, this approach tends to underestimate the spin splitting and gives a lower limit.

D. Radiative lifetimes

The global, spectrally integrated PL behavior is determined by the recombination rate or its inverse, the radiative lifetime τ. We calculate τ using an expression which assumes completely thermalized distributions of the excited electrons and holes.[50] The calculations are based on the independent-particle approximation. The solutions of the

Kohn-Sham equation are used for the single-particle states and energies. They also allow the reliable calculation of the optical oscillator strengths.[21] Room temperature is assumed. The calculations are performed for the ground-state geometries. Test calculations for the 83-atom Ge crystallite have shown that the influence of the modification of the geometry due to the excitation is weak, at least as long as the symmetry constraint is used, cf. the above discussion of the Stokes shifts. The radiative lifetime is reduced by about 5%. Our results are presented in Figs. 4 and 5 in dependence on the NC diameter (for Si and Ge) and on the pair-excitation energy (for Si). The results for Si and Ge (Fig. 4) are qualitatively different. In the size range of $1-2$ nm crystallite diameter the Si radiative lifetime is changed by more than five orders of magnitude. For the Ge crystallites this variation is less than one order of magnitude. The different radiative behavior of Si and Ge nanocrystals is a consequence of the remarkable differences in their oscillator strengths. In Ref. 21 these differences have been traced back to the fact that in bulk Ge the strong direct E_0 transition occurs close to the indirect gap. In bulk Si the situation is quite different. The E_0 transition and the indirect gap are separated by about 2.5 eV. As a consequence, the radiative lifetimes of Ge NC's are much shorter than those in the Si crystallites.

For the Si nanocrystals in Fig. 4(a) we compare our results with experimental results and with results based on different semiempirical descriptions of the electronic structure.[51–54] The trend of increasing lifetimes with the diameter is reproduced by all the theoretical approaches. For small diameters the various theories (with the exception of Ref. 54) seem to approach extremely small values. However, for large diameters the *ab initio* results seem to approach the lifetimes calculated within the effective-mass approximation.[52] All the other approaches underestimate the radiative lifetime in this size region. Unlike the calculations which assume defect-free crystallites with defined and saturated surfaces, the experimental samples are highly irregular and contain defects, reconstructed surfaces, and interfaces. Nonetheless, the agreement of our lifetimes with the experimental values is fair, despite the complications concerning the experimental determination of the diameter and the uncertainty as to precisely which physical system has been investigated by the measurements. In particular, the agreement with the measurements of Littau and Brus[55] for colloidal nanocrystals is excellent. The values measured by Wilcoxon *et al.*[56] are, however, smaller by orders of magnitude in comparison to all theoretical values. It is, therefore, apparent that a different physical mechanism has been measured.

There are more experimental data of radiative lifetimes for Si NC's. However, these are data given in terms of the PL energies rather than in terms of the diameters. The corresponding comparison for the Si lifetimes given versus PL energies is shown in Fig. 5. In general, our lifetimes agree well with some of the experimental results. The agreement with the data of Heitman *et al.*[57] is excellent, whereas the other experimental values envelope our theoretical lifetimes. However, the measurements of Heitmann *et al.*[57] have been performed at a temperature of 100 K. With the lowering of the temperature one expects an increase of the lifetimes as
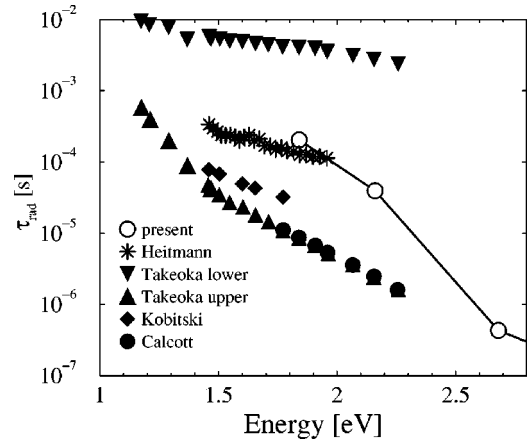

FIG. 5. Radiative lifetimes for Si nanocrystals vs excitation energy. We compare the calculated values (circles) with the PL results of Heitmann *et al.* (Ref. 57), Takeoka *et al.* (Ref. 38) for their lower and their upper transitions, those of Kobitski *et al.* (Ref. 9), those of Calcott *et al.* (Ref. 7), and those of Kanemitsu *et al.* (Ref. 63) for α-Si and c-Si.

also shown experimentally.[52] Moreover, the measurements of Takeoka *et al.*[38] are not directly related to quantum-confined states of the NC's. Rather, these authors have measured luminescence in which different defect or interfaces states are involved.

Again, there are no experimental data for Ge NC's with different diameters or excitation energies. Therefore, the results for the Ge crystallites in Fig. 5 remain predictive. There is only another calculation of Niquet *et al.*[58] based on the electronic structure and optical transition matrix elements from a semiempirical tight-binding method. We point out that the lifetimes calculated within our *ab initio* method are shorter by two orders of magnitude than the results obtained from the TB calculations.[58] The main difference, however, is probably related to the transition matrix elements which are remarkably underestimated in the TB method. Single rough experimental values are also reported which are close to our findings. Takeoka *et al.*[59] reported the lifetime of Ge nanocrystals to be shorter than 40 ns. Moreover, the PL intensity variation of Takeoka *et al.*[4] is very similar to the (inverse) lifetime dependence of our results in the same size range. Aoki *et al.*,[60] on the other hand, do not find a nanosecond PL lifetime component. We think that much work has to be done for clarifying the influence of defects etc. on the experimental and theoretical results.

IV. CONCLUSION

In order to determine the pair-excitation energies of Si and Ge NC's, we have carried out ΔSCF calculations which include the Coulombic electron-hole interaction. The results have been successfully compared to experiment and other theoretical approaches. In particular, we have shown that our LDA-based approach is able to reproduce the TDLDA results of Ref. 17. Lattice contributions to the luminescence Stokes shift has been calculated and compared successfully to values from resonant photoluminescence. The ΔSCF method

also allows the computation of the spin splitting between the energies of singlet and triplet excitons. A clear relationship to the excitation energy and, hence, the quantum confinement is confirmed. However, the local-spin-density approximation seems to underestimate the spin exchange splitting. A possible reason is discussed in the text. Finally, the range of lifetimes given by the results of both theory and experiment is extremely wide. Our results present a reasonable description of those systems which exhibit PL from quantum-confined excitons.

Note added in proof. The role of the symmetry lowering due to the excitation with respect to the Stokes shift has also been discussed in a recent publication by Franceschetti and Pantelides.[64]

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