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Ab initio absorption spectra of Ge nanocrystals

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Ab initio absorption spectra and optical gaps for hydrogen-passivated Ge nanocrystals are calculated using time-dependent density functional theory within the adiabatic local density approximation. The results are compared to previous effective mass, tight-binding, empirical pseudopotential, and "Δ self-consistent field" calculations and shed light on the validity of the various approximations used. By comparing our results with calculations for hydrogen-passivated Si nanocrystals, we predict that the Ge optical gap is smaller than that of Si for any nanocrystal size.

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Semiconductor quantum dots have received considerable attention due to their unusual optical and electronic properties and their promising applications in advanced electronic devices.[1,2] One of the most striking and best studied effects in semiconductor quantum dots is the quantum size effect—an inverse correlation between the optical gap and the quantum dot size. This effect has been used, e.g., to tune the fundamental absorption, and hence color, of CdSe semiconductor nanocrystals across the entire visible spectrum.[3,4] Significant quantum size effects were also observed experimentally in hydrogen-passivated nanocrystalline Si.[5–7] By decreasing the Si crystallite size, its optical gap was increased to a value of up to ~2.4 eV (in contrast to a bulk value of ~1.1 eV) and the optical transition had a direct character (in contrast to an indirect one in the bulk).

The optical gap of bulk Ge, ~0.68 eV, is significantly smaller than that of Si. In 1992, Takagahara and Takeda,[8] using an effective mass theory, predicted that because the effective mass of charge carriers in Ge is much smaller than in Si, surface-passivated Ge nanocrystallites smaller than a critical radius of ~30 Å would exhibit an optical gap larger than that of Si. Later, Hill *et al.*,[9] using a tight binding approach, reached a qualitatively similar conclusion but revised the critical radius value to ~12 Å. This predicted "crossover" between the optical gaps of Si and Ge has since been questioned. Reboredo and Zunger,[10] using an empirical pseudopotential approach, argued that there is no clear crossing of optical gap vs size curves for Si and Ge nanocrystals having a radius as small as ~10 Å. More recently, Weissker *et al.*[11–13] estimated the optical gaps of Si and Ge nanocrystals using the delta self-consistent field (ΔSCF) method, i.e., by taking the total energy difference between the ground-state configuration and a configuration where one electron was promoted to the lowest unoccupied molecular orbital (LUMO), leaving a hole in the highest occupied molecular orbital (HOMO). They did so within both the local density approximation[11,12] (LDA) and the local spin-density approximation[13] (LSDA) of density functional theory (DFT) calculations, without[11] and with structural relaxation,[12,13] and did not find a clear crossover in any case. These different comparisons between the quantum size effect in Ge and Si nanocrystals are summarized in Fig. 1. For completeness, the figure also contains data computed in the present work (discussed below).

Different theoretical predictions for the quantum size effect in Ge nanocrystals are summarized in Fig. 2 (again including data from the present work that is discussed below). It is readily observed that all of them obtain the same qualitative trend of an increasing optical gap with decreasing nanocrystal size, but have little else in common. Most of these studies were semiempirical in nature and usually relied on parameters coming from fitting (measured or computed) properties of bulk Ge. This may be a source of difficulty: the effective mass approximation is known to overestimate optical gaps for crystallites on the nanoscale.[14,15] Tight binding

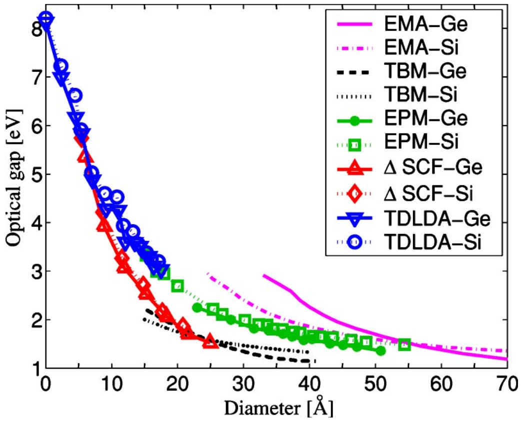

FIG. 1. (Color online) Optical gap of Ge and Si nanocrystals as a function of diameter, computed using TDLDA (this work, in blue, down triangles with solid line: Ge, open circles with dotted line: Si), effective mass approximation (Ref. 8, magenta, Solid line: Ge, dash-dotted line: Si), tight binding (Ref. 9, black, dashed line: Ge, dotted line: Si), empirical pseudopotentials (Ref. 10, green, solid circles with solid line: Ge, open squares with dotted line: Si), and ΔSCF (Ref. 13, red, up triangles with solid line: Ge, diamonds with dotted line: Si).

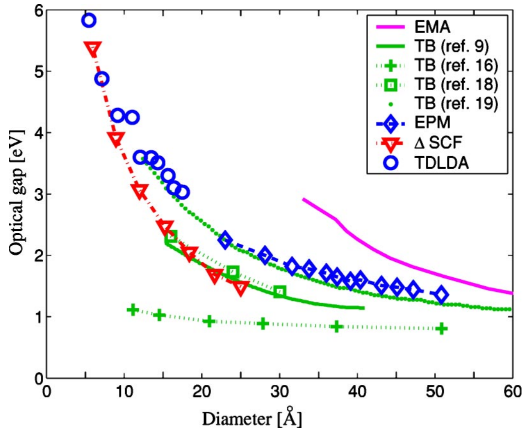

FIG. 2. (Color online) Optical gap of Ge nanocrystals as a function of diameter, computed using TDLDA (blue circles, this work), effective mass approximation (magenta solid line, Ref. 8), tight binding (green lines; solid line: Ref. 9, plus signs: Ref. 16, squares: Ref. 18, dotted line: Ref. 19), empirical pseudopotentials (blue diamonds: Ref. 10), and ΔSCF (red up triangles: Ref. 13).

parametrization of bulk Ge is not unique and the extent to which this parametrization remains valid for small nanocrystallites is unknown. Indeed, as clearly seen in Fig. 2, tight binding calculations of Ge nanocrystals performed by different groups[9,16–19] exhibit significant scatter in the results. Empirical pseudopotential calculations are, in principle, subject to the same limitations (although to the best of our knowledge only one such study for Ge nano crystals has been reported[10]). The question of the Si—Ge crossover (or lack thereof) then centers on which parametrization is more trustworthy. This makes finding a definitive answer difficult, especially as the reported magnitude of the crossover is of the same order as the discrepancy between different calculations. Furthermore, a crossover for very small crystallite sizes (where bulk parametrizations are surely suspect) is not ruled out.

Experimental data for Ge nanocrystals are of little help in obtaining further understanding: Optical spectra have been reported for only a few sizes of hydrogen-passivated Ge nanocrystallites,[20,21] but no focus on the gap energy has been made. Furthermore, Gerion *et al.* recently reported that optical properties of solution synthesized Ge nanocrystals could not be determined due to a large amount of residual byproducts in the powders.[22]

Clearly, such a situation calls for *ab initio* calculations that do not employ any parametrization and do not require any experimental input. The only *ab initio* investigations of the crossover effect that we are aware of are the ΔSCF calculations of Weissker *et al.*[11–13] (the data of Ref. 13, which include both structure and spin effects, are shown in Figs. 1 and 2). However, ΔSCF is not rigorously anchored within DFT because of the use of a partially filled orbital that is not the highest occupied state. It may therefore introduce uncontrolled errors in estimating the electron-hole interaction, and consequently the optical gap, correctly.[23] Put differently, ΔSCF presupposes that the optical transitions are dominated by a single transition between a Kohn-Sham occupied state and a Kohn-Sham unoccupied state, whereas the two-particle electron-hole wave function created upon optical excitation may involve many such Kohn-Sham transitions.[23–25] Optical spectra of hydrogen-passivated Ge nanocrystals based on conventional DFT have also been reported.[12,26] However, LDA spectra may (and often do) underestimate the correct gap value significantly, nor are they expected theoretically to yield adequate optical gap values.[28] Therefore, they cannot be relied on for a first-principles quantitative determination of the optical gap, especially in the absence of experimental data.

A different technique for calculating optical gaps which is rigorously grounded within DFT is time-dependent DFT (TDDFT).[27–30] Formally an exact approach, it is in practice an approximate one owing to the typical use of the local density approximation (LDA) instead of the exact spatial dependence, and an adiabatic approximation instead of the exact temporal dependence of the exchange-correlation functional. This approximate implementation is usually known as time-dependent LDA (TDLDA). Compared to other *ab initio* methods for computing excited states, TDLDA requires a substantially smaller computational effort and can handle a much larger number of atoms. Indeed, this method has been shown to yield very good results for optical excitations in molecules, clusters, and nanocrystals, in general,[24] and for quantum size effects in Si (Ref. 31) and CdSe (Ref. 32) nanocrystals, in particular. Here we present TDLDA calculations for the optical spectra and the size-dependent optical gap in hydrogen-passivated Ge nanocrystals and compare it to previous TDLDA calculations preformed for hydrogen-passivated Si nanocrystals.[31]

A detailed discussion of TDLDA formalism,[24,29,30,33] implementation,[25] and applications[24] has been given elsewhere. Briefly, we first solve the Kohn-Sham equation

$$\left(-\frac{\nabla^2}{2}+\sum_{\vec{R}_a} V_{ps}(\vec{r}-\vec{R}_a)+V_H[\rho(\vec{r})]+V_{\mathrm{xc}}[\rho(\vec{r})]\right)\psi_n(\vec{r}) = E_n\psi_n(\vec{r}). \tag{1}$$

In Eq. (1), E_n and $\psi_n(\vec{r})$ are the nth Kohn-Sham eigenvalue and orbital, respectively, $\rho(\vec{r})$ is the valence charge density, $V_{\mathrm{ps}}(\vec{r}-\vec{R}_a)$ is the pseudopotential associated with an atom situated at $\vec{R}_a$, $V_H[\rho(\vec{r})]$ is the Hartree (electron-electron) potential, $V_{\mathrm{xc}}[\rho(\vec{r})]$ is the exchange-correlation potential, and atomic units are used throughout. We then use the Kohn-Sham orbitals to construct a coupling matrix K given by

$$K_{ij,kl} = 2\int\int \psi_i^*(\vec{r})\psi_j(\vec{r})\left(\frac{1}{|\vec{r}-\vec{r}\,'|}+\frac{dV_{\mathrm{xc}}[\rho(\vec{r})]}{d\rho(\vec{r})}\right) \times \psi_k(\vec{r}\,')\psi_l^*(\vec{r}\,')d\vec{r}d\vec{r}\,', \tag{2}$$

and use it to construct another matrix Q given by

$$Q_{ij,kl} = \delta_{ik}\delta_{jl}\omega_{kl}^2 + 2\sqrt{\lambda_{ij}\omega_{ij}}K_{ij,kl}\sqrt{\lambda_{kl}\omega_{kl}}, \tag{3}$$

where $\omega_{ij}=E_j-E_i$ are the Kohn-Sham transition energies and $\lambda_{ij}=f_i-f_j$ are the differences between the occupation numbers of the ith and the jth states. Finally, optical transition energies Ω_I are obtained from solving the eigenvalue problem

$$QF_I = \Omega_I^2 F_I, \qquad (4)$$

and oscillator strengths are calculated from the eigenvectors F_I.

All calculations were performed using PARSEC—a software suite based on a real-space approach using the higher-order finite difference method.[34] We used the Ceperley-Alder form of the local density approximation[35] in conjunction with norm-conserving Troullier-Martins pseudopotentials,[36] with a cutoff parameter of 2.8 a.u. for Ge and 1.2 a.u. for H.[37]

We carefully tested the convergence of the computed absorption spectra with respect to the real-space grid spacing, the size of the domain in which the equations were solved, and the number of empty Kohn-Sham orbitals included in the calculation. We used a spherical domain such that the outermost atom of the nanocrystals was at least 17 a.u. from the boundary, a grid spacing of 0.3–0.5 a.u. for coordinate relaxation, a grid spacing of 0.45–0.7 a.u. for TDLDA calculations, and a number of unoccupied states that was at least twice as large as the number of the occupied states.

Approximately spherical hydrogen-passivated Ge nanocrystals were considered, where all Ge atoms were assumed to be located at their ideal bulk positions, and hydrogen atoms were placed so as to passivate every Ge dangling bond. The smallest "nanocrystal" thus constructed was GeH_4 (which is simply the germane molecule), and the largest nanocrystal studied here was $Ge_{147}H_{100}$. Initially, Ge—Ge and Ge—H bond lengths of 4.55 and 2.89 a.u., respectively, were used. Because bigger colloidal Ge nanocrystals are known to retain their bulklike structure,[20] atomic coordinates were relaxed completely only for small clusters (up to and including $Ge_{29}H_{36}$). For larger nanocrystals, only the two outer shells were relaxed. Even the unrelaxed Ge atoms did not experience a force exceeding $\sim 10^{-2}$ Ry/Bohr after relaxation.

Computed TDLDA spectra for the optical absorption cross section (in units of area),[33] for each of the Ge clusters studied, are shown in Fig. 3. Each spectrum is compared with a (time-independent) LDA spectrum obtained by considering filled and empty Kohn-Sham orbitals as true one-electron wave functions. Both LDA and TDLDA spectra were broadened by convolving with a 0.1 eV Gaussian for simulating finite temperature, lifetime, and experimental resolution effects.[38] With increasing nanocrystal size, both LDA and TDLDA spectra feature a gradual decrease in the absorption and a gradual evolution from discrete spectra for the smaller systems to quasicontinuous spectra for the larger ones. It is readily observed that the TDLDA spectra display a significant blueshift with respect to the LDA spectra. It can also be observed that in the low-energy region the LDA spectra present much larger oscillator strengths than that of the TDLDA spectra. Both effects are typical of TDLDA and have been observed in many other nanocrystalline and cluster systems.[24]

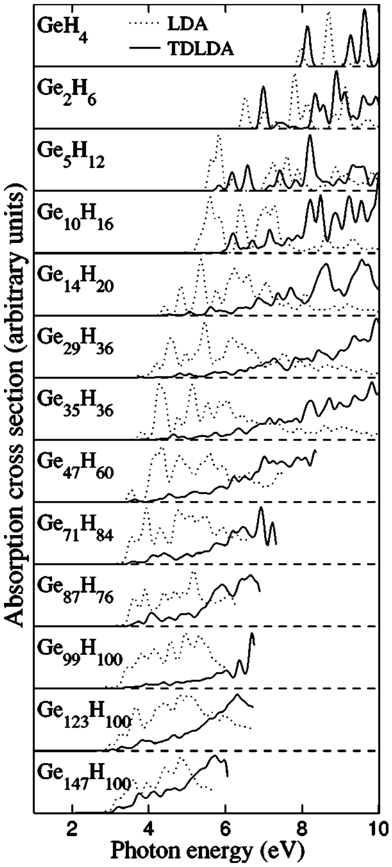

FIG. 3. Absorption spectra of Ge nanocrystals calculated using TDLDA (solid lines) and LDA (dashed lines).

Two factors enter into ascertaining the existence of an induced dipole transition: the existence of a transition energy and its corresponding oscillator strength. Within our frequency domain TDLDA approach, both terms are obtained and should always be considered together when predicting optical properties. This is because a large number of low-intensity transitions may exist near the absorption edge (especially for the larger clusters studied, where the absorption spectra become essentially quasicontinuous). Taken individually, the oscillator strengths of these transitions would be located far below the experimentally detectable limit.[24] In order to extract an optical gap from the present set of spectra, we took the absorption edge as the energy threshold at which the absorption is 2% of the total absorption. The same criterion was used previously for determining optical gaps in Si (Ref. 31) and CdSe (Ref. 32) nanocrystals and was found to yield good agreement with experiment. The extracted gaps are shown in both Figs. 1 and 2. In the former, they are accompanied by the gaps calculated previously for Si nanocrystals using the same methodology.[31]

Because of the large number of near-gap transitions, TDLDA predictions for near-gap optical activity are meaningful only if one averages the oscillator strengths over a relatively narrow energy window (in this case, 0.1 eV) around the optical gap. These calculated average oscillator strengths for near-gap transitions are shown in Fig. 4. Clearly, the oscillator strength of dipole-allowed transitions near the absorption edge decreases strongly with increasing cluster size. This diminishing optical activity is consistent with a shift from direct absorption for the smallest molecules

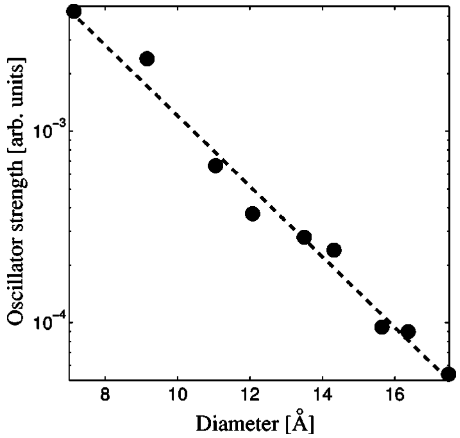

FIG. 4. Average oscillator strengths for near-edge optical transitions in Ge nanocrystals as a function of size. The dashed line is a linear fit.

and clusters to a formation of an indirect bandgap in the limit of bulk Ge. A similar behavior has been noted previously for TDLDA calculations of Si nanocrystals.[24,31]

In the absence of experimental data for the Ge nanocrystalline sizes studied here, our only point of experimental reference is the optical measurement of Itoh *et al.*[39] for germane—which serves here as the limiting case of the "zero diameter" nanocrystal. Here, our TDLDA-calculated optical gap value is 8.15 eV, which compares very well to the experimental value of 8.3 eV.

Compared to other theoretical calculations shown in Fig. 2, our new Ge results appear to be in very good agreement with the tight binding calculations of Niquet *et al.*[19] and agree with them to within ~0.2 eV where there is an overlap in the data. The data of Niquet *et al.*,[19] in turn, agree very well with the empirical pseudopotential calculations of Reboredo and Zunger for larger crystallite sizes.[10] By extrapolation, we consider our data to be in good agreement with the empirical pseudopotential data as well. This brings about another interesting point: it is well known that even though TDLDA works quite well for strongly localized systems, it yields optical gaps similar to those predicted by LDA for the bulk.[40] At present, it is unclear at what system size TDLDA should start to fail appreciably and how that failure may depend on the specifics of the system studied. In our case, the agreement with the results of Refs. 10 and 19 strongly suggests that we have not reached appreciable failure of TDLDA for the Ge nanocrystals studied here.

We do not find a quantitative agreement between our results and any of the other computations. Our results show yet again that the effective mass calculations of Takagahara and Takeda[8] significantly overestimate more sophisticated theories at small nanocrystals sizes. Furthermore, we do not find *ab initio* support for the results of any tight binding calculation other than that of Niquet *et al.*[19]

As compared to the ΔSCF calculations of Weissker *et al.*,[13] we find excellent agreement for the smallest crystalline sizes. For larger sizes, however, the ΔSCF results become increasingly smaller than our TDLDA data (as well as the data of Refs. 10 and 19). Interestingly, Weissker *et al.*[13] have previously noted an increasing difference between their Si nanocrystalline absorption data and the experimental data of Furukawa and Miyasato.[5] They have suggested that this may indicate that the ΔSCF method becomes less accurate with increasing nanocrystal size. Perhaps the same is true for the Ge nanocrystals. We do not believe that this difference between the TDLDA and the ΔSCF results is due to structural effects. First, as already noted the residual forces in the structures used are quite small. Second, previous ΔSCF work has shown that relaxation tends to increase the optical gap of Ge nanocrystals.[12] If further relaxation were to play a major role in our calculations, we would expect an increase in the optical gap values, making them even more different than the ΔSCF ones. Similarly, a failure of TDLDA (values tending towards the LDA ones) would again mean that the difference between the ΔSCF results and the "true" TDDFT results would be even larger.

We now turn to the Si/Ge crossover question. Figure 1 compares TDLDA results for both Si and Ge with all previous calculations known to us where an explicit comparison between Si and Ge was made by the original authors. For a meaningful comparison, we deliberately avoided including other data, where different approximations, methodologies, or passivation method may contribute to the difference in optical gap as much as (and perhaps more than) the difference in materials. Clearly, we do not find a crossover between the Si and Ge optical gap curves for any crystallite size, although for small enough crystallites the curves closely track each other. As explained above, our nanocrystals are taken such that the limiting case ("zero diameter" nanocrystal) is GeH_4 (germane) or SiH_4 (silane), for the Ge or Si nanocrystals, respectively. Figure 1 clearly predicts that the optical gap order is preserved even for this molecular limit. Indeed, experimentally the optical gap of germane is smaller than that of silane (8.3 vs 8.8 eV, respectively).[39]

Qualitatively, our results provide *ab initio* support for the conclusions of Reboredo and Zunger[10] and of Weissker *et al.*[11–13] and disagree with the earlier predictions of Takagahara and Takeda[8] and of Hill *et al.*[9] Quantitatively, our results agree very well with those obtained from semiempirical pseudopotentials,[10] but again differ from the ΔSCF results,[13] the latter being similar to the TDLDA ones for the smallest nanocrystals, but lower in energy for the larger ones.

In conclusion, we have calculated absorption spectra and optical gaps for hydrogen-passivated Ge nanocrystals using first-principles time-dependent LDA calculations. This made a critical assessment of previous calculations possible, and appears to validate the empirical psuedopotential and tight binding calculations of Refs. 10 and 19, respectively. Our *ab initio* calculations, obtained from a rigorous excited-state formalism, provided fresh first-principles evidence for a lack of "crossover" between the optical gaps of Si and Ge nanocrystals. Clearly, our TDLDA calculations are not capable of computing nanocrystals as large as those made possible by semiempirical approaches. We find, however, that such calculations may lend credence and confidence to some semiempirical results, thereby making the two approaches complementary.

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[38] Our LDA spectra of $Ge_{35}H_{36}$, $Ge_{87}H_{76}$, and $Ge_{100}H_{147}$ agree reasonably with those of Ref. 26, to within small differences stemming from the higher numerical accuracy used in the present work and the lack of structural relaxation in Ref. 26.

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