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The optical gap of small Ge nanocrystals

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Abstract. Using the Density Functional Theory (DFT) with the hybrid nonlocal exchange correlation functional of Becke and Lee, Yang and Parr (B3LYP), we have calculated the optical gap of small Ge nanocrystals passivated by hydrogen and with diameters between 2 and 20 Å. Our results show that the optical gap exhibits a size dependence (due to quantum confinement) with many similarities as in the case of Si quantum dots. The diameter of the smallest Ge nanocrystal emitting in the visible region of the spectrum, is approximately 19 Å. This critical dimension is smaller than the one found for the case of Si nanocrystals [Phys. Rev Lett. 87 276402 (2001)].

1. Introduction

The optical properties of semiconductor (IV) nanocrystals, have been a very promising field of research over the last decade. A large number of experimental and theoretical investigations have been carried out in order to explore the interesting physical properties that arise of “zero-dimensionality” structures, or else quantum dots. The optical behaviour of such nanostructured materials is dramatically different compared to the corresponding bulk materials.

Initially, the observation of intense photoluminescence (PL) from Si nanocrystals [1] stimulated considerable efforts towards the understanding of the key parameters responsible for visible light emission. Because of the large increase of the optical gap with respect to the bulk Si band-gap energy (1.2 eV), it was proposed that the luminescence in the visible was mainly due to quantum confinement. However, several alternative models challenged or complemented this hypothesis in an effort to make diverse experimental and theoretical results consistent with each other. From the theoretical point of view, the experience gained by the investigation of the optical properties of Si dots [2][3], so far, shows that in order to achieve the accuracy required to resolve the fundamental issues that dominate the emission of light, high level calculations are needed with well tested approximations, which include an accurate account of electron correlation [3].

The extension of research interest to Germanium nanocrystals is rather straightforward, as both Si and Ge are group IV semiconductors. Furthermore, Ge has a smaller band gap than Si, thus making it possible for smaller structures to produce visible PL. Experimentally PL has been observed in the range 350-700 nm from Ge nanocrystals 2-5 nm in size [4], while there are also studies concerning much larger nanoparticles [5].

It should be noted that up to date the optical properties of Ge quantum dots have been studied only in the framework of either semiempirical methods [6], or simple local density (LDA) ground state calculations without gradient corrections [7][8].

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2. Outline of the calculations

In this work we present ab initio calculation of the optical gap of small Ge nanocrystals based on time dependent density functional theory (TDDFT) [9] employing the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP) [10]. The accuracy of the TDDFT/B3LYP calculations for the optical gap has been tested for the case of Si nanocrystals, against MR-MP2, with excellent results [3]. Furthermore, it has been shown that the B3LYP functional can efficiently reproduce the band structure of a wide variety of materials, including crystalline Si, with no need for ad hoc numerical adjustments [11].

The size of the quantum dots considered here ranges from 5 to 99 Ge atoms, with 12 to 100 H atoms (a total of about 199 atoms). The diameter of the larger cluster studied here Ge99H100, shown in figure 1 is 19 Å. All dots have $T_d$ symmetry, as in figure 1, and their geometries have been fully optimized within this symmetry constrain, using the hybrid B3LYP functional [10]. As we have shown for the case of Si nanocrystals [3], the partially exact Hartree-Fock (HF) exchange that is included in the B3LYP method is very important for the correct description of the optical properties. The inclusion of exact HF exchange remedies the well-known deficiency of local-density approximation (LDA) to underestimate the band gap. The DFT and the TDDFT calculations were performed with the TURBOMOLE [12] suite of programs using Gaussian atomic orbital basis sets of split valence [SV(P)]: [4s3p1d]/[2s] [13] quality which involves 3400 basis functions for the largest system studied. The B3LYP functional has been used for both, the self-consistent solution of the Kohn-Sham equation for the ground state, and the solution of the linear response problem.

The optical gap in our calculations has been identified as the lowest allowed electronic transition (i.e., with nonzero oscillator strength) and it is identical with the so called fundamental optical gap.

![Figure 1. The structure of Ge99:H100.](image)

**Figure 1.** The structure of Ge99:H100.

**Figure 2.** Variation of the fundamental optical gap and the HOMO-LUMO gap as a function of the diameter of the nanocrystal.

**Figure 3.** Variation of the exciton binding energy.

Results and discussion

In figure 2, we have plotted the variation of both HOMO – LUMO gap and the fundamental optical gap as a function of the diameter of the Ge nanocrystals. The two curves, compared to the corresponding of Si nanocrystals, are shifted to lower energies but they reveal almost the same size dependence. The diameter of the smallest Ge quantum dot, for which the fundamental optical gap lies in the visible area of the spectrum, is in the range of 19-20Å. The corresponding critical diameter for the case of Si quantum dots was around 22Å [3].

In the same figure we can see the LDA/ΔSCF results of Weissker et al [7], which successfully describe in a qualitative manner the effect of quantum confinement on the fundamental optical gap. However, their absolute values are significantly shifted to smaller gap energies. This is not surprising since it is well known that simple LDA calculations, seriously underestimates the value of the HOMO-LUMO gap. Moreover, as we have shown elsewhere [14], the ΔSCF approximation, even when used with the B3LYP functional tends to underestimate the value of the optical gap. Consequently, the combination of the two approximations adopted by Weissker et al unavoidably leads to a serious underestimation of the optical gap. As a result, the conclusion that the fundamental optical gap of a 20Å Ge nanocrystal lies well below the visible area of the spectrum is wrong and is in clear conflict with the experimental results of Wilcoxon et al [4]. In contrast, our results are in a general agreement with the results and conclusions of Wilcoxon et al [4], although the size of the larger nanocrystal studied in this work (Ge99H100) has an approximate diameter of 19 Å (including the surface hydrogen atoms) which too small to compare directly with existing experiments. The optical gap for this nanocrystal is at 2.95eV (420nm).

Furthermore, our results seem to have a better agreement with the LDA ground state calculations of Melnikov and Chelikowsky [8]. This can be attributed to the fact that, the underestimation of single particle excitation energies derived by ground state LDA calculations is of the same order with the exciton binding energy in our calculations. However, the agreement deteriorates when the authors subtract from their single particle energies the electron-hole (exciton) Coulomb interaction energy. Although this is physically correct, the LDA single particle transition energies are already underestimated and further subtraction of the exciton binding energy makes them worse. This conclusion is in full accord with the well known fact (at least for the case of Si nanocrystals) that the corrections incorporated by TDLDA produce an optical gap which is slightly larger than the LDA single particle HOMO-LUMO gap. This has been also observed earlier by Vasiliev, Öğüt and Chelikowsky [2].

In figure 3 we have plotted the difference between the HOMO-LUMO gap and the fundamental optical gap. This quantity can be considered to approximate the binding energy $E_B$ of the exciton.
formed due to the electronic excitation. As expected by the quantum confinement hypothesis, $E_B$ must decrease as the diameter of the dot increases. For diameters around 20 Å, the value of $E_B$ is found to be approximately 0.45 eV. Compared to the case of Si quantum dots, we see that although the Si and Ge nanoparticles with $d=20$ Å contain different number of atoms, the values of $E_B$ practically coincide.

To facilitate the simple comparison of the energy structure (“band structure”) for nanocrystals of different size, we have plotted in figure 4 the energy level diagrams and the corresponding DOS for two nanocrystals of “medium” and “large” sizes (as far as the present investigation is concerned). The DOS curves were generated from the eigenstates of the ground state calculations with a suitable gaussian broadening. As we can see, the decrease of the gap with increasing size of the nanocrystals is practically “symmetrical” with respect to the conduction and valence band edges.

Also, to show the similarity of the electronic structure of Si and Ge nanocrystals, in figure 5 we have plotted the density of states for Ge$_{47}$:H$_{60}$ and Si$_{47}$:H$_{60}$. As we can clearly see, the two structures are fully homologous. In general the electronic structure of Si and Ge nanocrystals is homologous, and the same is more or less true for the optical properties. However, due to the smaller energy gap of Ge, the diameter of the smallest Ge nanoparticle which could emit in the visible region of the spectrum is found to be around 19-20 Å, smaller than the corresponding “critical” diameter of Si nanocrystals (22 Å). This seems to be verified by the experimental results of Wilcoxon et al[4].

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