Real space optical gap calculations in oxygenated Si nanocrystals

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Abstract. We have calculated the optical gap of small oxygenated Si nanocrystals with diameters in the range between 2 and 10 Å using the Density Functional Theory (DFT) with the hybrid nonlocal exchange correlation functional of Becke an Lee, Yang and Parr (b3LYP), which includes partially exact Hartree-Fock exchange. The optical gap is obtained from the B3LYP HOMO-LUMO gap by a well established correlation relation. Our results are in very good agreement with experimental measurements in oxygen containing samples, and confirm our earlier conclusions [Phys. Rev Lett. 87 276402 (2001)] for the role of oxygen in the optical gap of Si nanocrystals.

1. Introduction
The optical properties of silicon nanocrystals, have been a very promising field of research over the last decade. A large number of experimental and theoretical approaches have been carried out in order to explore the properties and resolve the origins of the observed visible Photoluminescence (PL) [1-11]. However, there are still issues, which are considered by several researchers as unsettled. For instance, the majority of the earlier experimental work gives diverse results as for the size of the Si dots capable of emitting in the visible. The results of Wolkin et al [2] revealed optical gaps as small as 2.2 eV, for nanoclusters with a diameter of 18Å. For nanoclusters of about the same size Wilcoxon et al. [1] obtained a similar result (2.5 eV) together with a much larger gap of about 3.2 eV for highly purified samples of the same dot diameter. Furthermore, Schupler et al [4] have estimated the critical diameter for visible PL to be less than 15 Å. As we have suggested earlier[6], the existing discrepancies in the experimental results are due to either oxygen contamination, or experimental uncertainties in the determination of the nanocrystal diameter. The discrepancies in the ab initio theoretical results are due to a poor treatment of exchange and (to a lesser degree) of correlation. For the phenomenological calculations the inconsistencies are due to unsuitable fittings of bulk parameters to small nanocrystal sizes. For the oxygen containing nanocrystals the role of surface passivants is also a controversial issue. Recent studies about the role of surface oxygen on the optical properties of silicon nanoclusters have reported conflicting levels of importance, ranging from minimal to crucial. In many experiments, the presence of oxygen is considered as a means to effectively passivate the surface dangling bonds or as a means to reduce (through oxidation) the size of the silicon nanoparticles. In most of the cases oxygen is just a contaminant, which is very difficult to remove.

From the theoretical point of view, only recently [6][21][23], calculations have appeared which employ high level ab initio techniques. These high-level ab initio calculations offer a more realistic description of the mechanism and the processes involved with the emission of light from Si nanocrystals. Although quantum confinement retains its key role in the heart of any explanation of
light emission, there is still place for additional or complementary channels of visible radiation, especially in the small cluster regime. Despite the evidence given by the experiments [1][2][4][9][10][11] as far as the role oxygen in the surface of Si dots is concerned, there has been a lack of realistic model calculations towards this direction until recently [22][23][24][26][27]. Here we present the largest, so far, accurate calculations of the optical gap, based on time dependent density functional theory (TDDFT)[12] employing the functionals of Becke and Perdew BP86 [19] and the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP)[18]. For hydrogen passivated nanocrystals we have tested [6] the reliability of the TDDFT/B3LYP method against sophisticated multi-reference second order perturbation theory (MR-MP2[13]) with excellent results. Furthermore, it has been shown that the B3LYP functional can efficiently reproduce the band structure of crystalline Si, without the need for ad hoc numerical adjustments[20].

**Figure 1.** The $Si_{99}H_{76}O_{12}$ and $Si_{147}H_{52}O_{24}$ nanocrystal. The oxygen atoms are red while the hydrogen atoms are white.

### 2. Outline of the calculation

The quantum dots considered here are $Si_{17}H_{12}O_{12}$, $Si_{29}H_{12}O_{12}$, $Si_{35}H_{24}O_{6}$, $Si_{47}H_{48}O_{6}$, $Si_{71}H_{72}O_{6}$, $Si_{99}H_{76}O_{12}$, $Si_{147}H_{52}O_{24}$. All dots have $T_d$ symmetry and their geometries have been fully optimised within this symmetry constrain using the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP)[18]. To maintain the $T_d$ symmetry of the cluster, which is very important for practical and physical reasons, we have to take certain steps before we optimize the nanocrystal geometry. The starting point was a selected set from the hydrogen containing nanocrystals we used earlier [6]. For each nanocrystal selected we chose a surface silicon atom having a bonding scheme of the form $R_{n}Si_i <Si>H_i$. In the above notation, $R_{n}$ is the main body of the nanocluster, $S_i$ are the two silicon atoms bonded to the atom of interest $<Si>$ and $H_i$ are the hydrogen passivants. For this site, we found the equivalent by symmetry Si atoms and replaced the two hydrogen passivants by one doubly bonded oxygen atom.

The DFT and the TDDFT calculations were performed with the TURBOMOLE [14] suite of programs using Gaussian atomic orbital basis sets of split-valence SV(P): [4s3p1d]/[2s] [15] quality. The TDDFT calculations have been described in detail in ref. [6] using the B3LYP functional consistently 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 TDDFT is identified as the energy of the lowest allowed electronic transition (i.e. with non-zero oscillator strength). According to prior experience [16][17][6], the TDDFT/B3LYP method has an estimated accuracy of about 0.3 eV for the excitation energies.

### 3. Results and discussion

In figure 2, we present the TDDFT/B3LYP optical gap of both the hydrogen [6] and hydrogen-oxygen passivated nanocrystals together with the experimental results of Wilcoxon et al [1] for the oxygen passivated quantum dots. For the same nanoparticles we have also performed TDDFT calculation with
the non-hybrid BP86 functional [19]. The trend established in ref [6] for the functional BP86 to underestimate the value of the optical gap still holds. In particular, it is found that the BP86 results are consistently lower than the corresponding B3LYP results by 0.5-0.6 eV.

This difference has approximately the same magnitude as in the case of the pure hydrogen passivated nanocrystals [6], where the BP86 gap was found to be shifted 0.6-0.7eV lower. The slightly smaller shift in the case of oxygen related calculations may arise from stronger electron-hole binding energy due to the more localized oxygen-like states. Assuming that this is a systematic trend, we have used the TDDFT/BP86 result of $\text{Si}_{147}H_{52}O_{24}$ to make an estimation of the TDDFT/B3LYP value of the gap of $\text{Si}_{147}H_{52}O_{24}$.

The dependence of the optical gap on the number of surface oxygen atoms is also investigated by performing additional calculations on several variants of $\text{Si}_{29}H_{12}O_{12}$ nanoparticle. In particular, the calculated optical gap of $\text{Si}_{29}H_{12}O_{3}$ (2.39eV), $\text{Si}_{29}H_{12}O_{4}$ (2.36eV) and $\text{Si}_{29}H_{12}O_{12}$ (2.32eV) demonstrate that, in practice, there is only a negligible dependence on the number of the surface oxygen atoms. However, additional calculations showed that there is a significant dependence on the relative distribution and interatomic distances of these oxygen atoms.

Our TDDFT/B3LYP results on oxygen containing dots are in very good agreement with recent Quantum Monte Carlo ΔSCF like calculations of Puzder et al [22] and the experimental data of Wilcoxon et al [1]. Additionally they establish the same trends with the corresponding results of ref [23][24][25][26] and expand them to larger oxygen containing nanocrystals.

![Figure 2](image)

**Figure 2.** Figure analogous to figure 10 of Wilcoxon et al[1], where the oxygen related results lie in the shaded area

Compared to the corresponding optical gap of the oxygen free nanocrystals of ref [6], the nanoclusters $\text{Si}_{147}H_{52}O_{24}$, $\text{Si}_{99}H_{76}O_{12}$, $\text{Si}_{71}H_{72}O_{6}$, $\text{Si}_{147}H_{52}O_{24}$ show a decrease of 2.04eV, 1.43eV, 0.94eV, 1.34eV of the optical gap. For the larger dots, this is consistent with the result of Wolkin et al [2] who have demonstrated that even a 3 min exposure of the samples in air produces a red shift as large as 1 eV, due to the formation of oxygen bonds on the surface. Figure 2, actually reproduces the experimental results of Wilcoxon et al [1] as they are depicted in figure10 of reference [1], where the oxygen containing nanocrystals are lying in the shaded area exhibiting a significantly lower optical gap. It becomes clear from figure 2 that the diverse experimental conclusion as for the size of the nanocrystals capable to emit in the visible can easily be clarified through the existence of doubly bonded oxygen atoms in the surface of the nanoparticles. In the case where Si=O bonds are present, the dimensions of the dots capable to emit in the visible can even be smaller than 15Å, as predicted by Schuppler et al [4]. On the other hand, in the cases where the nanocrystals are oxygen free, the critical dimension for light emission can be significantly larger and well above the 22Å.
Our conclusions are also consistent with the experimental results of Kamenev et al [28] which show that for sizes of the order of 15Å, there are two different mechanisms of radiative recombination with emission at wavelengths very close to each other. The one of them is ascribed to radiative recombination of electrons trapped in Si=O bonds with free or trapped holes and the other one to recombination of self-trapped excitons.

In conclusion, the present calculation is the largest, so far, on oxygen containing Si nanocrystals. Our results are in excellent agreement with existing experimental measurements and give sound evidence for the role of surface oxygen on the optical properties of small Si quantum dots. The trends reported by other theoretical treatments [22][23][24][25][26] for smaller clusters are verified and expanded to sizes for which accurate experimental data exist.

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