Ab Initio Study of functionalized 1 nm Silicon Nanoparticles

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Abstract. Functionalization of silicon nanoclusters reveals electronic and optical phenomena that can be utilized in a range of applications, including optical sensing, biological imaging and optoelectronic devices. Using density functional theory calculations, light-absorption and luminescence processes are modelled at the quantum mechanical level. In this study, a number of chemical functional groups are attached to the surface of silicon quantum dots (Si-QDs) of \( \sim1 \) nm diameter via either \( \text{C}_4\text{H}_8 \) or \( \text{C}_8\text{H}_{16} \) alkane chains. In these results, the impact of the functional groups upon the electronic structure and optical absorption spectra of composite systems depend upon the chemical nature of the functional group and the alkane chain length.

1. Introduction
In recent years, silicon nanocrystalline materials have become an interesting area in physics, chemistry, material science and biophysics. Various applications have resulted in biomedical applications, semiconductor nanomaterials and quantum dot devices\[1, 2\].

According to experimental observations and theoretical predictions, the properties of large Si-QDs are close to bulk silicon material in terms of the energy gap and emission wave length \[3\]. However, when Si-QDs have a diameter less than 5 nm, PL emission is in the visible range with high intensity. Quantum confinement is a key factor, but because there are up to around 50% of the atoms at the surface, the role of surface states is likely to be important.

Termination using hydrocarbon chains is an effective way of stabilizing the surface against oxidation \[4\]. Furthermore, functionalization of Si-QDs with different chemically active molecules is currently being investigated for possible applications as luminescent labels in biological applications, since the intense luminescence of Si-QDs are at wavelengths where biological systems do not absorb strongly. Theoretically, the role of surface functional groups with regards to their optical properties is an area still in development. For complete coverage, as the polarity of the Si-QD interface increases, the optical band-gap becomes increasingly affected by charge transfer at the interface rather than by quantum confinement \[5\].

Previous studies of surface functionalization largely involved functional groups bonded directly to the Si-QD rather than at the end of the long alkane chains. In this paper we present a quantum chemical study into the impact upon the electronic and optical properties of Si-QDs for various functional groups which terminate the alkane chains bonded to the Si-QD surface.
2. Computational Method
Calculations were carried out using the density functional technique, which is implemented in AIMPRO code (ab initio modelling program) [6, 7]. All calculations presented here use the generalized gradient approximation [8] for total energies and forces, and core electrons are treated using norm-conserving pseudo potentials [9].

The Si-QD is modeled starting from tetrahedral, hydrogen-terminated cluster, Si$_{35}$H$_{36}$, which is illustrated in Fig. 1. The non-functionalized cluster was first structurally relaxed, and the resulting geometry analyzed for its electronic structure and optical absorption. The main features of the electronic structures are the energies of the electronic-states, which represent the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Optical absorption spectra are obtained from the calculated complex dielectric function [10]. Each electron state is assigned an width using a polynomial broadening, characterized by a width of 0.1 eV.

For each functional group, one of the surface hydrogen atoms of the Si-QD is substituted by a linear alkane chain, and the functional group is attached to the other end of this chain. In all cases there are either four or eight methylene units (CH$_2$) between the “functional group” and the Si-QD, as shown in Fig. 1. The functional groups explored in this study are listed in table 1. To determine how significant the impact that functionalization has upon electronic and optical properties of the Si-QDs, in addition to varying the chemical functional group, we change the length of alkane chain from C$_4$H$_8$ to C$_8$H$_{16}$ with every functional group.

![Figure 1](image-url)  
**Figure 1.** Schematic showing the fully-hydrogenated silicon dot Si$_{35}$H$_{36}$, The left side is undecorated fully-hydrogenated silicon dot, while the right side is the Si-QD after the functionalization with a single functional group. Pink, white, grey and red atoms are silicon, hydrogen, carbon and oxygen, respectively.

3. Results
Calculations for Kohn-Sham energy levels, and the electronic spectra are given for functionalized and non-functionalized Si-QD systems. They can be viewed from the HOMOs and LUMOs energy levels with the associated optical gap, as illustrated in table 1.

The results divided into three main groups depending upon the electronic states introduced into the optical gap. Firstly, group(A) which contains alcohol, alkane, alkene, nitride, carbonic acid chloride, and halogens functional groups. As in table 1, in this group(A), the attached functional groups to the Si-QDs introduce no new electronic state into the optical gap. Fig. 2
Figure 2. The Kohn-Sham levels for 1 nm Si-QD of (A), (B) and (C) for alkane, carbonic-acid and aldehyde respectively, when (a), molecule with four carbon chain length (b) Si-QD attached to four carbon chain length, (c) undecorated H-terminated Si-QD, (d) molecule with eight carbon chain length and (d) molecule with eight carbon chain length. The shaded regions indicate the position of the bands for undecorated Si-QD (c).

Figure 3. Plot of the calculated optical absorption spectra corresponding to the undecorated hydrogen terminated Si-QD (black full line) in three graphs, (A) alkane functional group on silicon quantum dot (purple line), (B) carboxylic acid functional group (red line) and (C) aldehyde functional group (dashed green line).

(A) is represents alkane functional group Kohn-Sham energy levels as an example of this group. From the plot we can see that the chain of eight alkane chain has no new electronic state in the gap. This confirms that the length of alkane chain does not affect the states in the gap. At the same time, from Fig.3(A), the optical absorption spectrum for the same alkane functional group, produces no difference in terms of optical absorption coefficient compared to the undecorated Si-QD.

Secondly in group (B), which includes alkyne, arene and carboxylic acid. Shallow gap-states are introduced just above the HOMO of the Si-QD. Carboxylic acid functional group (carboxylic acid contains a carbon-oxygen double bond and carbon-oxygen-hydrogen single bonds) is chosen as an illustration to represent this group in Fig. 2 (B). From Fig. 3 (B), we can see a minor shift in absorption spectra.

Finally, group(C) which contains amide, thiole, amine, aldehyde, sulfide and ferrocene. We can see deep electronic states introduced into the optical gap. As a clear example, Fig. 2 (C) shows the electronic structure of aldehyde functionalized Si-QD (aldehyde contains a carbon-oxygen double bond). Here, a electronic state localised on the functional group lies well above the HOMO of the Si-QD. In Fig. 2 (C) we can see that the electronic state in HOMO-LUMO
gap corresponding with optical energy shift in the optical absorption by eV in Fig. 3 (C).

Table 1. Electronic structure data contain HOMO and LUMO energies for various functional groups attaches to the Si-QD via (C₄H₈ and C₈H₁₆). HOMO and LUMO energies are in eV relative to the vacuum level at zero. The groups are ranked by increasing energy of the HOMO and divided into the three groups as indicated in the text.

| Category | Family | Functional group | C₄H₈ HOMO | C₄H₈ LUMO | C₈H₁₆ HOMO | C₈H₁₆ LUMO |
|----------|--------|-----------------|-----------|-----------|-----------|-----------|
| A        | Pure QD |                 | -2.39     | -6.03     | -2.39     | -6.03     |
|          | Nitrile | (CN)            | -6.10     | -2.49     | -6.05     | -2.44     |
|          | Carbonic acid chloride | (COCl) | -6.06     | -2.44     | -6.02     | -2.41     |
|          | Chloride | (Cl)            | -6.04     | -2.43     | -6.01     | -2.39     |
|          | Bromide | (Br)            | -6.03     | -2.42     | -6.00     | -2.39     |
|          | Fluoride | (F)             | -6.03     | -2.42     | -6.00     | -2.39     |
|          | Alcohol | (OH)            | -5.99     | -2.38     | -5.95     | -2.37     |
|          | Alkene | (C₂H₃)         | -5.98     | -2.37     | -5.94     | -2.37     |
|          | Alkane | (H)             | -5.97     | -2.36     | -5.96     | -2.35     |
| B        | Alkyne | (C₂H₁)         | -5.78     | -2.38     | -5.73     | -2.37     |
|          | Arenne | (C₆H₅)         | -5.66     | -2.37     | -5.61     | -2.37     |
|          | Carboxylic acid | (C(OH)O) | -5.62     | -2.38     | -5.55     | -2.36     |
| C        | Amide | (CONH₂)         | -5.51     | -2.40     | -5.45     | -2.39     |
|          | Thiol | (SH)            | -5.50     | -2.41     | -5.45     | -2.40     |
|          | Amine | (N₂)           | -5.44     | -2.37     | -5.36     | -2.35     |
|          | Aldehyde | (CHO)    | -5.11     | -2.39     | -5.04     | -2.38     |
|          | Sulfide | (SCH₃) | -5.02     | -2.40     | -4.96     | -2.39     |
|          | Ferrocene | ((C₅H₅)₂Fe) | -4.07     | -2.37     | -4.01     | -2.37     |

4. Discussion and Conclusions
The presence and location of electronic states in the band-gap of the 1 nm Si-QD is strongly dependent upon the chemical nature of the functional group. In our calculations the increase in the chain length from four to eight carbon atoms results in only a small perturbation of the electronic structure, but dramatically reduces any sub-band-gap optical absorption due to the associated decrease in the overlap between the HOMO and LUMO molecular orbitals. The role of oxidation is the subject of future investigations.

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