Photo-absorption spectra of small hydrogenated silicon clusters using the time-dependent density functional theory

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We present a systematic study of the photo-absorption spectra of various SiHn clusters (n=1-10, m=1-14) using the time-dependent density functional theory (TDDFT). The method uses a real-time, real-space implementation of TDDFT involving full propagation of the time dependent Kohn-Sham equations. Our results for SiH4 and Si2H6 show good agreement with the earlier calculations and experimental data. We find that for small clusters (n<7) the photo-absorption spectrum is atomic-like while for the larger clusters it shows bulk-like behaviour. We study the photo-absorption spectra of silicon clusters as a function of hydrogenation. For single hydrogenation, we find that in general, the absorption optical gap decreases and as the number of silicon atoms increase the effect of a single hydrogen atom on the optical gap diminishes. For further hydrogenation the optical gap increases and for the fully hydrogenated clusters the optical gap is larger compared to corresponding pure silicon clusters.

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I. INTRODUCTION

Recently, there has been a renewed interest in understanding the optical properties of clusters because confinement of electrons changes the physical properties. Thus by varying size of the clusters the optical properties can be tuned according to the desired application. In particular, optical properties of silicon and hydrogenated silicon clusters have been of great interest due to the observation of photo luminescence (PL) in porous silicon. The structure and properties of silicon clusters can be tuned by varying the cluster size as well as doping. An important dopant for silicon clusters is hydrogen and it plays an important role in structural stability. Experimental studies also confirm this fact, but in spite of several investigations many issues about hydrogenated silicon clusters have not been understood. It is not clear how the structure and optical properties of the cluster evolves with size and as a function of hydrogenation. It is therefore interesting to calculate the photo-absorption (PA) spectra and compare it with experiment.

There has been a considerable amount of work experimental as well as theoretical on silicon and hydrogenated silicon clusters. Suto and Lee measured the photo-absorption and fluorescence of silane in the energy range 8-12 eV using synchrotron radiation. The optical absorption of silane and disilane has been measured by Itoh et. al. in the energy range 6-12 eV. Cheshnovsky et. al. have measured the photo-electron spectra of charged silicon and germanium clusters. Rinnen and Mandich have measured the photo-dissociation spectra of neutral silicon clusters Si18(n=18-41). Murakami and Kanayama investigated the stability of some silicon and hydrogenated silicon clusters using a quadrupole ion trap. More recently Antonietti et. al. deduced the photo-absorption spectra of charged silicon clusters from photo-dissociation of charged xenon-silicon clusters. On the theoretical side Chantranupong et. al. performed a configuration interaction (CI) calculation for a large number of low lying states in silane. Rubio et. al. calculated the photo-absorption spectra of silicon and alkali metal clusters using time dependent local density approximation (TDLDA). Rohlfing and Louie calculated the optical absorption spectra of hydrogen terminated silicon clusters by solving the Bethe-Salpeter equation. Vasiliev et. al. and Marques et. al. calculated the optical absorption spectra of SiHm clusters using linear response theory within TDLDA. Rao et. al. measured the photo luminescence of a dispersion of 1 nm silicon particles obtained from crystalline silicon that is dispersed into nanoparticles through electrochemical etching with HF and H2O2. They also calculated the photo-absorption spectra of Si29H34 using time dependent density functional theory (TDDFT). Lehtonen and Sundholm calculated the absorption spectra of three hydrogen terminated silicon clusters using TDDFT.

The earlier studies on the optical properties of silicon and hydrogenated silicon clusters focused on the size dependence of the PL and photo-absorption. Some of these studies ignored the influence of oscillator strength’s (electric dipole matrix elements) and hence were not in good agreement with the experimental data. Calculations based on DFT using LDA and the generalised gradient approximation (GGA) which included the dipole matrix elements suffered from the drawback that is inherent in LDA/GGA i.e. the energy gaps were underestimated because these calculations ignored the effect of excited states. To overcome this drawback, the configuration interaction method or the methods based on solving the Bethe-Salpeter equation along with the GW approximation have been suggested. These methods require a lot of computer time and hence have been restricted to small clusters. A computational technique based on linear response theory within TDLDA had been proposed by Vasiliev et. al. This is a natural extension of the LDA ground state density functional formulation designed to include excited states. This method is faster than the BS and GW methods and can therefore be used for larger clusters. Vasiliev et. al. have shown the vi-
ability of their method by performing calculations on silicon and hydrogenated and oxygenated silicon clusters. Another implementation of TDDFT has been formulated by Castro et al. which allows the calculation of the excited state energies and optical absorption spectra. In the present work, we have used this method.

Most of earlier calculations have considered only hydrogen terminated silicon clusters. There seems to be a lack of a systematic study on small hydrogenated silicon clusters. In this paper we report calculations for the hydrogen and hydrogenated silicon clusters in addition to some hydrogen terminated silicon clusters. Thus our calculations will show the effect of hydrogenation on the optical properties of silicon clusters. Our emphasis is on the smaller clusters so as to bring out the evolution of the optical properties as we increase the number of silicon and hydrogen atoms in the cluster.

The plan of the paper is as follows. In section II, we briefly discuss the method and give computational details. In section III we present our results and discussion. In section IV we present our conclusions.

II. METHOD AND COMPUTATIONAL DETAILS

We have used TDDFT for our calculation of the photoabsorption spectrum\(^{22,23}\). For the sake of completeness we shall summarise the essentials of the method. In TDDFT, the basic variable is the one electron density \(n(r,t)\), which is obtained with the help of a fictitious system of non-interacting electrons, the Kohn-Sham system. The time-dependent Kohn-Sham equations are

\[
\frac{i}{\hbar}\frac{\partial}{\partial t} \psi_i(r,t) = \left[-\nabla^2/2 + v_{KS}(r,t)\right] \psi_i(r,t)
\]

(1)

where \(\psi_i(r,t)\) are Kohn-Sham one electron orbitals. In terms these orbitals \(n(r,t)\) can be written as

\[
n(r,t) = \sum_{\alpha} |\psi_{\alpha}(r,t)|^2
\]

(2)

The Kohn-Sham potential can be written as

\[
v_{KS}(r,t) = v_{ext}(r,t) + v_{Hartree}(r,t) + v_{xc}(r,t)
\]

(3)

where the first term is the external potential, the second Hartree potential and the last the exchange and correlation potential. For obtaining this potential we use adiabatic local density approximation (ALDA).

In our work we shall use the TDDFT scheme which calculates propagation of the time-dependent Kohn-Sham equations in real time. In this scheme the electrons are given some small momentum(\(\kappa\)) to excite all the frequencies\(^{24}\). This is achieved by transforming the ground state wave function according to

\[
\psi_i(r,\delta t) = e^{i\kappa r}\psi_i(r,0)
\]

(4)

and then propagating these wave functions for some finite time. The spectrum is then obtained from dipole strength function \(S(\omega)\)

\[
S(\omega) = \frac{2\omega}{\pi} Im\alpha(\omega)
\]

(5)

where the \(\alpha(\omega)\) is the dynamical polarizability and is given by

\[
\alpha(\omega) = \frac{1}{\kappa} \int dt e^{i\omega t}[d(t) - d(0)]
\]

(6)

where \(d(t)\) is dipole moment of the system.

We can also define a quantity know as the oscillator strength to express the strength of the transition.

\[
f_I(x) = \frac{2}{3} \omega \sum_{n\in x,y,z} |<\phi_0|\phi_I>|^2
\]

(7)

where \(\phi_0\) and \(\phi_I\) are the ground and excited state respectively. The oscillator strength is related to the dipole strength function defined earlier using the following relationship

\[
S(\omega) = \sum_I f_I \delta(\omega - \omega_I)
\]

(8)

The sum over the oscillator strength gives the number off active electrons in the system,

\[
\sum f_I = N
\]

(9)

where \(N\) is the number of active electrons in the system.

The initial structures of the clusters used for our calculations have been obtained by Balamurugan and Prasad\(^ {21}\), earlier from their analysis based on the Car-Parrinello molecular dynamics (CPMD)\(^ {22}\). The resulting structures have been further optimised using the electronic structure method implemented in VASP (Vienna Ab-initio Simulation Package)\(^ {23}\). We do not find any significant changes in the structures compared to the CPMD results. In fact the starting CPMD configuration gives forces that are around 0.5 eV/Å which eventually reduce to around 0.05 eV/Å in VASP. VASP employs density functional theory (DFT) and we have employed the local density approximation (LDA) for the exchange correlation using norm conserving pseudo-potentials. The optimisation is done only by relaxing the ions via the conjugate gradient (CG) method and using a k-point Monkhorst-Pack mesh of 4x4x4. All calculations have been performed in a cubic supercell of length 20 Å.

In this work the photo-absorption spectra of the optimised structures were studied using OCTOPUS code\(^ {24,25}\) where the above approach is implemented. All calculations are expanded in a regular mesh in real space, and the simulations are performed in real time. The local density approximation was employed to keep consistency with the geometry optimisation process. OCTOPUS uses a uniform grid in real space, which is located inside the sum of n spheres, one around each atom of the n-atom cluster. For all clusters a minimisation of energy with respect to the radius and the grid spacing was carried out. We required the radius of each sphere to be 6-8 Å and the grid spacing 0.28-0.4 Å for optimal energy minimisation.

For the TDDFT the propagation in real time has been performed with 30,000 time steps with a total simulation time.
of around 124 fs. This gives a good resolution of the spectra. Throughout the calculations the ions were kept static and in order to approximate the evolution operator the approximated enforced time reversal symmetry (aefts) method was employed. Numerically the exponential of the Hamiltonian, which is used to approximate the evolution operator was evaluated using a simple Taylor expansion of the exponential.

III. RESULTS AND DISCUSSIONS

In order to verify our calculations with the experimental data, we chose to compare the two most stable clusters SiH$_6$ and Si$_2$H$_6$ with the available experimental data as our benchmark. In optical properties we are interested in transitions form the occupied levels to the unoccupied levels. The structures in the photo-absorption spectra are identified with these transitions. It is therefore interesting to calculate these energy differences and compare them with the energy differences deduced from the experimental spectra. Table I shows such a comparison. For our calculations, we have checked that the f-sum rule is satisfied. In Table I we have also included the Bethe-Salpeter results of Rohlfing and Louie, the TDLDA results of Vasiliev et al and the TDLDA results of Marques et al, along with the transitions identification. The uppermost occupied states result from a hybridisation of the silicon and hydrogen states while the lowest unoccupied states are primarily silicon states. Thus the energy gap is dependent on the the bonding and anti-bonding silicon states. The transition between these states have been identified as 4s, 4p, 4d states (these refer to the angular momentum character of the final states). We find good agreement with the experimental data of Itoh et. al and Suto and Lee, and other theoretical calculations. In particular, we get very good agreement with the results of Marques et. al. As compared to the work of Marques et. al we obtain an additional peak at 8.3 eV for SiH$_6$ which is observed in other works and the experiments. Our simulations pick up this additional peak because our broadening factor, which is the inverse of the time steps in the TDDFT run is quite narrow as compared to Marques et. al. Fig. 1 shows the structures and photo-absorption spectra of the current work, Vasiliev et al and Marques et. al for SiH$_6$ and Si$_2$H$_6$ clusters. The calculated photo-absorption cross-section (using TDDFT) seems to be in good agreement with the TDLDA results of Vasiliev et. al and the TDLDA results of Marques et. al using Octopus.

In order to see the effect of increasing the size of silicon clusters on the optical spectra, we present in Fig. 2 I the optimised structures of silicon clusters Si$_n$ [n=1-10] along with the photo-absorption spectra. To see the effect of adding a single H atom to these clusters, we have also calculated the photo-absorption spectra of Si$_n$H clusters which are also shown in Fig. 2 II along with the silicon clusters results. Each figure shows the structure of silicon and hydrogenated silicon clusters and the calculated photo-absorption cross-section. Consider first the silicon clusters. For small clusters (up to n=7) we find that the photo-absorption spectra is a combination of many peaks and looks like that of isolated atoms. However for n>7, the optical spectra looks bulk-like. This can be understood using a simple tight-binding picture. In a larger silicon cluster, the overlap between electronic wave-functions lifts the degeneracy of the energy levels resulting in bunching of energy levels in a narrow energy range. This results in broadening of PA spectrum for larger clusters. In Fig 2 we see that the main structure in the PA spectra is located at around 9 eV and a minor structure starts to build up at around 15 eV. The same trends are found in the singly hydrogenated clusters. For smaller clusters (n<7) the PA spectrum changes significantly as we increase the number of hydrogen atoms, while for larger clusters this change is small.

To see the effect of further hydrogenation, we present the PA spectra of hydrogenated silicon clusters where the number of hydrogen atoms is increased in Fig. 3. We have performed...
calculation for $\text{Si}_3\text{H}_4$, $\text{Si}_4\text{H}_4$ and $\text{Si}_4\text{H}_5$, $\text{Si}_5\text{H}_6$ and $\text{Si}_5\text{H}_{12}$ and $\text{Si}_6\text{H}_7$ and $\text{Si}_6\text{H}_{14}$ clusters. The different positions of the hydrogen atoms in $\text{Si}_3\text{H}$ and $\text{Si}_3\text{H}_3$ makes the two structures very different. Hence there is a large difference between the PA spectra. In going from $\text{Si}_3\text{H}$ to $\text{Si}_3\text{H}_3$ we find that the number of structures in the PA spectra increases and some of the new structures have larger peaks. In fact the PA spectrum goes from atom-like to bulk-like. We see similar trends in $\text{Si}_4\text{H}_4$ and $\text{Si}_4\text{H}_5$ except that the silicon backbone is a rhombus. We find that the new structures in $\text{Si}_3\text{H}_6$ PA spectrum have significantly larger peaks compared to $\text{Si}_3\text{H}_4$. In these hydrogenated clusters ($\text{Si}_3\text{H}_3$, $\text{Si}_3\text{H}_4$, $\text{Si}_4\text{H}_5$, $\text{Si}_5\text{H}_6$, $\text{Si}_5\text{H}_{12}$, $\text{Si}_6\text{H}_7$ and $\text{Si}_6\text{H}_{14}$) which have different silicon backbones, we observe that the bulk-like behaviour seems to start at $n=4$ which is much earlier than in singly hydrogenated and silicon clusters. This effect may be attributed to the large number of hydrogen atoms.

We obtained two very closely related structures of $\text{Si}_3\text{H}$ having a difference of about 0.043 eV in their total energy. Both the structures have been shown in Fig. 4 and the corresponding PA spectra in Figure 2 II. The silicon backbone in both these clusters remains the same and the only difference is found in the position of the hydrogen atom. In the ground state structure (solid line in the PA spectra) hydrogen is bonded to two silicon atoms while in the other (dashed line in the PA spectra) it is bonded to only one silicon atom. The PA spectra of the two structures is quite different. This shows that the PA spectrum is sensitive to small changes in the structure. Thus the PA spectrum can be used to identify the structure of the clusters which differ by a very small energy.

In Table II we present the optical absorption gaps of the various clusters. We define the optical gaps through the integral of the oscillator strength rather than as the energy of the first dipole allowed transition in the absorption spectra. The integral of the oscillator strength gives the total number of active electrons in the system. In this approach the value of the optical absorption gap is determined at a very small but non-zero fraction of the complete oscillator strength. We set this threshold to $10^{-4}$ of the total oscillator strength. This value is chosen because it stands above the value of “numerical noise” and at the same time it is sufficiently small so as to not suppress the experimentally detectable dipole allowed transitions. This definition of absorption gap doesn’t affect the values of optical gaps for small clusters, since the intensity of first transitions is well above the selected threshold.

| Transition | Present Work | Marques et. al. | Rohlfing & Louie | Vasiliev et. al. | Experiment |
|------------|--------------|-----------------|-----------------|-----------------|------------|
| $\text{SiH}_4$ | 4s | 8.2 | 8.2 | 9.0 | 8.2 | 8.8\text{a}, 9.0\text{b} |
| | 4p | 9.2 | 9.4 | 10.2 | 9.2 | 9.7\text{a}, 9.7\text{b} |
| | 4d | 9.8 | 10 | 11.2 | 9.7 | 10.7\text{a}, 9.7\text{b} |
| $\text{Si}_3\text{H}_6$ | 4s | 7.3 | 7.3 | 7.6 | 7.3 | 7.6\text{a} |
| | 4p | 8.3 | - | 9.0 | 7.8 | 8.4 \text{a} |
| | 8.6 | 8.7 | | | 9.5\text{a} |
| | 10.6 | 10.6 | | | 9.9 \text{a} |

In Fig. 5 we plot the optical gap as a function of the number of silicon atoms ($n$) for various $\text{Si}_n$ (solid Line) and $\text{Si}_n\text{H}$ (dashed Line) clusters ($n=1-10$). It shows a general trend that the addition of a single hydrogen atom reduces the optical gap as compared to the silicon clusters. As the number of silicon atoms in the cluster increase we find that the effect of a single hydrogen atom reduces the optical gap and the difference between the optical gap of $\text{Si}_n$ and $\text{Si}_n\text{H}$ gradually decreases with the increase in silicon atoms. In the bulk limit a single hydrogen atom should not distort the optical gap and thus in that limit the optical gap of the silicon will be the same as the optical gap of the singly hydrogenated silicon.

To see the effect of further hydrogenation, we list the op-
Figure 5: Optical absorption gap of various Siₙ (solid line filled circle) and SiₙH (dashed line empty circle) clusters as a function of the number of silicon atoms (n).

IV. CONCLUSIONS

The photo-absorption spectra of silicon and hydrogenated silicon clusters have been calculated using TDDFT. Our calculations show very good agreement for the benchmarks of SiH₄ and Si₂H₆ with the earlier theoretical calculations and experimental results. We find that the changes in the photo-absorption spectra correlate well with the changes in the structure of the cluster. In the singly hydrogenated clusters we find bulk-like behaviour for larger clusters (n>7) while for the smaller clusters we find the PA spectra is composed of numerous peaks as in atoms. We find that the PA spectra of two structures of Si₃H which are close in energy to be quite different. For the other hydrogenated clusters the bulk-like behaviour appears for smaller n which can be attributed to the larger number of hydrogen atoms. The addition of a single hydrogen to the silicon cluster shows a decrease in the absorption optical gap. The optical gap decreases gradually with the number of silicon atoms in the cluster giving the bulk limit in which an addition of a single hydrogen to the silicon should not affect the optical gap of silicon. With further hydrogenation the optical gap increases and for the fully clusters the optical gap is larger than the corresponding gap for pure silicon clusters.

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Table II: Optical gaps of various clusters.

| Cluster | Absorption Optical Gap (eV) |
|---------|-----------------------------|
| Si      | 4.7                         |
| SiH     | 3.8                         |
| SiH₄    | 8.2                         |
| Si₂     | 5.3                         |
| Si₂H    | 4.4                         |
| Si₂H₆   | 7.3                         |
| Si₃     | 4.9                         |
| Si₃H    | 4.3                         |
| Si₃H₃   | 4.6                         |
| Si₄     | 5.4                         |
| Si₄H    | 4.5                         |
| Si₄H₄   | 5.5                         |
| Si₄H₈   | 5.6                         |
| Si₅     | 4.9                         |
| Si₅H (gs) | 4.5                     |
| Si₅H (he) | 5.4                     |
| Si₅H₆   | 5.2                         |
| Si₅H₁₂  | 6.4                         |
| Si₆     | 5.4                         |
| Si₆H    | 5.1                         |
| Si₆H₇   | 4.3                         |
| Si₆H₁₄  | 6.3                         |
| Si₇     | 5.3                         |
| Si₇H    | 5.1                         |
| Si₈     | 5.5                         |
| Si₈H    | 5.3                         |
| Si₉     | 6.1                         |
| Si₉H    | 5.6                         |
| Si₁₀    | 6.0                         |
| Si₁₀H   | 5.6                         |
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