Ab Initio Absorption Spectra and Optical Gaps in Nanocrystalline Silicon

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The optical absorption spectra of $\mathrm{Si}_n\mathrm{H}_m$ nanoclusters up to ~250 atoms are computed using a linear response theory within the *time-dependent* local density approximation (TDLDA). The TDLDA formalism allows the electronic screening and correlation effects, which determine exciton binding energies, to be naturally incorporated within an *ab initio* framework. We find the calculated excitation energies and optical absorption gaps to be in good agreement with experiment in the limit of both small and large clusters. The TDLDA absorption spectra exhibit substantial blueshifts with respect to the spectra obtained within the time-independent local density approximation.

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The study of optical excitations in hydrogen terminated silicon clusters is essential for understanding absorption and emission of visible light in porous silicon [1]. Over the last decade, $\mathrm{Si}_n\mathrm{H}_m$ clusters in the form of quantum dots have been the subject of intensive experimental [2–4] and theoretical [5–12] research. However, disagreements among different theoretical models used for describing electronic excitations in these systems remain a subject of significant controversy. For the most part, the disagreements arise from the formulation of the optical gap in confined systems and the calculation of different components such as image charges, self-energies, and excitonic contributions that compose the optical gap [13,14].

Most theoretical studies focus primarily on the size dependence of photoluminescence energies and photoabsorption gaps [5–11]. In many cases, such calculations do not evaluate oscillator strengths and cannot explicitly identify optically allowed and dark transitions. This creates an uncertainty in the theoretical interpretation of the experimentally measured optical absorption. Only one of the published works [12] presents calculations for the entire absorption *spectra* of a few small ($n + m \leq 34$) $\mathrm{Si}_n\mathrm{H}_m$ clusters. The lack of theoretical studies dealing with the optical spectra for larger clusters can be explained by the extreme complexity of these calculations, e.g., the difficulty in describing many body effects in confined systems. The common techniques for excited state properties, such as the configuration-interaction method [15] or the method based on solving the Bethe-Salpeter equation within the *GW* approximation [12,16], are limited to very small clusters because of the high computational demand. Our work employs a computational technique based on linear response theory within the time-dependent local density approximation (TDLDA) [17]. This technique can be viewed as a natural extension of the ground state density-functional formalism and the local density approximation (LDA), designed to include the proper representation of excited states. Compared to other theoretical methods, the TDLDA approach requires considerably less computational effort and can be applied to much larger systems.

Despite its relative simplicity, the TDLDA formalism incorporates electronic screening and relevant correlation effects for electronic excitations [18,19]. In this sense, the TDLDA method represents a fully *ab initio* formalism for excited states. As such, the TDLDA calculations for the optical gaps are removed from the theoretical disagreements mentioned above. Unlike time-independent LDA calculations for clusters, the TDLDA approach does not require any artificial adjustment of the electronic excitation energies and absorption gaps to account for the LDA self-energy correction [9]. A model screening dielectric function is not required within TDLDA to estimate the screened Coulombic interactions in excitons [10]. TDLDA has previously been applied to atoms, metallic and bare semiconductor clusters, as well as small molecules; the calculated excitation energies and absorption spectra are in good agreement with available experimental data [17,20–23]. We have also demonstrated that in many cases the TDLDA absorption spectra for clusters are almost as accurate as the spectra obtained with much more complex theoretical methods [17,20]. However, until now the TDLDA formalism has not been applied to *hydrogenated* semiconductor clusters and quantum dots.

Our computational technique is based on the higher-order finite-difference pseudopotential method [24]. All calculations, including the TDLDA part, are performed directly in real space, so that the TDLDA formalism is straightforward and does not require any additional steps, such as setting up an intermediate basis grid [17]. Within TDLDA, the true excitation energies and oscillator strengths are obtained from the poles and residues of the dynamic polarizability, which are calculated by setting up and solving the eigenvalue problem for the coupling matrix. A detailed description of TDLDA theory can be found elsewhere [18,19].

Structures of $\mathrm{Si}_n\mathrm{H}_m$ clusters were obtained by starting with the coordinates of the bulk silicon and minimizing the total energy and interatomic forces acting on silicon and hydrogen atoms. For the silane molecule, SiH_4, our calculated Si-H interatomic distance of 1.472 Å is in excellent agreement with the experimental value of 1.480 Å [25]. We optimized the structures of all clusters up to $Si_{14}H_{20}$. For the larger clusters we started with spherical fragments of the silicon bulk lattice and further relaxed the outer layers by minimizing forces acting on the surface hydrogen atoms. The structures of selected Si_nH_m clusters are shown in Fig. 1.

Before proceeding with TDLDA calculations, we carefully tested for convergence of the computed excitation energies and absorption spectra with respect to the size of the spherical boundary domain, the grid spacing, and the total number of electronic states included in calculations. For all clusters, we required at least a 10 to 12 a.u. separation between the surface atoms and the spherical boundary. In the calculation of the TDLDA transition matrix elements, we included at least 2 to 3 times as many unoccupied states as the number of occupied states. These conditions were sufficient to achieve complete convergence of the computed spectra in the experimentally important region below 10 eV.

The calculated absorption spectra of Si_nH_m clusters are shown in Fig. 2. To reduce the memory requirements and the overall computational load, spectra of the last four clusters were calculated including only electronic transitions below a chosen energy threshold. Along with the TDLDA spectra, we also included the spectra of time-independent Kohn-Sham LDA eigenvalues. As in the case of metallic and semiconductor clusters with open surfaces [17,20,21], the TDLDA spectra of Si_nH_m clusters are blueshifted with respect to the Kohn-Sham eigenvalue spectra. However, unlike optical spectra of "bare" semiconductor clusters, the TDLDA spectra of hydrogenated silicon clusters do not display low energy transitions associated with the surface states. Consequently, the values of the calculated photoabsorption gaps for Si_nH_m clusters are much larger than those of Si_n clusters with open surfaces [10,12,21]. As the size of the cluster increases, the absorption gaps gradually decrease, and the discrete spectra for small clusters evolve into quasicontinuous spectra for silicon nanocrystals. At the same time, the oscillator strength of dipole-allowed transitions near the absorption edge decreases with

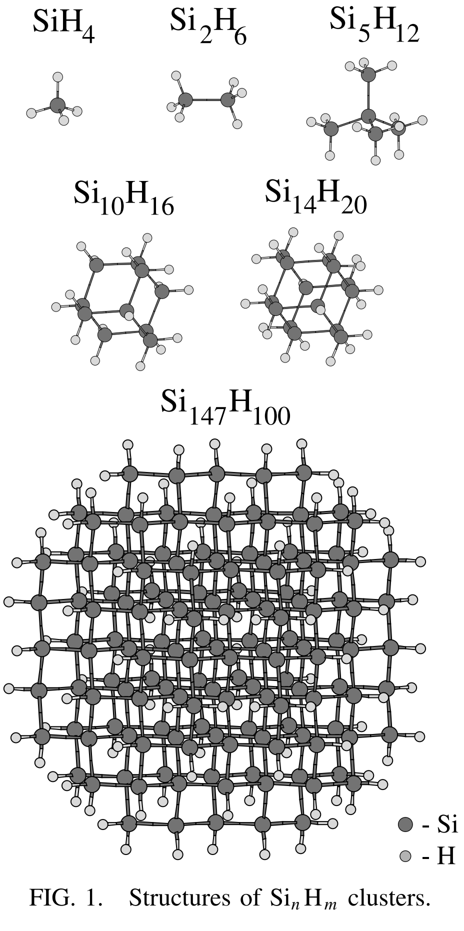

FIG. 1. Structures of Si_nH_m clusters.

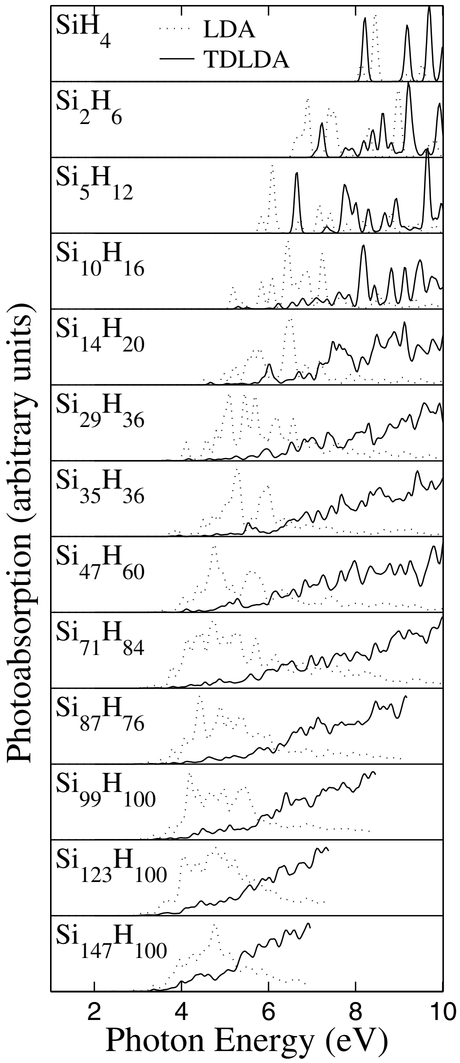

FIG. 2. Calculated TDLDA absorption spectra of Si_nH_m clusters (solid lines). Spectra of time-independent Kohn-Sham LDA eigenvalues (dotted lines) are shown for comparison. A Gaussian function of 0.06 eV has been used to simulate a finite broadening.

increasing cluster size. This fact is consistent with the formation of an *indirect* band gap in the limit of bulk silicon [9].

In Table I, we compare TDLDA values for the excitation energies of the first three $\mathrm{Si}_n\mathrm{H}_m$ clusters with experimental data [2,9] as well as with the values calculated using the Bethe-Salpeter technique [12]. The last column in Table I shows the Kohn-Sham LDA "ionization potentials" of the clusters $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$, given by the negative values of the energies for the highest occupied LDA molecular orbitals. It has been shown that, while TDLDA calculations usually provide good agreement with experiment for the excitation energies below $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$, they often tend to underestimate electronic excitation energies above this threshold [22]. As Table I demonstrates, the calculated TDLDA excitation energies for the transitions below or close to $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$ agree well with the experimental data and the Bethe-Salpeter values. The agreement deteriorates for higher excitations, which lie above $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$. However, as the size of the cluster increases, the energy of the first allowed excitation moves further down from the LDA "ionization" energy, and the agreement with experiment improves. For large $\mathrm{Si}_n\mathrm{H}_m$ clusters, we found that the first allowed optical transitions are always located below $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$. On this basis, we believe that the TDLDA should provide an accurate description for the photoabsorption gaps and the low energy optical transitions in all larger $\mathrm{Si}_n\mathrm{H}_m$ clusters.

The optical absorption gaps for small clusters can be defined directly by the energy of the first dipole-allowed transition in their absorption spectra. For large clusters, the absorption spectra become essentially quasicontinuous. A large number of low intensity transitions exist near the absorption edge. Taken individually, the oscillator strengths of these transitions would be located far below the experimentally detectable limit. As a result, identifying the first allowed optical transition in the case of large clusters is not a trivial task. Rather than associating the optical gaps with the individual transitions, we define them through the integral oscillator strength. With this approach, the value of the optical absorption gap is determined at a very small but nonzero fraction of the complete electronic oscillator strength [20]. In the present work, we set this threshold value at 10^{-4} of the total oscillator strength for a cluster. The chosen value of 10^{-4} stands above the level of numerical "noise," but is sufficiently small as to not suppress the experimentally detectable dipole-allowed transitions. Defining the absorption gaps in such a way does not affect the values of the optical gaps for small $\mathrm{Si}_n\mathrm{H}_m$ clusters, since the intensity of their first allowed transitions is much higher than the selected threshold. At the same time, it offers a simple way to evaluate the optical absorption gaps in large clusters. A similar definition for the photoabsorption gaps in clusters is commonly used in experimental work [26].

TABLE I. Excitation energies of hydrogenated silicon clusters. The experimental optical absorption energies are taken from Ref. [2] (silane and disilane) and Ref. [9] (neopentasilane). The assignment of electronic excitations for silane and disilane corresponds to the Rydberg transitions. The Bethe-Salpeter (BS) excitation energies are adapted from Ref. [12]. $-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$ is the time-independent LDA "ionization" energy. All values are in eV.

Cluster	Transition	Experiment	BS	TDLDA	$-\epsilon_{\mathrm{HOMO}}^{\mathrm{LDA}}$
SiH_4	4*s*	8.8	9.0	8.2	8.6
	4*p*	9.7	10.2	9.2	
	4*d*	10.7	11.2	9.7	
$\mathrm{Si}_2\mathrm{H}_6$	4*s*	7.6	7.6	7.3	7.5
	4*p*	8.4	9.0	7.8	
$\mathrm{Si}_5\mathrm{H}_{12}$	···	6.5	7.2	6.6	7.3

The variation of the optical absorption gaps as a function of cluster size is shown in Fig. 3. Along with the TDLDA values, we included optical gaps calculated by the Bethe-Salpeter (BS) technique [12]. For very small clusters, SiH_4, $\mathrm{Si}_2\mathrm{H}_6$, and $\mathrm{Si}_5\mathrm{H}_{12}$, the gaps computed by the TDLDA method are close to the BS values, although for $\mathrm{Si}_{10}\mathrm{H}_{16}$ and $\mathrm{Si}_{14}\mathrm{H}_{20}$ our gaps are considerably smaller than the BS gaps. At the same time, our TDLDA gaps for clusters in the size range from 5 to 71 silicon atoms are larger by ~1 eV than the gaps calculated by the Hartree-Fock technique with the correlation correction included through the configuration-interaction approximation (HF-CI) [11]. These differences are consistent with the fact that the BS calculations systematically overestimate and the HF-CI calculations underestimate the experimental absorption gaps. For example, for the optical absorption gap of $\mathrm{Si}_5\mathrm{H}_{12}$ the BS, TDLDA, and HF-CI methods predict the values of 7.2, 6.6, and 5.3 eV, respectively, compared to the experimental value of 6.5 eV. However, it is not clear whether the gaps of Ref. [11] refer to the optically allowed or

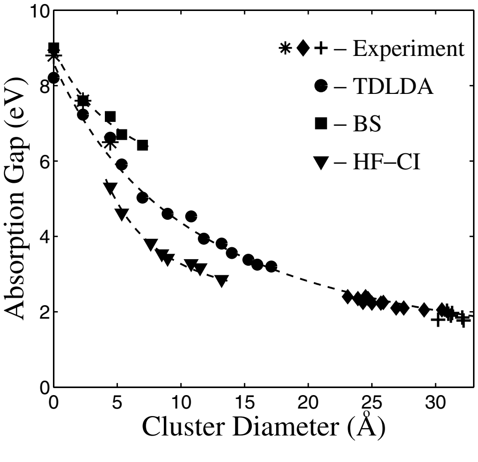

FIG. 3. Variation of optical absorption gaps as a function of cluster diameter. Theoretical values shown in the plot include the gaps calculated by the TDLDA method (this work), by the Bethe-Salpeter technique (BS) [12], and by the Hartree-Fock method with the correlation included through the configuration-interaction approximation (HF-CI) [11]. Experimental values are taken from Refs. [2,3,9]. The dashed lines are just a guide for the eye.

optically forbidden transitions, which may offer a possible explanation for the observed discrepancy. In the limit of large clusters, we find the TDLDA optical gaps to be in generally good agreement with the photoabsorption gaps evaluated by the majority of self-energy corrected LDA [9,10] and empirical [7,8] techniques. At present, the full TDLDA calculations for clusters larger than 20 Å in diameter remain beyond our capabilities. Nevertheless, the extrapolation of the TDLDA curve in the limit of large clusters comes very close to the experimental values for the photoabsorption gaps.

It is well known that time-independent LDA calculations typically underestimate the experimental photoabsorption gaps. Recent calculations for the frequency-dependent dielectric function in crystals [27] suggest that TDLDA and LDA gaps might converge for an infinite system. We did not observe this trend for the clusters we have examined in this work. On the contrary, for all clusters considered, our calculations show a substantial difference between the optical spectra and photoabsorption gaps calculated by the TDLDA and the time-independent LDA methods. At this stage, one cannot rule out the possibility that the TDLDA optical transitions will converge with the regular time-independent LDA spectra for much larger systems. Nevertheless, our calculations suggest that such convergence does not occur at least up to several hundred atoms, which is sufficient for a large variety of prospective TDLDA applications. As such, it is not necessary to invoke *ad hoc* empirical assumptions to examine systems comparable in size to experimentally measured quantum dots [8].

In summary, we have implemented a linear response theory within the time-dependent local density approximation to calculate the optical absorption spectra of $\mathrm{Si}_n\mathrm{H}_m$ nanoclusters. The calculations were performed in the cluster size range up to several hundred atoms. We have shown that the TDLDA technique provides an efficient, robust alternative to much more complex theoretical methods for the excited state properties. The excitation energies and optical absorption gaps computed with our technique were found to be in good agreement with experiment in the limit of both small and large clusters.

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