

Time-dependent density functional theory calculations for the Stokes shift in hydrogenated silicon clusters

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Experimental evidence suggests that the Stokes shift may be considerable in silicon clusters. Multiple theoretical methods have been used to study this problem, with varying results: predicted Stokes shifts can differ in energy by several electron volts, and predicted minimum-energy structures can have either relaxed cores or relaxed outer shells. Here we present the lowest energy configuration for excited states and the Stokes shift for a series of silicon clusters in two separate ways. First, by energy minimization using density functional theory and changing the electronic occupation such that an electron is moved from the highest occupied molecular orbital to the lowest unoccupied molecular orbital; and second, by total-energy minimization using time-dependent density functional theory to calculate the energy of the first electronic transition with non-negligible oscillatory strength.

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I. INTRODUCTION

Understanding the unprecedented size-dependent electronic and optical properties of nanoscale systems, such as atomic clusters, is critical to the fabrication of novel materials, which could greatly impact the technological industry. Silicon clusters, both bare and hydrogenated, have been the focus of an extensive research effort owing to the importance of silicon in the fabrication of electronic materials.¹⁻⁶ Still, fundamental questions remain regarding the optical properties of silicon clusters.⁷

Experimental evidence suggests that hydrogenated silicon clusters may have large Stokes shifts.⁸⁻¹³ The processes of absorption and emission of a photon are not symmetric because the cluster may undergo structural relaxation while it is in an excited state. Multiple theoretical methods have been used to study this problem,¹⁴⁻¹⁷ with varying results: predicted Stokes shifts can differ in energy by several electron volts, and predicted minimum-energy structures can have either relaxed cores¹⁷ or relaxed outer shells.¹⁶

The problem is particularly challenging as it involves structural relaxations in excited states; calculations of such systems are very computationally demanding owing to the presence of numerous degrees of freedom and the complexity of correlated interactions. One approach that has been used quite extensively is to promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and finding the relaxed structure by using a ground-state theory such as density functional theory (DFT) in such an occupation constrained configuration. The Stokes shift is then approximated by the difference in the HOMO-LUMO gap from the ground-state structure and the structure with an electron promoted to the LUMO (Fig. 1). A second approach is to use time-dependent theory to calculate the gap for each of the two structures found with DFT, and to then calculate the

difference in energy gaps. This approach fixes the shortcoming of the first approach by a better treatment of the excitation process, i.e., the excited-state electronic state includes the presence of the hole state, at least in an approximate fashion. However, the relaxed structure may not be the lowest energy structure in the excited state as it is calculated with a ground-state theory

Expanding on previous work,¹⁸ we present two types of calculations for hydrogenated silicon clusters ranging in size from Si₅H₁₂ to Si₃₅H₃₆. First, we calculate the Stokes shift by promoting an electron from the HOMO to the LUMO, using the DFT method combined with the local-density approximation (LDA) and generalized gradient approximation (GGA) exchange-correlation functionals. In the second approach, which we believe is more suitable given its explicit treatment of excited states, the Stokes shift is calculated by employing

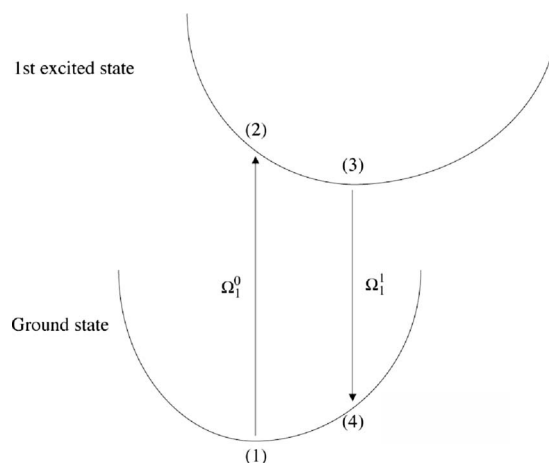


FIG. 1. Schematic illustration of the Stokes shift. The Stokes shift is defined as the difference between the absorption, (1)→(2), and emission, (3)→(4), energies: $\Omega_1^0 - \Omega_1^1$.

time-dependent DFT (TDDFT) formalism. In this approach, the relaxed structure in the excited state is found by minimizing the total energy of the system in the excited state.

II. COMPUTATIONAL METHODS

We calculate ground-state properties using the real-space pseudopotential method within density functional theory. We describe the electronic problem by a Kohn-Sham equation of the form

$$\left\{ -\frac{\nabla^2}{2} + \sum_a v_{ion}^p(\mathbf{r}-\mathbf{r}_a) + v_H[\rho(\mathbf{r})] + v_{xc}[\rho(\mathbf{r})] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (1)$$

where $v_{ion}^p(\mathbf{r}-\mathbf{r}_a)$ is a norm-conserving pseudopotential¹⁹ that replaces the all-electron potential of each ion at \mathbf{r}_a , $v_H[\rho(\mathbf{r})]$ is the Hartree potential, and $v_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation potential, which is approximated by a parametrized analytical expression of the charge density. We use two common approximations for the exchange-correlation functional: the LDA (Refs. 20 and 21) and the GGA.^{22,23} We use atomic units ($\hbar=e=m=1$) throughout.

Equation (1) is solved self-consistently on a real-space grid within a spherical boundary (outside of which the wave functions vanish), using a finite-difference expansion for the Laplacian operator. A more detailed description of the real-space pseudopotential method can be found in Refs. 24–27.

Electronic excitations can be calculated in the framework of TDDFT by considering a linear response to an external periodic perturbation.^{28,29} A linear-response formalism is used to derive a density functional expression for the dynamic polarizability. The excitation energies Ω_I , which correspond to the poles of the dynamic polarizability, are obtained from the solution of an eigenvalue problem

$$\mathbf{Q}\mathbf{F}_I = \Omega_I^2 \mathbf{F}_I, \quad (2)$$

where the matrix \mathbf{Q} is given by

$$Q_{ij\sigma,kl\tau} = \delta_{i,k} \delta_{j,l} \delta_{\sigma,\tau} \omega_{kl\tau}^2 + 2\sqrt{\lambda_{ij\sigma} \omega_{ij\sigma}} K_{ij\sigma,kl\tau} \sqrt{\lambda_{kl\tau} \omega_{kl\tau}}. \quad (3)$$

In this equation, the indices i, j , and σ (k, l , and τ) refer to the space and spin components, respectively, of the unperturbed static Kohn-Sham orbitals $\phi_{i\sigma}(\mathbf{r})$, $\omega_{ij\sigma} = \epsilon_{j\sigma} - \epsilon_{i\sigma}$ are the differences between the eigenvalues of the single-particle states, $\lambda_{ij\sigma} = n_{i\sigma} - n_{j\sigma}$ are the difference between their occupation numbers, and the coupling matrix \mathbf{K} in the adiabatic approximation is given by

$$K_{ij\sigma,kl\tau} = \int \int \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta^2 E_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r}) \delta\rho_\tau(\mathbf{r}')} \right) \times \phi_{k\tau}(\mathbf{r}') \phi_{l\tau}^*(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (4)$$

where E_{xc} is the exchange-correlation energy of the system. The oscillator strengths f_I , which correspond to the residues of the dynamic polarizability, are given by

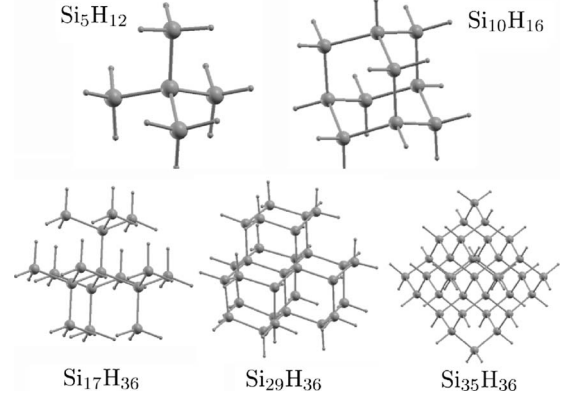


FIG. 2. Structures of hydrogenated Si clusters.

$$f_I = \frac{2}{3} \sum_{\beta=\{x,y,z\}} |\hat{\beta} \mathbf{R}^{1/2} \mathbf{F}_I|^2, \quad (5)$$

where \mathbf{F}_I are the eigenvectors of Eq. (2), $R_{ij\sigma,kl\tau} = \delta_{i,k} \delta_{j,l} \delta_{\sigma,\tau} \lambda_{kl\tau} \omega_{kl\tau}$ and $\hat{\beta}$ is the dipole matrix element, $\hat{\beta}_{ij\sigma} = \int \phi_{i\sigma}(\mathbf{r}) \beta \phi_{j\sigma}(\mathbf{r}) d\mathbf{r}$, $\beta = \{x, y, z\}$. The static Kohn-Sham orbitals $\phi_i(\mathbf{r})$ and their eigenvalues ϵ_i used in Eqs. (2)–(5) are obtained from the solution of the *time-independent* Kohn-Sham equations.

Compared to other *ab initio* methods for excited states, such as the configuration interaction method,³⁰ quantum Monte Carlo simulations,³¹ or the Green's function method based on the GW approximation,^{32,33} the TDDFT approach is less computationally demanding.^{1,2} This makes it feasible to find the minimum-energy structures of the silicon clusters studied using a direct total-energy minimization approach.

The clusters were constructed as spherical portions of bulk silicon capped by hydrogen atoms. We obtained the relaxed ground-state cluster structures using the Broyden-Fletcher-Goldfarb-Shanno minimization scheme^{34,35} implemented within the PARSEC electronic-structure code.³⁶ These calculations were carried out using a grid spacing of 0.6 a.u. (1 a.u.=0.5292 Å). The capping hydrogen atoms and the boundary of the spherical domain are at least 6 a.u. apart. The optimized structures of the hydrogenated silicon clusters are shown in Fig. 2. As in all the studies to date, the lifetime of the electronic excitation is assumed to be long enough to allow for structural relaxation.

In the first approach, which we call DFT-LDA (density functional theory within the local-density approximation) or DFT-GGA (density functional theory within the generalized gradient approximation), four separate calculations were made for each cluster: (1) the relaxed ground-state structure and its HOMO energy were found, (2) using the ground-state structure, an electron was promoted from the HOMO to the LUMO and the LUMO energy was found, (3) the structure with an electron promoted from the HOMO to the LUMO was relaxed (the structure was first distorted in order to break symmetry) to find the excited-state structure, and (4) using the excited-state structure, the HOMO energy was calculated. The Stokes shift was then computed as the difference [(1)→(2)]–[(3)→(4)], as shown in Fig. 1.

TABLE I. Absorption gaps, E_{abs} , emission gaps E_{em} , and Stokes shifts, E_{ss} , calculated by promoting an electron from the HOMO to the LUMO. The results of our PARSEC calculations are shown along with the previous results obtained using the ABINIT (Ref. 16) and JEEP (Ref. 15) codes. All values are in eV.

Cluster	ABINIT			JEEP	PARSEC LDA (GGA)		
	E_{abs}	E_{em}	E_{ss}	E_{ss}	E_{abs}	E_{em}	E_{ss}
Si ₅ H ₁₂	6.09	0.42	5.67		5.49 (5.81)	0.33 (0.21)	5.16 (5.60)
Si ₁₀ H ₁₆	4.81	0.41	4.40		4.62 (4.77)	0.73 (0.58)	3.89 (4.19)
Si ₁₇ H ₃₆					4.15 (4.17)	1.34 (0.50)	2.81 (3.67)
Si ₂₉ H ₃₆	3.65	2.29	1.35	0.69	3.04 (3.55)	2.49 (2.91)	0.55 (0.64)
Si ₃₅ H ₃₆	3.56	2.64	0.92	0.57	3.30 (3.46)	2.36 (2.70)	0.94 (0.76)

Several methods have been proposed for the calculation of excited-state forces.^{37–41} We used the frequency domain approach within TDDFT (Ref. 41) to compute the excited-state forces of the hydrogenated silicon clusters. The energy derivatives were calculated by explicit small displacements of the nuclei. Although this approach is computationally inefficient when compared to an explicit perturbative approach, it does have the advantage of being straightforward and easy to implement.

First, we calculated the optical absorption gap of the DFT-LDA ground-state structure. We then searched for the relaxed structure in the excited state by breaking the Td symmetry of the Si_mH_n clusters and systematically moving each of the atoms in the cluster. The total excited-state energy (LDA+TDLDA) was calculated for each new structure and the atoms were moved until a minimum-energy structure was found. This approach is very computationally intensive since the excited-state cluster configurations lack symmetry and because it is necessary to perform a large number of atom movements to find the minimum-energy structure. However, this approach should result in more accurate values of the Stokes shift than methods based purely on ground-state calculations.

As mentioned above, in both of the approaches we use it is necessary to break symmetry and distort the clusters in order to find the minimum-energy structure in the excited state. This may result in reordering of mixing of the energy levels. However, because it is no longer possible to characterize the different energy levels by their symmetry, and since they can be closely spaced, we cannot determine whether level crossings occurred. Projecting final states into initial states is likewise inconclusive. The overlap between states can be small due to the fact that the final geometry may be quite different from the initial geometry of the cluster, as discussed in the following section.

III. RESULTS

Table I and Fig. 3 show the Stokes shifts of hydrogenated silicon clusters calculated by promoting an electron from the HOMO to the LUMO. For smaller Si_mH_n clusters, the Stokes shifts were found to be on the order of a few electron volts, while for the larger clusters the Stokes shifts were less than 1 eV. As expected, the value of the Stokes shift strongly de-

creases with increasing cluster size, although a slight increase is seen from Si₂₉H₃₆ to Si₃₅H₃₆ in our calculations. Degoli *et al.*¹⁶ previously computed the Stokes shifts of hydrogenated Si clusters using the ABINIT package. They also observed a decrease in the value of the Stokes shift with increasing cluster size. Puzder *et al.*¹⁵ calculated the Stokes shifts for the Si₂₉H₃₆ and Si₃₅H₃₆ clusters using the JEEP code. Both the ABINIT and JEEP codes utilize plane-wave basis sets. Our values of the Stokes shifts are in reasonable agreement with the previous calculations of Degoli *et al.*¹⁶ and Puzder *et al.*¹⁵

In previous studies different minimum-energy structures of hydrogenated Si clusters with either relaxed cores¹⁷ or relaxed outer shells¹⁶ have been used. The ground-state structures and the lowest energy structures of Si_mH_n clusters obtained in our calculations when an electron is promoted from the HOMO to the LUMO are shown in the left and right panels of Fig. 4, respectively. The Si₅H₁₂ cluster has one Si atom at the center and a shell of four Si atoms around it. In the ground state, the distance from the shell Si atoms to the central atom is found to be 4.38 (4.42) a.u. within LDA (GGA). When an electron is promoted to the LUMO, one SiH₃ unit is projected out and the cluster cleaves. The

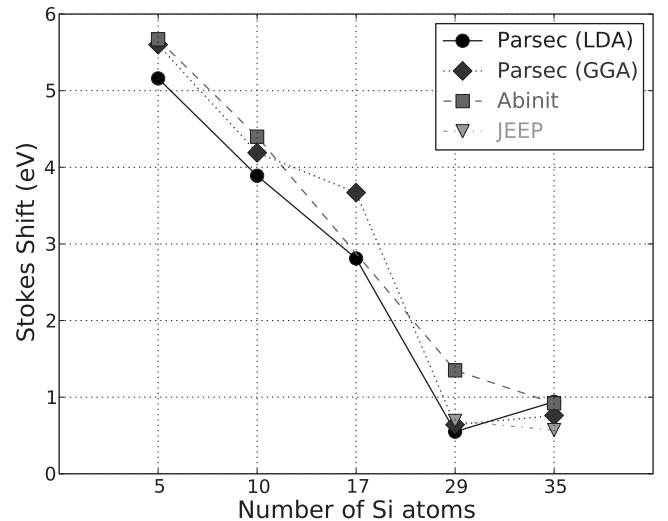


FIG. 3. Stokes shifts calculated by promoting an electron from the HOMO to the LUMO. Our results (PARSEC) are shown along with the previous ABINIT (Ref. 16) and JEEP (Ref. 15) calculations.

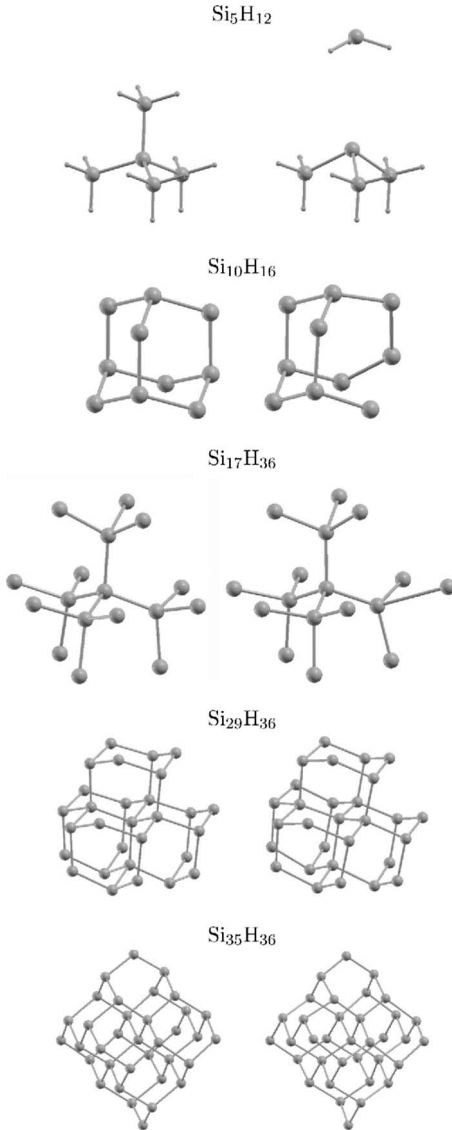


FIG. 4. Left panel: ground-state structures of Si_mH_n clusters. Right panel: lowest energy structures of Si_mH_n clusters when an electron is promoted from the HOMO to the LUMO within DFT-LDA. For clarity, only the Si atoms are shown for larger clusters.

$\text{Si}_{10}\text{H}_{16}$ cluster has a cage structure with no Si atom at its center. In this case, when an electron is promoted to the LUMO, the shell expands and the average distance from the center of the cluster increases from 4.79 to 4.96 a.u. within LDA and from 4.85 to 4.88 a.u. within GGA. When an electron is promoted to the LUMO in the $\text{Si}_{17}\text{H}_{36}$ cluster, one SiH_3 unit is projected from the cluster. For the two largest clusters, $\text{Si}_{29}\text{H}_{36}$ and $\text{Si}_{35}\text{H}_{36}$, the atomic displacements are relatively small.

Table II and Fig. 5 show the Stokes shifts of hydrogenated Si clusters computed by minimizing the total (LDA+TDLDA) energy. Again, we find that the Stokes shifts decrease with increasing cluster size. It is interesting to note the large difference between the Stokes shifts of the $\text{Si}_{10}\text{H}_{16}$ cluster calculated using the DFT-LDA and TDLDA methods. In the DFT-LDA calculation for this cluster, we find an absorption gap of 4.62 eV, and an emission gap of

TABLE II. Absorption gaps, E_{abs} , emission gaps, E_{em} , and Stokes shifts, E_{ss} , calculated using the QMC method, Ref. 15, TDDFTB (Ref. 17) and TDLDA approach (this work). All values are in eV.

Cluster	QMC	TDDFTB		TDLDA			
	E_{ss}	E_{abs}	E_{em}	E_{ss}	E_{abs}	E_{em}	E_{ss}
Si_5H_{12}		6.40	2.29	4.11	6.49	1.49	5.00
$\text{Si}_{10}\text{H}_{16}$					3.60	3.54	0.06
$\text{Si}_{17}\text{H}_{36}$		4.47	2.40	2.07	4.93	2.64	2.29
$\text{Si}_{29}\text{H}_{36}$	1.0	4.42	2.57	1.85	3.58	1.93	1.65
$\text{Si}_{35}\text{H}_{36}$	0.8	4.37	2.89	1.48	3.84	2.41	1.43

0.73 eV, leading to the Stokes shift of 3.89 eV. In the TDLDA calculation, the absorption gap is 3.60 eV and the emission gap is 3.54 eV, resulting in the Stokes shift of only 0.06 eV. There is a TDLDA eigenvalue at 0.73 eV in the emission spectra of $\text{Si}_{10}\text{H}_{16}$. However, this transition has a very small oscillator strength. The first transition with a non-negligible oscillator strength in the absorption spectrum of $\text{Si}_{10}\text{H}_{16}$ is at 3.54 eV, which results in the small Stokes shift reported. We believe that the TDLDA Stokes shift of this cluster would be closer to the experimental value. This also highlights the problem with using DFT-LDA for calculation of Stokes shift. Within DFT, one does not take any optical oscillator strength into account. While in most cases, the transition from the HOMO to the LUMO is the first optically allowed transition, in some cases that is not the case. Using TDLDA one can easily avoid this problem.

The results of previous calculations for the Stokes shifts of hydrogenated Si clusters using the quantum Monte Carlo (QMC) (Ref. 15) and TDDF tight-binding (TDDFTB) (Ref. 17) methods are also shown in Table II and Fig. 5. In these calculations the structures of Si_mH_n clusters were not relaxed

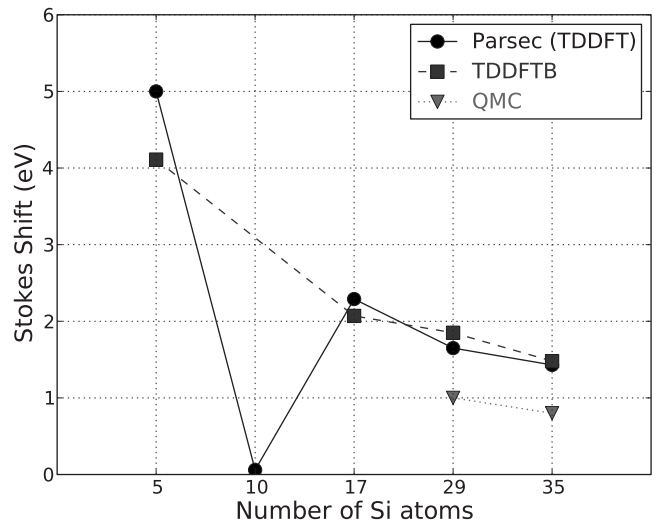


FIG. 5. Stokes shift calculated by minimizing the total (LDA+TDLDA) energy. Our results (TDLDA) are shown along with the previous QMC (Ref. 15) and TDDFTB (Ref. 17) calculations.

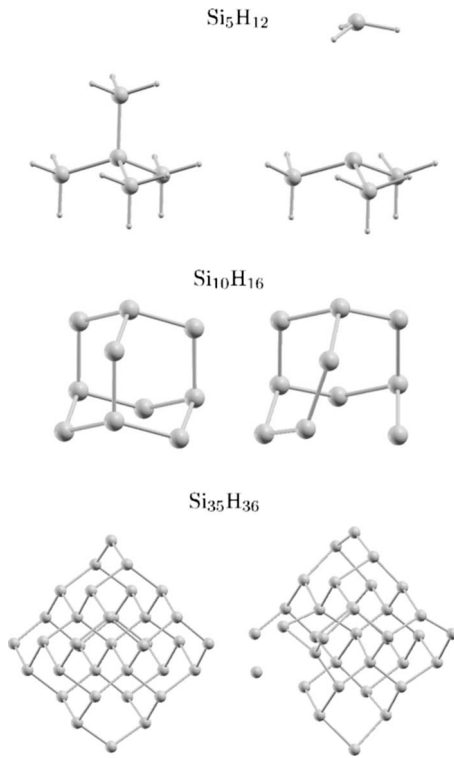


FIG. 6. Left panel: ground-state structures of Si_mH_n clusters. Right panel: lowest energy structures of Si_mH_n clusters obtained by TDLDA total-energy minimization. For clarity, only the Si atoms are shown for the larger clusters.

in the excited state. Instead, time-dependent calculations were carried out using the ground-state structures and the structures that resulted from promoting an electron from the HOMO to the LUMO within time-independent DFT-LDA. However, the structures of Si_mH_n clusters obtained by promoting an electron from the HOMO to the LUMO may not be the same as those found by performing the total-energy minimization. Figure 6 shows the ground-state and relaxed excited-state structures of the hydrogenated Si clusters obtained in our calculations. The comparison of clusters shown in Figs. 4 and 6 indicates that the cluster structures resulted from promoting an electron from the HOMO to the LUMO appear to be similar to those obtained by the total-energy minimization. There are, however, some noticeable differences between the structures of Si_mH_n clusters shown in the right panels of Figs. 4 and 6. For the Si_5H_{12} cluster, the TDLDA structure has somewhat longer Si-Si bonds (4.57 a.u.) than the DFT-LDA structure (4.47 a.u.) and the SiH_3 unit is projected further outward by almost 1 a.u. A similar situation occurs in the $\text{Si}_{10}\text{H}_{16}$ cluster, where the average distance from the Si atoms to the cluster center increases by 0.13 a.u. In the excited-state TDLDA structure of $\text{Si}_{17}\text{H}_{36}$, the inner shell contracts by about 1% and the outer shell expands by approximately 2%, with an SiH_3 unit projecting outward. In contrast, in the DFT-LDA excited-state structure, both the inner and outer shells contract by about 1% of the ground-state bond length.

The $\text{Si}_{29}\text{H}_{36}$ DFT-LDA and TDLDA structures are very similar—in both cases symmetry is broken, and atoms in the inner shell contract while atoms in the outer shell expand slightly. The case of $\text{Si}_{35}\text{H}_{36}$ is similar to that of $\text{Si}_{10}\text{H}_{16}$ in that an SiH_3 unit is projected from the cluster. In $\text{Si}_{35}\text{H}_{36}$ we also find that atoms in the inner shell contract while atoms in the outer shell expand slightly. It is interesting to note that although the TDLDA and DFT-LDA excited-state structures are different, the calculated Stokes shifts shown in Fig. 5 for “Parsec (TDDFT)” and “TDDFTB” are remarkably similar for the larger clusters.

IV. SUMMARY

We have calculated the Stokes shifts of a series of hydrogenated silicon clusters using two different approaches: within LDA, by promoting an electron from the highest unoccupied molecular orbital to the lowest (previously) unoccupied molecular orbital, and within TDLDA, by directly minimizing the total energy. Because the latter approach treats the excited states explicitly, we believe it to be more appropriate in describing the Stokes shift in hydrogenated silicon clusters.

In both cases, we find that the magnitude of the Stokes shift is strongly size dependent, decreasing as cluster size increases. Our LDA calculations show Stokes shifts as large as 5 eV, and structures that are significantly distorted from the ground-state structures. These findings are in good agreement with previous studies on these systems.^{14–17}

Our TDLDA calculations also show distorted structures in the excited state. For Si_5H_{12} there is not much difference between the LDA and TDLDA calculated Stokes shifts. However, for $\text{Si}_{10}\text{H}_{16}$, we find that the first few TDLDA transitions are not optically allowed. This makes the TDLDA emission gap much larger than the LDA emission gap. Consequently, the TDLDA calculated Stokes shift is much smaller than the LDA calculated Stokes shift (0.06 eV, compared to 3.89 eV). We expect TDLDA to be much closer to the experimental situation—that the molecule will get excited to the first optically allowed transition rather than the transition from the HOMO to the LUMO. This highlights the necessity of using an excited states formalism to study the Stokes shift problem.

As mentioned in the introduction, different calculations have shown either core or surface silicon atoms relaxing in the excited state. For the largest cluster run with the TDLDA method, $\text{Si}_{35}\text{H}_{36}$, we find that atoms near the center of the cluster move inwards (i.e., closer to the center of the cluster), while the outer shell expands and projects out an SiH_3 unit.

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