# Excitons in small hydrogenated Si clusters

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The excitonic states of four small hydrogenated Si clusters ($SiH_4$, $Si_2H_6$, $Si_5H_{12}$, and $Si_{10}H_{16}$) are studied using the diffusion quantum Monte Carlo approach. The importance of using accurate guiding wave functions is stressed and we show that the quantum chemical singles-only configuration interaction method and the time-dependent density functional theory within the adiabatic local-density approximation can provide suitable zeroth-order approximations in these systems.

Hydrogenated silicon clusters are of significant interest because they may be used to model the absorption and emission of visible light in quantum dots[1] and porous silicon.[2] The optical properties of these systems are strongly influenced by exciton formation, and the accurate prediction of their excitonic gap energies is one of the most challenging theoretical problems in these materials.

Excitation energies in hydrogenated silicon clusters have been studied using many theoretical methods, including tight-binding and density-functional methods, and many-body perturbation theory. In this paper we present a study of the excitonic states of small $Si_nH_m$ clusters using the diffusion quantum Monte Carlo (DMC) technique.[3–5] The small clusters that we study ($SiH_4$, $Si_2H_6$, $Si_5H_{12}$, and $Si_{10}H_{16}$) are at the molecular limit of semiconductor nanostructures. Small clusters have the advantage that a significant amount of experimental and theoretical data exists with which we can compare our results. Any method capable of giving an accurate description of excitonic behavior in semiconductor clusters at the microscopic level should be able to describe excitons in these clusters, which are therefore important systems for the benchmarking of theoretical methods.

DMC is a stochastic method for evolving the imaginary-time Schrödinger equation. The fermionic symmetry is maintained using the fixed-node approximation[6] in which the nodal surface of the wave function is constrained to equal that of a guiding wave function. DMC presents an attractive approach for studying electronic systems because it can achieve very high accuracy and the computational cost scales as $N^3$, where $N$ is the number of electrons, which is much more favorable than other correlated wave-function methods.

Accurate DMC calculations of ground-state energies have already been demonstrated and in principle such accuracy can also be attained for excited states. The DMC method gives the lowest energy consistent with the nodal surface of the guiding wave function[7,8] and it is therefore crucial that the guiding wave functions give a reasonable description of the excited states of the system. We use guiding wave functions of the Slater-Jastrow type where the Slater part, consisting of a sum of determinants, is multiplied by a nodeless Jastrow correlation factor

$$\Psi = \exp(\mathcal{J}) \sum_i c_i \mathcal{D}_i^{\uparrow} \mathcal{D}_i^{\downarrow} \qquad (1)$$

where $\exp(\mathcal{J})$ is the Jastrow factor and $\mathcal{D}_i^{\uparrow}$ and $\mathcal{D}_i^{\downarrow}$ are Slater determinants of one-particle up- and down-spin orbitals. The Jastrow factor does not alter the nodal surface of the guiding wave function, which is therefore fixed by the Slater part.

For the Jastrow factors we used parametrized forms depending on the distances between electrons and their relative spins and the distances of electrons from the ions. The Jastrow factors contained up to 48 variable parameters whose optimal values were obtained using efficient variance minimization techniques.[9,10] We have investigated a variety of methods for obtaining the Slater part of the wave function, including singles-only configuration interaction (CIS), time-dependent density-functional theory within the adiabatic local-density approximation (TD-LDA), and the complete active space self-consistent field (CASSCF) technique.

A CIS wave function consists of a linear combination of determinants each of which involves a single excitation from the Hartree-Fock (HF) ground state. Although the CIS wave function neglects correlation effects due to double and higher excitations, this approach has considerable merit for our purposes. The CIS wave functions are orthogonal to the ground state HF determinant and therefore CIS is a rather natural extension of the HF theory to excited states. The CIS wavefunction is flexible enough to give a reasonable description of electron-hole interactions. CIS is also size-consistent,[11] so that it is appropriate to use CIS-based guiding wave functions for studying excited-state properties as a function of system size. In addition, and very importantly for our purposes, the CIS wave function can always be resummed into a number of determinants equal to the number of electrons in the system, so that the number of determinants rises only linearly with system size. Moreover, because each of these determinants differs from the ground-state HF determinant in only a single column they can be evaluated very efficiently using rank-one updates of the cofactor matrices.[12] Within the pair approximation, the TD-LDA wave function also involves only single excitations from the ground state, but in this case the orbitals are LDA orbitals instead of HF ones. For our purposes the TD-LDA method therefore offers similar computational advantages to CIS. The CASSCF method includes multiple excitations and is capable of giving very high accuracy but is computationally extremely expensive.

We have performed calculations for the vertical-ionization and electron-affinity energies and the vertical sin-

TABLE I. Vertical ionization potentials $I_P$ and electron affinities $E_A$ in eV calculated within DMC.

| Cluster | $I_P$ | $E_A$ |
|---|---|---|
| $SiH_4$ | 12.88(3) | −0.26(2) |
| $Si_2H_6$ | 10.90(3) | −0.26(4) |
| $Si_5H_{12}$ | 9.8(1) | 0.0(1) |
| $Si_{10}H_{16}$ | 9.6(1) | 0.0(1) |

glet and triplet excitation energies of $SiH_4$, $Si_2H_6$, $Si_5H_{12}$, and $Si_{10}H_{16}$, using geometries identical to those of Ref. 13. The Slater parts of the guiding wave functions for the ground states of the clusters were obtained from HF calculations in the correct charge states, thereby allowing for electronic relaxation effects. The HF, CIS, LDA, TD-LDA, and CASSCF calculations in this study were performed using the GAUSSIAN98 package,[14] while for the DMC calculations we used the CASINO quantum Monte Carlo code.[15] Optimized uncontracted valence Gaussian basis sets consisting of 12 $s$ functions, 6 $p$ functions, and 2 $d$ functions centered on the Si atoms, and 13 $s$ functions and 2 $p$ functions centered on the H atoms were used to represent the single-particle orbitals. The Si core electrons were modeled by a norm-conserving HF pseudopotential. In the DMC calculations we added the core polarization potential of Shirley and Martin,[16] and the nonlocal energy was evaluated within the locality approximation.[17]

First we discuss the DMC results for the ionization potentials $I_P$ and electron affinities $E_A$, which are shown in Table I. The ionization potential is defined as $I_P = E(N-1) - E(N)$, where $E(M)$ is the energy of the $M$-electron system, and the electron affinity is defined as $E_A = E(N) - E(N+1)$. The photoelectron spectrum of $SiH_4$ shows a double-peaked structure arising from the Jahn-Teller distortion of the ionized state.[18] The most appropriate comparison is between our calculated vertical $I_P$ of 12.88(3) eV and the average of the two Jahn-Teller-split peaks, which gives 12.61 eV.[18] For $Si_2H_6$ a range of experimental values of 10.53-10.7 eV has been reported,[19,20] which is in reasonable agreement with our value of 10.90(3) eV. The ionization energies slowly decrease as the cluster size increases and the electron affinities are small because each of the clusters has a closed-shell electronic configuration. From Table I we can deduce the quasiparticle band gaps ($E_{qp} = I_P - E_A$) and, for example, for $SiH_4$ we obtain 13.14(4) eV, which is in reasonable agreement with the results of Grossman *et al.*[21] who obtained 12.8(1) eV within DMC and 13.0 eV within the $GW$ approximation.

In Fig. 1 we plot the energies of the lowest-triplet, lowest-bright (dipole-allowed)-singlet, and lowest-dark (dipole-forbidden)-singlet transitions against cluster size for the CIS, TD-LDA, and DMC calculations, together with the available experimental data.[22] The DMC values were obtained using guiding wave functions obtained from CIS calculations, but we repeated some of the calculations using TD-LDA guiding wave functions and obtained almost the same energies. The energies of the lowest singlet and triplet energies of the clus-
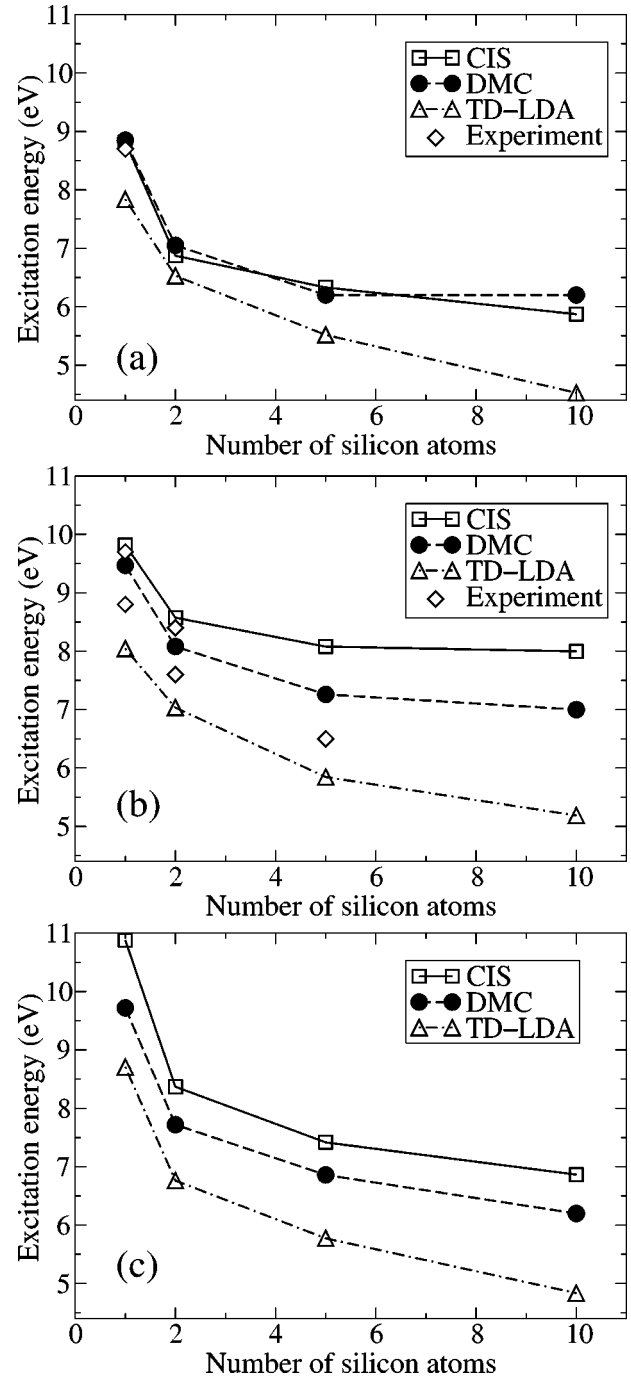


FIG. 1. Excitonic energies versus the number of silicon atoms in the cluster. (a) The lowest-triplet excitation, (b) the lowest-bright (dipole-allowed)-singlet excitation (Ref. 22), and (c) the lowest-dark (dipole-forbidden)-singlet excitation. In (b) the positions of the two lowest peaks in the measured absorption spectrum for $SiH_4$ and $Si_2H_6$ are shown. For the DMC values the error bars are smaller than the symbols.

ters generally decrease with increasing cluster size because of the reduction in the quantum-confinement effect.

The comparison with experiment is unfortunately not straightforward. The absorption spectrum of $SiH_4$ shows three broad peaks at energies of 8.8, 9.7, and 10.7 eV.[23] According to our CIS, TD-LDA, and DMC calculations, and

the multireference single- and double-excitation configuration interaction (MRCI) calculations of Chantranupong *et al.*,[24] there are only *two* strong absorption peaks in the relevant energy range. Chantranupong *et al.* suggested that the experimental peaks at 8.8 and 9.7 eV derive from a Jahn-Teller splitting of the triply degenerate $2t_2 \rightarrow 4s$ transition. The theoretical results presented here do not include the effects of the Jahn-Teller distortion and should therefore lie between 8.8 and 9.7 eV. Our DMC value of 9.47(2) eV for the $2t_2 \rightarrow 4s$ transition lends support to this interpretation. This interpretation is, however, different from that of Grossman *et al.*,[21] whose DMC excitation energy for the lowest singlet state of 9.1(1) eV is closer to the experimental energy of the lowest absorption peak at 8.8 eV. For $Si_2H_6$, Itoh *et al.*[23] have reported the lowest optically allowed excitation at 7.6 eV, which is lower than our DMC energy, while Fehér[27] gives a corresponding value for $Si_5H_{10}$ of 6.5 eV, which is also lower than our DMC value. In general the experimental values for the lowest optically allowed transitions are a little lower than the calculated ones. In $SiH_4$ there is good evidence that this discrepancy arises largely from a lowering of the first allowed transition due to the Jahn-Teller distortion of the excited state.[24] We note that each of the lowest optically allowed transitions plotted in Fig. 1(b) is orbitally degenerate and therefore subject to a Jahn-Teller distortion, although the magnitude of this effect is unknown in the larger clusters. Our DMC value for the lowest triplet excitation in $SiH_4$ is in good agreement with the experimental result of Curtis and Walker.[25] Given the uncertainties in the comparison with experiment due to the breadth of the peaks in the measured absorption spectra and the likely role of vibrational and Jahn-Teller effects, the agreement between theory and experiment is quite good.

Our DMC results for the cluster excitation energies are a little higher than the values of Rohlfing and Louie,[13] who solved the Bethe-Salpeter equation (BSE) using the results of *GW* self-energy calculations. Recently, however, these authors have found that their neglect of the off-diagonal matrix elements of the self-energy leads to some inaccuracies and that inclusion of these terms increased the lowest singlet and triplet excitation energies of $SiH_4$ by 0.4 eV and 0.8 eV,[21] respectively, which brings their results into much better agreement with ours. Our results for $SiH_4$ are in good agreement with the MRCI calculations of Chantranupong *et al.*[24] Grossman *et al.*[21] also calculated excitation energies of $SiH_4$ using the DMC method, obtaining results in good agreement with ours. The differences between our DMC results and those of Grossman *et al.*[21] are, however, outside of the statistical error bars. The reasons for these differences are unclear, but they could arise from the use of different pseudopotentials, different Gaussian basis sets, and the differences in the theoretical methods used for constructing the multideterminant guiding wave functions, or other differences in the DMC algorithms used.

For the CIS calculations the ground state is the HF ground state. The CIS singlet excitation energies are too high because the correlation energy, which is poorly described in CIS, is larger in the excited states than in the ground state. The error in the CIS triplet states is expected to be smaller because the large electron-hole exchange interaction in the triplet states is well described by CIS so that the electron-hole correlation energy, which is poorly described, is smaller than for the singlet. For these clusters the CIS triplet excitation energies are actually very close to the DMC energies, although this results from a large cancellation of errors between the CIS excited-state energies and the HF ground-state energy, which will not necessarily occur in other systems. The TD-LDA excitation energies are significantly lower than the DMC values. The excitation energies studied here are close to the TD-LDA ionization threshold, which is equal to the negative of the eigenvalue of the highest occupied LDA orbital. It is well known that TD-LDA gives excitation energies that are too low for excited states close to or greater than the TD-LDA ionization threshold,[26] which is too small because of the exponential decay of the LDA exchange-correlation potential into the vacuum.

An examination of the CIS and TD-LDA wave functions reveals that for each of the excitonic states of Fig. 1 only excitations from the highest occupied molecular orbital (HOMO) are significant[28] for $SiH_4$, $Si_2H_6$, and $Si_5H_{12}$, although for $Si_{10}H_{16}$ several occupied orbitals are involved. The number of unoccupied molecular orbitals with significant weight depends on the theoretical method used and the particular excitonic state. In general, more unoccupied molecular orbitals have a significant weight in the low-energy CIS wave functions than in the TD-LDA ones. For example, in $SiH_4$ the lowest-energy singlet has significant weight on four unoccupied orbitals in CIS but only the lowest unoccupied molecular orbital (LUMO) is significant in TD-LDA.

The simplest possible excited-state wave functions are those obtained by replacing a HOMO in the ground-state determinant by a LUMO and symmetrizing appropriately. Within HF theory this approach works poorly for $SiH_4$, giving DMC energies that are too high, with errors of 1.2 eV for the lowest singlet state and 1.3 eV for the lowest triplet state. However, this approach works much better within LDA. These conclusions are consistent with our analysis of the CIS and TD-LDA wave functions given above. For crystalline silicon, accurate DMC energies for low-lying states have been obtained using guiding wave functions formed by replacing a single occupied LDA orbital by an unoccupied one.[29] In this case the mixing in of other states is small because of the weaker electron-hole interaction and the momentum-selection rule. The LDA orbitals therefore appear to form an efficient basis for describing the low-energy excited states of hydrogenated silicon clusters and of crystalline silicon. However, the simple approach of using single excitations from the LDA ground-state determinant does not work in all cases. For example, in $Si_5H_{12}$ there are two low-energy orbitals, differing in energy by only 0.02 eV, which mix strongly into both the lowest bright and dark singlets. A multideterminant approach is necessary to correctly describe the nature of these states. For the $SiH_4$ cluster we have also obtained guiding wave functions within CASSCF. For the lowest bright singlet of $SiH_4$, for example, the DMC excitation energies obtained from CIS-, TD-LDA- and CASSCF-

based guiding wave functions differ by less than 0.1 eV, indicating that the extra expense of calculating and using the CASSCF wave function is unnecessary in this case.

Finally, we use our results to test the remarkably simple formula for the excitonic energies of semiconducting clusters developed by Delerue et al.,[30] which is based on the strong cancellation between the self-energy and Coulomb corrections to the excitonic gap. These authors showed that, to a good approximation, the triplet exciton energy in hydrogenated silicon clusters satisfies

$$\epsilon_g^{\text{exc}} \approx \epsilon_g^{\text{LDA}} + \delta\Sigma_b, \qquad (2)$$

where $\epsilon_g^{\text{LDA}}$ is the LDA band gap and $\delta\Sigma_b$ is the self-energy correction to the LDA band gap in bulk silicon, which is approximately 0.65 eV. Delerue found that this formula described their tight-binding $GW$-BSE results almost exactly for clusters containing more than 50 Si atoms, and worked well even down to much smaller sizes. We have evaluated the right-hand side of Eq. (2), obtaining values of 8.6 eV $(SiH_4)$, 7.3 eV $(Si_2H_6)$, 6.4 eV $(Si_5H_{12})$, and 5.3 eV $(Si_{10}H_{16})$, which are in quite good agreement with the DMC triplet excitonic energies shown in Fig. 1(a). It would be very interesting to test whether such a simple formula works well in other materials.

In summary, we have shown that the DMC method, combined with suitable methods for generating guiding wave functions, is a viable and accurate method for calculating the excited states of hydrogenated silicon clusters. Our DMC results are in good agreement with the best theoretical results obtained from other methods. The need for sophisticated guiding wave functions has been emphasized and we have shown that the CIS and TD-LDA methods can provide suitable zeroth-order approximations in these systems. The CIS and TD-LDA wave functions have properties that make them highly suitable for use in DMC calculations and they are sufficiently computationally tractable to be used for systems with of the order of 100 atoms. The techniques described here will therefore allow application of the DMC method to excited states of a broad range of systems with strong electron-hole interactions.

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