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Final Report on Project 01-ERD-017

“Smart Nanostructures from Computer Simulations”

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Smart Nanostructures from Computer Simulation: Final Report

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Purpose:

This project had two main objectives. The first major goal was to develop new, powerful computational simulation capabilities. It was important that these tools have the combination of the accuracy needed to describe the quantum mechanical nature of nanoscale systems and the efficiency required to be applied to realistic, experimentally derived materials. The second major goal was to apply these computational methods to calculate and predict the properties of quantum dots – initially composed of silicon, but then of other elements – which could be used to build novel nanotechnology devices. The driving factor of our purpose has been that, through the development and successful application of these tools, we would generate a new capability at LLNL that could be used to make nanostructured materials “smarter”, e.g., by selectively predicting how to engineering specific, desired properties.

Activities:

To carry out the necessary work to successfully complete this project and deliver on our goals, we established a two-pronged effort from the beginning: (1) to work on developing new, more efficient algorithms and quantum simulation tools, and (2) to solve problems and make predictions regarding properties of quantum dots which were being studied experimentally here at Livermore. Below, we highlight the main activities and accomplishments in each of these areas.

Algorithmic development and enhancement of simulation tools:

We have integrated 3 separate quantum simulation codes in such a manner that they work together and can read one another's input and output. This was a crucial first step as the three codes play a unique and important role in our simulations. In particular, the quantum Monte Carlo (QMC) code is used to calculate highly accurate total energies, which can be used to determine binding energies, optical excitation energies, and reaction pathway energies. The planewave density functional theory (DFT) code is used to provide accurate structural and dynamical properties, and also to predict correct trends of materials properties. The output of the DFT code is needed as input to the QMC code. We also integrated an empirical pseudopotential code, which is used to calculate optical properties of larger systems. As a result, we created a comprehensive quantum simulation suite of simulation codes that serves as a powerful means to carry out a wide range of calculations.

We have developed a new algorithm in our QMC calculations that changes the way the method scales with the number of particles in the system from N^3 to N

(see attached paper 1). As a result, our new, LLNL linear scaling QMC code can be applied to much larger systems. As an example, using the old algorithm, if a 10-atom system took 10 minutes to simulate, a 100-atom system would take 2.8 days to simulate. Using our new algorithm, a 100-atom system would take only 100 minutes or 1.7 hours. This improvement has greatly enriched our ability to apply one of the most accurate ab initio methods (QMC) to real nanoscale systems which are of interest to experimentalists and designers of nanoscale devices. We have also carried out an extensive benchmarking of the QMC approach, calculating the binding energy of 55 different molecules (see attached paper 2). This helps to standardize the QMC method and determine its broad applicability and near chemical accuracy.

Application to Nanoscale Systems: Silicon and Germanium Quantum Dots

One of our first major applications of these simulation tools was to predict and understand the optical properties of silicon quantum dots (see attached papers 3,4). There is enormous academic and industrial interest in the ability of silicon nanoparticles to emit visible light as the size of the particles is made smaller. Since it is extremely challenging both to reliably fabricate silicon quantum dots and to measure their optical characteristics, this is an ideal problem for accurate quantum simulations. In addition, there are several experimental efforts at LLNL dedicated to studying these same systems for use as efficient optical tags or sensors. We have carried out a comprehensive analysis of the optical properties of these quantum dots in their diamond structure phase as a function of size up to 2 nm, and we have determined that the effect of a single contaminant atom on the surface of the nanoparticle such as oxygen can dramatically alter its optical properties. These results, and other predictions we have made regarding the surface chemistry of silicon nanostructures, have helped explain recent experimental efforts, and have already become a benchmark in the theoretical community.

In addition to the effects of surface chemistry, we have considered the impact of the synthesis process on the resulting optical properties (see attached paper 5). Specifically, we carried out dynamical simulations using DFT molecular dynamics to reproduce several different synthesis techniques. The optical properties of the resulting structures were then computed using QMC and compared with the corresponding experiments. We found, surprisingly, that completely amorphous nanoparticles can still have emission and absorption in the visible spectrum, and that these non-symmetric particles would be more robust to changes in the surface chemistry than their symmetric counterparts. These are the first ever, accurate simulations using ab initio methods of the dynamical processes involved in real experiments. This is also an excellent example of the benefit of coupling different quantum simulation methods to address a single problem (DFT for the dynamics and QMC for the optical properties).

Technical Outcome:

The technical outcome of our LDRD project is that we have developed a powerful new capability at LLNL to investigate the properties of nanostructure systems and devices. As an example, we have resolved a number of important questions regarding the structural, optical and electronic properties of silicon and germanium nanoparticles. Perhaps more importantly, we have devised a unique combination of quantum simulation tools with enhanced performance that are generally applicable to a wide range of activities. Using these simulation tools we are able to accelerate the design of smart, functional nanoscale materials by providing valuable predictions and interpretations to nano-device designers.

Linear Scaling Quantum Monte Carlo Calculations

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Linear Scaling Quantum Monte Carlo Calculations

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A method is presented for using a maximally localized Wannier functions to introduce sparsity into the Slater determinant part of the trial wavefunction in quantum Monte Carlo calculations. When combined with an efficient numerical evaluation of these localized orbitals, the dominant cost in the calculation, namely the evaluation of the elements of the Slater determinant, scales linearly with system size. This technique is applied to the accurate calculation of the total energy of hydrogenated silicon clusters and carbon fullerenes containing 20-1000 electrons.

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Over the past two decades, considerable progress has been made using quantum Monte Carlo (QMC) methods to calculate the electronic structure of realistic materials [1]. One of the great strengths of QMC has been the combination of favorably “soft” scaling as N^3 , where N is the number of electrons, and high accuracy (e.g., exact exchange plus a full many-body description of correlation effects). Mean field methods such as Hartree-Fock and density functional theory possess a similar N^3 scaling, but may lack the desired level of accuracy. On the other hand, quantum chemistry approaches such as configuration interaction or coupled cluster may achieve a high accuracy, but typically scale as N^{5-7} leading to prohibitive sizes even at only a few atoms.

A number of algorithmic developments have made routine the application of fixed-node diffusion Monte Carlo (DMC) to small molecular and periodic solid systems [2–7]. Despite these and many other successful applications, QMC calculations for realistic atomic systems have been limited to studying systems with a few tens of atoms. This restriction arises from both the N^3 scaling already mentioned and a much larger prefactor than present in typical mean field calculations. The N^3 scaling is due to from the fact that to calculate the elements of the Slater determinant associated with a given configuration of electronic coordinates requires N orbitals to be evaluated for each of the N electrons and the cost of each orbital evaluation scales as the number of basis functions which is itself proportional to N [8]. The large prefactor arises from the large number of determinants evaluations that need to be performed to achieve a small enough statistical error bar. This prefactor can be dramatically improved by reducing the number of basis functions per electron by choosing more efficient basis sets. However, to date, the N^3 scaling has always remained, and the system size limitation is governed by this scaling.

In this letter we present, for the first time to our knowledge, QMC scalings that are linear in the number of electrons over a wide range of sizes (20-1000 electrons). We form QMC wavefunctions with significant sparsity in the Slater determinant by choosing single particle orbitals derived from the Maximally Localized Wannier function

construction [9]. A combination of a real space truncation of these functions and a representation in a numerical basis that is independent of system size, results in an improvement in scaling from N^3 to N . We demonstrate this $O(N)$ scaling for large hydrogenated silicon clusters and carbon fullerenes. Our results show that it is now feasible for QMC to routinely study systems containing up to 1000 electrons.

The introduction of sparsity into the Slater determinant part of the wavefunction is similar in concept to the introduction of sparsity into the overlap matrix of the Löwdin states in linear scaling density functional approaches [10,11]. However, the application of linear scaling to the quantum Monte Carlo formalism is not fraught with the same technical difficulties that have plagued linear scaling density functional approaches. Firstly, in QMC the Hamiltonian is not constructed from a self-consistent charge density, it is fixed. Therefore, when the MLW functions are truncated this does not affect the conservation of charge and introduce noise into the Hamiltonian. Secondly, the requirement to invert the overlap matrix in linear scaling density functional calculations imposes a large prefactor on these methods, such that the cross-over point with traditional N^3 scaling techniques occurs around 1000 atoms. In our linear scaling QMC approach, the prefactor is the same as for the traditional N^3 implementations and so the benefit is immediate.

In our QMC approach [1–5,12], we adopt the standard Slater-Jastrow trial wavefunction,

$$\Psi = D^\dagger D^\downarrow \exp \left[\sum_i^N \chi(\mathbf{r}_i) - \sum_{i<j}^N u(r_{ij}) \right] , \quad (1)$$

where D represents a Slater determinant, r_i and r_{ij} correspond to electron positions and separations, N is the number of electrons, χ is a one-body function, and u is a two-body correlation factor. The Slater determinant is constructed from a set of single particle states, $D_{ij} = \phi_i(\mathbf{r}_j)$. In our calculations, the states $\{\phi_i\}$ are obtained from an LDA calculation using the JEEP code [13], which uses a plane wave basis set with periodic

boundary conditions. We then use a conjugate gradient algorithm to search for the unitary transformation of the LDA eigenstates which yields Wannier functions with the maximum localization [9,14]. These Maximally Localized Wannier (MLW) functions are determined by the chemistry of the system and the procedure is analogous to the Boys localization procedure commonly used in quantum chemistry [15]. For finite systems the spread functional that is minimized becomes equal to $[\langle(\mathbf{r} - \mathbf{R}_n)^2\rangle]^{1/2}$, where $\mathbf{R}_n$ is the centroid of the MLW function. All QMC results presented here were performed using the CASINO code [12]. As the value of a determinant is unchanged by a unitary transform, the QMC energy evaluated with a set of MLW functions is numerically identical to that obtained from the original LDA orbitals. The orbitals used in the MLW functions can be occupied or unoccupied states in an insulator, semiconductor, or metal [16], and may correspond to ground or excited states.

Once the MLW functions have been constructed, there are two important steps we can implement to take advantage of the localized nature of these functions and reduce the QMC scaling. Each step reduces the scaling by an order of N .

First, we define a cutoff radius, R_{cut} , beyond which the MLW function is truncated to zero. This truncation insures that each electron only falls within the cutoff radius of a subset, M , of the MLW functions. For hydrogenated silicon clusters this number is typically $M \sim 35$. Therefore, when the system size increases beyond M atoms, the number of orbitals $\phi_i(\mathbf{r})$ required to be evaluated for each electron is fixed at M and the cost of the evaluating the Slater determinant then scales as MN^2 .

To determine appropriate values for R_{cut} , we require the truncated MLW function, ϕ_{trunc}^{MLW} , to reproduce at least 99.9% of the norm of the original MLW function, $\int |\phi_{trunc}^{MLW}(\mathbf{r})|^2 d\mathbf{r} > 0.999$ and the contribution to the kinetic energy from the Slater determinant should have an error of less than 0.1%. In Fig. 1 we plot the fixed node diffusion Monte Carlo (DMC) energy for SiH_4 obtained with different values of R_{cut} . Since SiH_4 has T_d symmetry, all four MLW functions are symmetry equivalent and the same value of R_{cut} is applied to each MLW function. In addition, we plot the norm of the truncated MLW function as a function of R_{cut} . Fig. 1 shows that the DMC algorithm is stable over a wide range of values of R_{cut} , i.e. truncation of the tails of the MLW functions does not significantly affect the nodal structure of the Slater determinant. In all the systems we have studied so far, the DMC energy is well converged for a value of R_{cut} chosen to reproduce a norm of 0.999.

A second step we take to improve the scaling is to remove the dependency of the number of basis functions on the number of electrons. Again taking advantage of the highly localized nature of the MLW functions, we choose to evaluate the MLW functions using 3 dimensional cubic splines [17,18]. In so doing, each orbital

$\phi_i(\mathbf{r})$ is evaluated by a single spline interpolation and the cost of evaluating the Slater determinant then scales as MN , i.e. a linearly scaling algorithm. The number of spline grid points, N_{grid} , was chosen to be consistent with the plane wave cutoff in the original LDA calculation, $N_{grid} = 2R_{cut}\sqrt{E_{cutoff}}/2\pi$, where E_{cut} is the plane wave cutoff in Rydbergs. For the systems we have studied, R_{cut} is independent of system size and hence the total memory required to store the spline grids for all orbitals grows only linearly with system size. This is in contrast to conventional implementations where the total storage grows as N^2 , due to the growth of the basis set with system size.

It is interesting to note that other basis sets for representing the MLW functions could lead to a similar reduction in scaling. For example, one could expand the MLW functions in a Gaussian basis and impose a cutoff radius on the evaluation of the Gaussians. However, for the systems studied here, the MLW functions represent the covalent bonds in the system and an expansion in atom or Wannier function centered Gaussians requires very high angular momentum components to faithfully describe the MLW function.

To demonstrate the improved scaling resulting from our spline interpolated, truncated MLW functions, we plot (Fig. 2) the CPU time on a 667MHz EV67 alpha processor required to move a single configuration of electrons a single time step for a series of hydrogenated silicon clusters and carbon fullerenes, ranging in diameter from 0.3 to 2.0 nm. Three different basis sets used to expand the original LDA wavefunctions are compared: (a) the truncated MLW functions interpolated using cubic splines, (b) a 6-31G* quality Gaussian basis set, and (c) a plane wave basis with 11 Rydberg energy cutoff. Figure 2 shows that the computational cost of evaluating the LDA wavefunctions in a plane wave basis scales as approximately N^3 . The exact scaling is determined by the volume of the supercell chosen for each system. The computational cost of the Gaussian basis also scales as N^3 , but with a smaller prefactor as the number of basis functions per atom is much smaller. We have tested implementing a fixed cutoff on the evaluation of these Gaussian basis functions which would in principle reduce the scaling to N^2 . However, the long range tails of the Gaussians mean that the N^2 regime is not reached for these system sizes. The calculations using the truncated MLW functions demonstrate that the CPU time required to move a single configuration of electrons scales approximately linearly with the number of electrons. In the case of the hydrogenated silicon clusters the deviation from linearity in the MLW curves is mainly due to differing ratios of hydrogen to silicon atoms, i.e. the surface to volume ratio; for the carbon fullerenes it is due to different strain in the clusters requiring slightly different cutoff radii for the MLW functions. Note that, for the systems we compared (SiH_4 and Si_5H_{12}) DMC total energies are

within statistical error bars for all three basis sets.

Once the cost of evaluating the elements of the Slater determinant has been reduced to an $O(N)$ scaling, it is interesting to ask how large a system one can study before other parts of the algorithm will begin to dominate and the linear scaling will be lost. For the $\text{Si}_{211}\text{H}_{140}$ system (984 electrons) approximately 10% of the calculation involves parts of the algorithm that scale as N^2 and N^3 , namely evaluating the electron-electron and electron-ion interactions, calculating the two-body term in the Jastrow function [$u(r_{ij})$ in Eq.(1)] and updating the value of the determinant after moving an electron. The electron-ion interaction can be rewritten with the sum over ions precomputed so the local part scales as $O(N)$. The non-local contribution already scales as $O(N)$ due to the cutoff in the range of the interaction. The electron-electron interaction can be rewritten to scale as $O(N)$ by writing it as a sum of short and long ranged pieces [1,7], or using Greengard's multipole expansion [19]. The Jastrow function can also be cast into an $O(N)$ form by using a cutoff based on the electron-electron separation [20]. To update the Slater determinant we adopt the procedure based on storing the inverse of the transpose of the matrix from Ref. [21]. This procedure traditionally scales as N^3 . Our introduction of sparsity into the Slater determinant allows us to significantly reduce the prefactor for this N^3 term. We believe that in larger systems where the determinant is increasingly sparse it should be possible to reformulate the determinant update procedure to utilize this sparsity and obtain a better size scaling. In summary, our algorithm yields a size scaling that is practically linear up to 1000 electrons. The relatively minor algorithmic improvements outlined above will extend this linear regime to several thousand electrons. However, even with 1000 electrons, the time limiting step is performing the initial LDA calculation to generate the single particle orbitals.

Note, if one is interested in the *total* energy of a system, then an additional factor of N should be included to account for the increase in the variance of the total energy with the number of electrons. If one is interested in *per electron* quantities, such as the binding energy of a bulk solid then the increase in the variance of the total energy is canceled by the increase in the number of electrons and the cost of calculating a *per electron energy* with a given error bar would indeed scale linearly with our method.

To illustrate the range of systems that can now feasibly be studied within QMC using truncated MLW functions in the Slater determinant, we have calculated total energies of a series of carbon fullerenes. In Fig. 3 we plot the binding energy per atom of C_{20} , C_{36} , C_{60} , C_{80} , C_{180} fullerenes. Line (a) shows the binding energies calculated using LDA, line (b) shows the binding energy calculated within fixed node DMC. The LDA calculations were performed at the Γ point of the Brillouin zone, using a cutoff

of 40 Rydbergs. The same pseudopotentials were used in the LDA and DMC calculations. The single particle orbitals for the DMC calculation were obtained by performing the MLW transform described above on the LDA eigenstates. Figure 3 shows that the LDA binding energies smoothly approach the bulk LDA binding energy for graphite as the size of the cluster increases. Comparison with the DMC results shows that the LDA overestimates the binding energy for each of the clusters. The general trend within DMC is similar to LDA, again asymptotically approaching the bulk binding energy with larger cluster size. In addition, the DMC calculations find that the binding energy per atom in C_{60} is anomalously large for its size. While initially surprising, this result provides additional support for the high stability of C_{60} . This result will be further discussed in a future publication.

In conclusion, we have demonstrated a method for using maximally localized Wannier functions to introduce sparsity into the Slater determinant part of the trial wavefunction in quantum Monte Carlo calculations. When combined with an efficient numerical evaluation of these localized orbitals, the cost of evaluating the Slater determinant is reduced to scaling linearly with system size for hydrogenated silicon clusters and carbon fullerenes containing 20-1000 electrons. Utilizing this linear scaling, it is possible to use quantum Monte Carlo methods to study system sizes that could previously only be examined within mean field methods. This development opens the possibility of accurately studying the effects of exchange and correlation in a range of scientifically and technologically important systems such as quantum dots, nanodevices, biological molecules, and the materials science of solids.

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FIG. 1. The dependence of the norm of the truncated MLW function and the fixed node DMC energy on the cutoff radius, R_{cut} of the MLW functions. DMC statistical error bars are smaller than the symbols.

FIG. 2. Computational cost of moving one configuration of electrons within diffusion Monte Carlo for SiH_4 , Si_5H_{12} , $\text{Si}_{35}\text{H}_{36}$, $\text{Si}_{87}\text{H}_{76}$, $\text{Si}_{123}\text{H}_{100}$, $\text{Si}_{211}\text{H}_{140}$, C_{20} , C_{36} , C_{60} , C_{80} , C_{180} .

FIG. 3. Binding energy per atom of carbon fullerenes as a function of the number of atoms. DMC statistical error bars are smaller than the symbols. For comparison, we have added an estimated 0.18 eV zero point energy to the bulk diamond experimental binding energy (7.37 eV) [22].

Fig. 1.

Fig. 2

Fig. 3

Quantum Monte Carlo Calculations for the Pople Set

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Quantum Monte Carlo Calculations for the Pople Set

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Abstract

Fixed node diffusion Monte Carlo (FN-DMC) atomization energies are calculated for a benchmark set of 55 molecules. Using single determinant trial wavefunctions, comparison with experiment yields an average absolute deviation of 2.9 kcal/mol, placing this simplest form of FN-DMC roughly at the same level of accuracy as the CCSD(T)/aug-cc-pVQZ method. However, unlike perturbative wavefunction expansion approaches, FN-DMC is applicable to systems containing thousands of valence electrons. For the P_2 molecule, a number of possible sources of error are explored in detail. Results show that the main error is due to the fixed-node approximation and that this can be improved significantly with multi-reference trial wavefunctions. It is also shown that for some molecules in the set a significant contribution to the error may be due to the use of pseudopotentials.

I. INTRODUCTION

Benchmark sets of molecules have proven to be a useful tool for gauging the accuracy and predictive abilities of a given computational method. The Pople set of 55 molecules, representing a broad range of chemical environments and originally grouped together to fit the semi-empirical Gaussian-1 (G1) [1] and Gaussian-2 (G2) [2] theories, has become very

popular for such purposes. Computed G1 energies for this set of molecules have a mean absolute deviation ϵ_{MAD} from experiment of 1.6 kcal/mol and a maximum deviation of 7.4 kcal/mol. These two numbers have become a standard benchmark for electronic structure approaches, including further G-n theories [3] as well as other state-of-the-art approaches such as the coupled cluster approximation with single, double, and perturbationally included triple excitations (CCSD(T)) [4,5], and density functional theory (DFT) methods [6,7].

Recently, the quantum Monte Carlo (QMC) approaches have been shown to provide highly accurate results when applied to a wide range of chemical systems (e.g., atoms, molecules, solids, nuclei, etc.) to calculate a wide range of properties (e.g., binding energies, reaction pathway energetics, optical gaps, momentum densities, etc.). A number of factors make QMC, which relies on a stochastic solution of the many-body Schrödinger equation, a highly attractive alternative to the more traditional mean-field and wavefunction expansion based techniques. Similar to the mean-field methods such as DFT, the computation time required in QMC scales as N^3 where N is the number of particles in the system. Yet, more closely related to post-Hartree-Fock wavefunction expansion methods, QMC solves the full $3N$ -dimensional Schrödinger equation directly, allowing for explicit evaluation of electron correlation. Typically, within the diffusion Monte Carlo (DMC) variant the method recovers $\sim 95\%$ of the total valence correlation energy. Furthermore, very recent algorithmic developments have shown that QMC can be implemented to scale *linearly* as the number of particles, with no loss of accuracy, by applying a unitary transform to localize the single-particle orbitals [8]. The combination of high accuracy and the ability to study systems with thousands of valence electrons makes QMC a very promising approach.

Despite the successes of QMC, comparisons with experiment have not been made systematically for a large data set, and the accuracy of QMC approaches has yet to be measured against a well-defined benchmark such as the G2 set. Recently, Manten and Lüchow have approached the subject of general accuracy for a small set of molecules and molecular reactions using all-electron fixed-node DMC [9], and found accuracies for reaction energetics comparable to CCSD(T)/cc-pVTZ. Indeed, such studies are necessary and long overdue to

answer many questions regarding the overall consistency and predictive capability of the approach. For example, when QMC is referred to as “highly accurate,” what exactly is meant? How big is the fixed-node error, on average? It is of great practical importance to answer these types of questions for a standard benchmark set of molecules such that one may better gauge the accuracy of QMC as well as develop further understanding of its limitations and methods for improvement.

In this work, results are presented for atomization energies calculated by single determinant, pseudopotential, fixed-node diffusion Monte Carlo (FN-DMC) for the 55 molecules in the G2 set. The average absolute deviation is 2.9 kcal/mol with a maximum deviation from experiment of 14 kcal/mol. These results support claims that QMC provides near “chemical” accuracy; however, it is also apparent that consistent accuracy of *less* than 1-2 kcal/mol is challenging within FN-DMC. Possible sources of error include: atomic orbital basis set, determinantal basis set, geometry, pseudopotentials, and zero-point energy. For the P_2 molecule, a detailed investigation of some of these potential sources of error has been carried out. Results show that one of the main sources of error is in the fixed node approximation which can be systematically improved by including multiple determinants in the QMC trial wavefunction. Another significant source of error for this particular case is in the use of pseudopotentials.

II. METHOD

In our QMC approach [10–14], we use the variational Monte Carlo method to find an optimized correlated many-body trial function. This trial function is a product of Slater determinants and a correlation factor [15]. In the Slater determinant part, we employ natural orbitals (NO) rather than Hartree-Fock or density functional orbitals [11]. To eliminate most of the remaining variational bias we use the diffusion Monte Carlo method, which is based on the property that the operator $e^{-\tau H}$, where H is the Hamiltonian, projects out the ground state of any trial function with the same symmetry and non-zero overlap. All QMC results

presented here are from the diffusion Monte Carlo approach.

Atomic cores are treated with Stevens-Basch-Krauss (SBK) effective core potentials [16] for all atoms except hydrogen. The natural orbitals are derived from small multi-configuration self-consistent field (MCSCF) calculations that include 15-30 virtual and all occupied valence orbitals in the active space.

FN-DMC calculations for all 55 molecules were carried out using a single determinant trial wavefunction except when noted. For multi-determinant FN-DMC calculations, weights from MCSCF were used. In each case a single particle basis of quality similar to 6-311++G(2d,2p) was employed. Geometries were taken from the original G1 set [1], i.e., optimized within MP2/6-31G(d). In order to make accurate comparisons with experiment, FN-DMC calculations were carried out for a long enough time to obtain stochastic error bars of < 1 kcal/mol (typically 0.2-0.4 kcal/mol). Careful time-step studies were performed for several cases and conservative time-steps were used for the entire set (i.e., DMC acceptance ratios were always greater than 99%).

All Hartree-Fock and MCSCF calculations in this work were performed using the GAMESS quantum chemistry package [17].

III. RESULTS FOR THE POPLI SET

The experimental data reported here are taken from a combination of NIST-JANAF tables [18] and Huber and Herberg [19], in the same manner as Ref. [5]. Experimentally measured atomization energies for the Pople set range from 17 kcal/mol (Na_2) to 709 kcal/mol (C_2H_2). Most experimental errors are small (i.e., < 0.5 kcal/mol), although several are somewhat larger (e.g., CS has an experimental error of 6 kcal/mol [18]). To compare with theory, zero point energies are taken from experiment when available and from the calculations of Ref. [5] otherwise. For several species experimental errors are unavailable.

Calculated FN-DMC atomization energies for the 55 G2 molecules are shown in Tab. I. For each molecule, both the experimental and calculated binding energies are listed.

Error bars are shown for experiment and theory (computational error bars originate from the statistical sampling inherent in the DMC energy evaluation).

The largest error between FN-DMC and experiment occurs for the SO_2 molecule, where the discrepancy is 14 kcal/mol. This makes SO_2 a somewhat special case as the next largest error in the set is only ~ 8 kcal/mol. The sensitivity of the atomization energy of SO_2 to the single particle basis has been studied carefully for the CCSD(T) approach [5,20,21]. In particular, it was found that SO_2 showed very slow convergence with respect to standard correlation consistent basis sets (e.g., CCSD(T)/aug-cc-pVQZ is 10 kcal/mol underbound), and that the addition of tight d and f functions on sulfur improved the convergence considerably. For the FN-DMC method employed here, additional tight d and f functions on sulfur in the generation of the trial function did not improve the energy. Because this molecule is somewhat larger and its error is so much greater than any other case, additional studies and ways for improving the FN-DMC result for SO_2 are relegated to a separate study.

After SO_2 , the molecules with the biggest discrepancy from experiment are P_2 , ClO , CN , LiF , and NO , with errors -8.2, -8.0, -7.6, +7.5, and -7.1 kcal/mol, respectively. Averaging over all molecules in the set yields a fairly good agreement between FN-DMC and experiment, with a mean absolute deviation of 2.9 kcal/mol (excluding SO_2 lowers this number to 2.5).

It is interesting to compare the FN-DMC results against other quantum chemical approaches. Previous studies have compared a number of DFT methods for the G2 test set, including local density approximation (LDA) and a variety of generalized gradient approximations (GGA) [6,7]. As expected, LDA overbinds for every molecule in the set (except LiF), with $\epsilon_{\text{MAD}} \sim 40$ kcal/mol. The GGAs offer significant improvements over LDA, with the best functionals (B3LYP and B3PW91) giving $\epsilon_{\text{MAD}} \sim 2.5$ kcal/mol. It was shown that the key ingredient to achieving this result was in the 3-parameter B3 exchange function [22], which uses a semi-empirical fit to incorporate a fraction of the exact Hartree-Fock exchange. It was also noted that while ϵ_{MAD} for a larger 93-molecule test set using the same B3 functional was only 1 kcal/mol higher than for the original 55-molecule test set, the *maximum*

deviation was doubled to 20 kcal/mol. This significantly larger range of error is evidence that accuracy trends in DFT methods are not always systematic and must be checked; a given functional working well for one problem does not necessarily imply it will work as well for another.

CCSD(T) has proven to be the most accurate ab initio electronic structure technique when applied with large basis sets to small molecules. Recent CCSD(T) calculations for atomization energies of the 55 G2 molecules provide a wealth of valuable information regarding the accuracy of CCSD(T) [4,5]. It was found that CCSD(T)/aug-cc-pVQZ has $\epsilon_{MAD}=2.8$ kcal/mol which is very similar to the FN-DMC results presented here. Using the CCSD(T) complete basis set limit, by extrapolating a series of correlation consistent basis sets, reduces ϵ_{MAD} by half to 1.3 kcal/mol. It would be interesting to attempt to formulate and apply such extrapolation techniques to FN-DMC.

Part of the advantage of having data for a benchmark set of molecules is the ability to look for trends within the set. There are several possible reasons for the errors in the present FN-DMC results (see discussion in next section), so it may be difficult to identify a single quantity or property that points to a trend. Indeed, as shown in Table II, a comparison of the 27 worst case molecules with the 28 best case ones does not seem to yield any visible trends for a number of properties; if anything, the trends appear to be counterintuitive. For example, one might expect closed-shell systems with large gaps to be, on average, better represented by a single Slater determinant. The results here show that while both subsets are mostly closed-shell in character, the better-performing half of the G2 set has more open-shell molecules, and the average gap over the closed shell cases is actually smaller than the same average over the worse half of the set. One might also guess that the weights of excited state determinants from MCSCF calculations may tend to be larger for the poorer performers (meaning that the true wavefunction is better represented with a multi-reference description). However, we find that the average weights are very similar, with only a very slight, essentially insignificant, difference (0.080 vs. 0.075) between the two subsets.

It is also interesting to note that the average error among the worst 27 cases is negative

at -2.7 kcal/mol, while the same average for the best 28 molecules is nearly zero at +0.2 kcal/mol. This difference may be indicative of the following general tendency. If FN-DMC fails to describe the atom and molecule with the same degree of accuracy, it is far more likely that the larger error will be made on the molecule.

IV. IMPROVEMENT OF THE P_2 MOLECULE

As mentioned, all of the FN-DMC results listed in Table I are obtained from trial wavefunctions using a single Slater determinant built from natural orbitals. In order to probe the main source of discrepancy from experiment, one can examine how changes to this trial wavefunction impact the FN-DMC result. For such a study, we choose one of the worst case molecules, P_2 , since its relatively small size allows for a number of thorough tests to be carried out.

A. Pseudopotentials

One possible source of error is due to the use of pseudopotentials. Although in this work the SBK [16] pseudopotentials are employed, a number of other types of pseudopotentials are available. Furthermore, in addition to the method of construction, there are different theories on which the pseudopotential can be based. For example, SBK pseudopotentials are based on Hartree-Fock, but others can be made from LDA, GGA or other correlated theories. A test on different pseudopotentials within FN-DMC would be interesting but is beyond the scope of the present work. Here we compare the SBK pseudopotential vs all-electron for Hartree-Fock, LDA, and several GGA atomization energies.

Results for the pseudopotential and all-electron atomization energies of P_2 are shown in Tab. III. In each case the dimer bond distance was reoptimized within the given method. Large basis sets (22s22p15d/22s22p15d) were used in order to ensure convergence to within 0.1 kcal/mol in the atomization energy. Note that the pseudopotential and all-electron

Hartree-Fock energies are in excellent agreement, as expected since the SBK pseudopotentials were generated using the Hartree-Fock theory. On the other hand, the LDA results show a large discrepancy of 8.6 kcal/mol between the pseudopotential and all electron atomization energies. This discrepancy is much smaller for the BPW91 and B3LYP methods, 3.2 and 1.1 kcal/mol, respectively. Note that for all of the methods shown in Table III the pseudopotential atomization is less than the all-electron value.

Based on these results, it is likely that the FN-DMC error, which is also negative, is partially due to an error in the pseudopotential. However, it is difficult to quantify this error since an all-electron FN-DMC calculation would contain additional contributions to the fixed-node error from the core electrons; therefore, making a comparison between pseudopotential and all-electron FN-DMC is somewhat ambiguous. Nonetheless, we can estimate that the error in FN-DMC due to the pseudopotential lies in between LDA and HF and given the GGA results is most likely around 2 kcal/mol. This error is in good agreement with previous work that estimated the errors related to the use of pseudopotentials in QMC calculations for transition metals by comparing accurate coupled cluster valence-only and all-electron results [23].

B. Geometry

The impact of how the P_2 bond distance is optimized is another important test in our attempt to improve the energy. Forces are still challenging to evaluate within QMC, although there has been recent progress [24,25]. In the case of the P_2 dimer, only a single bond distance needs to be optimized which can be done easily with a series of total energy calculations. Fig. 1 shows FN-DMC energies for the P_2 molecule at varying bond distances. Note that the optimal FN-DMC bond distance is 0.035 Å shorter than the MP2/6-31G(d) value. The difference in energy between these two structures is ~ 0.5 kcal/mol. This small difference indicates that the sensitivity of atomization energy to geometry is fairly minimal in this case and is not a large source of the error from experiment.

Since the geometry correction is an order of magnitude less than the missing binding energy, we focus on the quality of the nodal structure which is likely to have a far greater impact. The FN-DMC nodes are determined entirely by the nodes of the Slater determinant(s) which are constructed with single-body orbitals. There are a number of ways in which one can easily at least attempt to improve upon these nodes. First, the accuracy of the single-body orbitals may be improved by increasing the atomic orbital basis sets. Second, the orbitals themselves can be taken from any number of theories (i.e., Hartree-Fock, LDA, GGA, NO, etc.), some of which may lead to better nodes than others. Third, the determinantal basis can be expanded to include more than a single determinant.

C. Single-Particle Orbitals

For pseudopotential calculations, it is generally assumed that the fixed-node error is not effected much by the quality of the atomic orbital basis, as long as the basis is sufficient (i.e., 6-311G* quality or better). For P_2 , 3 atomic orbital basis sets were tested: 17s17p2d/4s4p2d, 27s27p3d/6s6p3d, and 32s32p8d/8s8p4d. Contractions for these basis sets were least squares fit to the orbitals of the exact Hartree-Fock solution for the P pseudo-atom. Uncontracted exponents were chosen to optimize the energy of the Hartree-Fock dimer. For each case FN-DMC total energies were computed with statistical error bars less than 0.0001 au. All 3 basis sets give the same total energy within error bars, indicating the relative insensitivity of the nodes to the atomic orbital basis in this case. It may be interesting to carry out this same kind of test systematically for other molecules in the set, although that is beyond the scope of the present work. Further, these atomic orbital basis set tests were performed with single determinant trial functions; it is possible that the effect of the atomic orbital basis becomes more important as the trial function is expanded to include multiple determinants.

A number of different single-particle orbitals have been used in the past to construct the Slater determinant part of QMC trial wavefunctions. In some cases, it was found that NO offer a slight improvement in the nodes over Hartree-Fock orbitals [11]. Other times,

DFT orbitals may be more appropriate. It is difficult to predict *a priori* which orbitals are better suited to a given system. In many cases, the resulting differences tend to be rather small. Table IV lists the total energy of the P_2 molecule using a single Slater determinant built from 5 different kinds of orbitals: Hartree-Fock, NO, LDA, BPW91, and B3LYP. Note that using the NO gives a small (~ 0.7 kcal/mol) improvement over Hartree-Fock, and the LDA and GGA orbitals are slightly better (~ 1.0 kcal/mol) than NO. While it is interesting that in this case the DFT orbitals are best, they only account for 1 of the 8 kcal/mol FN-DMC error found with NO. Of course, other single-body orbitals could be used, however it appears that, like geometry, the choice of single-body orbitals is a small contribution to the discrepancy with experiment.

D. Multiple Determinants

Another way to change and possibly improve the nodal surface of the trial QMC wavefunction is to use more than a single Slater determinant. Just as an expansion of the determinantal basis increases the variational freedom in the wavefunction and therefore lowers the total energy in post Hartree-Fock calculations, multi-determinantal trial wavefunctions can lead to better nodes which lower the FN-DMC total energy [26]. In general, however, a given determinantal expansion that improves the variational energy does not always lead to a similar improvement in the nodal surface. In fact, recent work has shown that MCSCF-based trial functions may not improve the FN-DMC energy [27] and in some cases can even worsen the fixed node error [28]. It has also been suggested recently that multi-determinantal trial functions based on pair natural orbital CI wavefunctions may improve the nodal surface more efficiently than MCSCF-based trial functions [29].

Table V shows the total FN-DMC energies for P_2 using several different multi-reference trial functions. In each case, determinants were taken from an MCSCF calculation in which all occupied electrons were singly and doubly excited into a given number of virtual states. The number of resulting determinants corresponds to a threshold of 0.01 for the weight

of the configuration state functions (CSF) to keep. Weights of these determinants in the FN-DMC calculations are taken to be the same as the MCSCF weights. Of course, these weights may not be ideal since they are taken from a minimization of the total energy which may not always correspond to improving the nodal surface. Nonetheless, MCSCF weights provide a good starting point and can help guide us in selecting the determinants.

Note that the energies are improved using a multi-reference trial function based on MCSCF orbitals and weights. Using a single determinant of MCSCF orbitals gives the same FN-DMC energy as Hartree-Fock orbitals, slightly higher than the NO single determinant energy (see Tab. IV). Taking excitations into just the first three virtual states lowers the FN-DMC energy by 2.1 kcal/mol compared with a single determinant.

In going from 3 to 8 virtual states in the MCSCF calculation, the FN-DMC energy is improved yet again rather substantially. With a 167-determinant wavefunction, the FN-DMC energy is 4.3 kcal/mol lower in energy than a single determinant. The additional improvement may be due to the fact that the 167-determinant expansion includes excitations into *d*-like orbitals not present in the smaller 54-determinant run. This explanation is in good agreement with previous work which found that significant improvement in the nodal structure of several atoms [30] and the N₂ molecule [31] relied on the inclusion of determinants with excitations into *d* states.

The largest determinantal expansion listed is for 269 determinants from an MCSCF calculation that included excitations into 16 virtual states. The energy for this case is only slightly improved (0.3(1) kcal/mol) compared to the 167-determinant case. This makes our best multi-determinant FN-DMC energy roughly 4.1(1) kcal/mol lower than the single-determinant NO result listed in Tab I.

Further excitations into more virtual states in the MCSCF calculations do not lead to further improvements in the FN-DMC energy. This may be partly due to the fact that we use here the same cutoff (0.01) for the CSF weights in all cases. As the number of virtual states increases, the total number of determinants increases and the weights of each determinant decrease. (This is also the reason why the number of determinants decreases

for the last two rows of Tab. V). Such an explanation cannot be complete, however, since the energy is improved in going from 25 to 40 virtual states (245 to 223 determinants).

We have so far only examined the improvement in total energy of the P_2 molecule. Of course, to compute the atomization energy one must also know the energy of the P atom. Therefore, it is reasonable that if multireference determinants are used for the molecule one should re-compute the atomization energy using a similar multideterminant wavefunction for the atom. A 66-determinant trial function for the P atom was generated from an MCSCF calculation with excitations into 24 virtual states. The energy was indeed lower than the single determinant FN-DMC energy, but only by 0.3(1) kcal/mol. The best correction above, then, is 3.5 kcal/mol when referring to the atomization energy.

In our quest to improve the FN-DMC atomization of the P_2 molecule, we have found $\sim$ 2.0 kcal/mol (pseudopotential), 0.5 kcal/mol (geometry), 1.0 kcal/mol (single-body orbitals), and 3.5 kcal/mol (determinantal basis). Previous work [5] found roughly 0.8 kcal/mol in core-valence correlation (not included here due to our use of pseudopotentials) and a 0.2 kcal/mol correction due to scalar relativistic effects. A sum of these individual effects would result in a 8.0 kcal/mol improvement in the atomization energy of P_2 , bringing the error with experiment to -0.2 kcal/mol. Although it is not entirely clear that one can sum these errors (i.e., that the correction terms listed above are unrelated) it is nonetheless evident that a substantial improvement can be made in this case.

Another, somewhat complicated source of error is the localization error [10] which is intimately connected with the fixed-node error. It was shown that the localization error scales as the error in the trial function squared [10]. Thus, with a good enough trial function, it is typically assumed that this error is minimal (i.e., significantly smaller than the statistical errorbars). However, in the current set of data we are exploring small energies with very small errorbars. It is likely that the 4.1 kcal/mol improvement found by expanding the determinantal basis is an improvement in *both* the nodal error and the localization error. To separate the two is, unfortunately, exceedingly difficult, particularly since improving the nodes also improves the localization error. For the purpose of this discussion, when referring

to the fixed-node error we mean more precisely a combination of fixed-node and localization errors.

V. CONCLUSIONS

The accuracy of the pseudopotential FN-DMC approach has been assessed for the 55 G2 molecules. For these calculations, the method was treated in as “black box” a way as possible. For example, all calculations were run systematically with the same basis sets and type of orbital for a single determinant trial function. With such an approach, a mean absolute deviation of 2.9 kcal/mol was achieved. The main source of error for the P_2 molecule was found in the fixed-node approximation, a second important error was in the use of the SBK pseudopotential, and smaller errors were due to geometry and choice of single-body orbitals. The nodes were shown to be substantially improved by using multiple determinants in the trial function. These results indicate that ϵ_{MAD} could be significantly reduced (i.e., by a factor of 2) if multi-reference trial wavefunctions were employed for the whole set.

Many more careful studies are needed to understand the best means of improving the fixed-node error. It is our hope that the benchmark results provided in this work will aid in some of these studies. For example, the 5 or 10 worst case molecules could provide a useful laboratory for tests and improvements. Furthermore, the results presented here put pseudopotential single determinant FN-DMC on the map as a benchmark, with its absolute mean deviation now a number that can be directly compared with other methods.

VI. ACKNOWLEDGEMENTS

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TABLES

TABLE I. Atomization energies (kcal/mol) for the 55 molecules in the Pople set [1]. Diffusion Monte Carlo (DMC) calculations and experimental (EXP) results are listed. For DMC, statistical error bars are given in parentheses. Experimental errors are listed in parentheses (a dash indicates no error was available).

Molecule	DMC	EXP
LiH	55.3(2)	56.00(1)
BeH	43.0(2)	46.90(1)
CH	79.5(2)	79.90(2)
CH ₂ (³ B ₁)	181.9(4)	179.6(4)
CH ₂ (¹ A ₁)	169.7(4)	170.6(4)
CH ₃	290.9(2)	289.3(2)
CH ₄	395.0(2)	392.5(1)
NH	78.2(4)	79.0(4)
NH ₂	169.2(4)	170.0(3)
NH ₃	276.5(2)	276.7(1)
OH	101.2(3)	101.4(3)
H ₂ O	219.4(2)	219.35(1)
HF	135.9(2)	135.2(2)
SiH ₂ (¹ A ₁)	145.5(2)	144.4(2)
SiH ₂ (³ B ₁)	125.8(2)	123.4(2)
SiH ₃	215.1(2)	214(1)
SiH ₄	305.8(2)	302.6(5)
PH ₂	143.7(2)	144.7(6)
PH ₃	224.8(2)	228.6(4)
H ₂ S	172.1(4)	173.1(2)
HCl	103.4(4)	102.2(5)

Li ₂	23.5(2)	23.9(7)
LiF	145.1(4)	138(2)
C ₂ H ₂	390.0(4)	386.9(2)
C ₂ H ₄	533.5(4)	531.9(1)
C ₂ H ₆	669.3(4)	666.3(-)
CN	170.5(4)	178(2)
HCN	302.0(8)	301(2)
CO	253.2(3)	256.2(2)
HCO	269.8(4)	270(2)
H ₂ CO	357.5(5)	357.2(1)
H ₃ COH	483.8(5)	480.8(-)
N ₂	221.0(8)	225.1(4)
N ₂ H ₄	406.8(9)	405.4(-)
NO	142.9(4)	150.06(4)
O ₂	111.7(5)	117.96(2)
H ₂ O ₂	246.6(3)	252.3(-)
F ₂	32.0(8)	36.9(1)
CO ₂	379.5(4)	381.93(1)
Na ₂	17.3(2)	16.8(3)
Si ₂	73.3(2)	74.0(-)
P ₂	107.9(2)	116.1(5)
S ₂	98.3(3)	100.66(7)
Cl ₂	54.3(2)	57.18(1)
NaCl	98.8(3)	97.3(5)
SiO	186.7(2)	190(2)
CS	165.4(5)	169(6)
SO	117.6(6)	123.4(3)

ClO	55.4(4)	63.42(2)
ClF	53.7(6)	59.1(1)
Si ₂ H ₆	505.8(4)	500.1(−)
CH ₃ Cl	371.6(8)	371.0(−)
H ₃ CSH	446.0(4)	445.1(−)
HOCl	152.8(4)	156.3(5)
SO ₂	240.0(8)	254.0(2)

TABLE II. FN-DMC Error, FN-DMC ϵ_{MAD} , Hartree-Fock HOMO-LUMO gap, and two largest CSF weights from MCSCF calculations averaged over the 27 worst and 28 best FN-DMC energies in the G2 set. A breakdown of the kinds of spin multiplicities is also given, where S=singlet, D=doublet, and T=triplet.

	27 Worst	28 Best
ϵ_{avg} (kcal/mol)	-2.7	+0.2
ϵ_{MAD} (kcal/mol)	5.0	0.9
spin multiplicities	20S, 4D, 3T	17S, 7D, 4T
HOMO-LUMO gap (eV)	14.4	11.6
ground state CSF weight	0.959	0.964
2nd largest CSF weight	0.080	0.075

TABLE III. Pseudopotential (PP) and all-electron (AE) atomization energies (kcal/mol, without zero-point corrections) for the P_2 molecule using the Hartree-Fock, LDA, BPW91, and B3LYP methods.

Method	Pseudopotential	All-Electron
Hartree-Fock	37.2	37.3
LDA	133.5	142.1
BPW91	116.2	117.3
B3LYP	111.8	115.0

TABLE IV. Total single determinant FN-DMC energy (au) of the P_2 molecule for different types of orbitals used to fill the Slater determinant.

Orbitals	Total Energy
Hartree-Fock Orbitals	-13.0628(1)
Natural Orbitals	-13.0636(1)
LDA Orbitals	-13.0652(1)
BPW91 Orbitals	-13.0652(1)
B3LYP Orbitals	-13.0651(1)

TABLE V. Total FN-DMC energy (au) of the P_2 molecule with differing number of determinants in the trial wavefunction. The number of virtual states in the MCSCF calculation is also listed. For each case, all configuration state functions with weight greater than 0.01 were included.

# of Determinants	# Virtual States	Total Energy
1	1	-13.0628(1)
54	3	-13.0660(1)
167	8	-13.0696(1)
269	16	-13.0701(1)
245	25	-13.0691(1)
223	40	-13.0698(1)

FIGURES

FIG. 1. FN-DMC energy of the P_2 molecule as a function of the bond distance. The solid line represents a quadratic fit to the QMC data. The x-axis has been shifted by the MP2/631G(d) bond distance.

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Passivation Effects of Silicon Nanoclusters

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Abstract

We employ density functional and quantum Monte Carlo calculations to show that significant changes occur in the gap of fully hydrogenated nanoclusters when the surface contains impurity passivants such as atomic oxygen. Our results show that quantum confinement is only one mechanism responsible for visible photoluminescence in silicon nanoclusters and that the specific surface chemistry must be taken into account in order to interpret experimental results. In the case of oxygen, the gap reduction computed as a function of the nanocluster size provides a consistent interpretation of several recent experiments. Furthermore, we predict that other double bonded groups also significantly affect the optical gap, while single bonded groups have a minimal influence.

I. INTRODUCTION

Reducing the size of a semiconductor to the nanometer scale changes the physical properties of the material in a fundamental way. For example, semiconductor nanoclusters exhibit an increased optical gap and narrower emission spectra compared to bulk values [1–3]. In addition, reducing the size to the nanometer scale causes a dramatic increase of surface area to volume ratio; therefore, the physical and chemical properties of semiconductor nanoclusters are greatly influenced by surface reconstruction, passivation, and ultimately by surface chemistry. The efficient photoluminescence (PL) observed in porous silicon [4] as

well as other free standing silicon nanoclusters [5–7] suggests that these structures may be exploited for specific applications in which they might be integrated within existing silicon technologies to create nanoscale optoelectronic devices. Additionally, the biocompatibility of silicon make these nanoclusters ideal candidates for biotags, replacing the inefficient fluorescent dyes. However, the size dependence of the optical gap is difficult to reproduce in silicon nanoclusters as surface effects play a prominent role. Developing a more thorough understanding of the electronic and optical properties of silicon nanoclusters, in particular the effect of the surface, is a crucial step towards the utilization of these structures for new technologies.

Most experiments designed to explore the optical properties of semiconductor nanoclusters have focused on II/VI materials such as CdSe, CdS, and CdTe [1,2,8–10] as these clusters are easier to synthesize with a narrow size distribution and with well passivated surfaces. Although the effect of surface reconstructions and different passivants has not been studied in detail, it is generally accepted that quantum confinement dominates the optical properties of these II/VI clusters. In contrast, silicon nanoclusters are much less well characterized, and the interplay of quantum confinement and surface properties is still unclear. In particular, few surface sensitive probes are available, and distinguishing bulk effects from surface effects is difficult. Theoretical modeling [11–16] is challenging within this size regime as a full quantum mechanical description of both the core and the surface is required to provide accurate and predictive data. Recent studies have, in general, shown that the surface can affect the optical properties including gaps and radiative lifetimes (strength of transition) [17,18]. The possibility of surface control of optical properties can provide opportunities to design nanoclusters with the desired properties.

Recent studies on the role of surface chemistry on the optical properties of silicon nanoclusters have reported conflicting levels of importance, ranging from minimal [19–22] to crucial [6,17,18,23]. In particular, experiments investigating the effect of oxygen in both porous silicon [17] and hydrogen passivated nanoclusters [18,20,21,23] have generated conflicting results. Oxygen exists in many experiments as a contaminant [21,22] and may also

be intentionally used to saturate dangling bonds [6,17,23]. Discrepancies between experiments have arisen both with respect to the shift in the emission spectra and the changes in intensity when oxygen is adsorbed onto hydrogenated silicon nanoclusters. With the exception of oxygen, very few detailed experimental studies of surface passivants have been undertaken to date.

In this paper, we present *ab initio* calculations of a number of hydrogen passivated silicon nanoclusters with diameters up to 2 nm. In our calculations, we replaced one or more of the hydrogen atoms with a number of different passivants including oxygen, sulfur, a CH₂ group, fluorine, chlorine, and a hydroxyl group (OH). We found that double bonded passivants significantly reduce the gap compared to that of a completely hydrogenated cluster. Conversely, we found that single bonded passivants have a minimal effect on the optical gap. Finally, we specifically present results for a common contaminant, oxygen, suggesting explanations for the discrepancies amongst experiments [5,20–23] and we calculate the size below which an “oxygen gap” will be observed.

The rest of the paper is organized as follows: Section II discusses the theoretical methods we used to perform our calculations, Section III discusses the specific DFT and QMC results, Section IV interprets these results, and Section V offers some concluding remarks.

II. COMPUTATIONAL METHODS

Large scale, atomistic calculations are needed to study the surface of silicon nanoclusters up to 2 nm in diameter. The calculations were performed using density functional theory (DFT) and quantum Monte Carlo (QMC). The diameters are calculated using the approximation $D = a(\frac{3}{4\pi}N)^{1/3}$ where N is the number of silicon atoms and a is the lattice constant. We studied completely hydrogenated silicon nanoclusters, and silicon clusters with a range of different passivants replacing one or two of the hydrogen atoms. We also replaced up to 12 hydrogens with oxygen.

Our *ab initio* DFT calculations are based on the local density approximation (LDA) and

the generalized gradient approximation (GGA). We adopt a pseudopotential plane wave approach [24] in which we design an artificial periodic system of clusters with a large enough spacing so that no resulting spurious interactions exist between them. All the clusters are placed in a periodically repeated box with 9 to 16 Å of vacuum region between clusters (the precise amount depends on the resulting structural relaxation of the different passivants and on convergence tests performed for each system). This amount proved sufficient for all square modulus of wavefunctions to have negligible values well before the box edge. The interaction between the silicon ionic cores and valence electrons are described by a fully norm conserving, non-local pseudopotential of the Hamann type [25] except for hydrogen in which we use a pseudopotential of the Giannozzi type [26]. In our DFT calculations, we use the Ceperley-Alder exchange-correlation energy functional and potential [27]. The Kohn-Sham orbitals are expanded in a plane wave basis set, with a kinetic energy cutoff of at least 35 Ry corresponding to about 10^5 plane waves. In cases with passivation groups different from hydrogen, we used up to 70 Ry for convergence tests. We found that the higher cutoff had no discernable effect on the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), that is, the single particle gap as defined within DFT (less than 0.3 % in all cases).

All silicon clusters were initially constructed in a diamond structure lattice with bulk silicon-silicon bond lengths. Dangling bonds were passivated with hydrogen initially placed along the appropriate tetrahedral direction at the experimental silicon-hydrogen distance in SiH_4 . The structures were then relaxed to zero temperature molecular dynamics simulations, where the ions are treated classically and the electrons quantum mechanically until the correct ground state structure is reached. In every case, each atom was relaxed until the residual forces were less than $2 \times 10^{-4} \text{ eV/\AA}$. We also performed GGA calculations using the PBE functional [28] on a number of representative clusters, including full geometry reoptimization, in order to test the effect of gradient corrections to the exchange-correlation potential. Despite slight changes to the structure (1.6 % longer silicon-silicon bond lengths) and total energies, we find that the single particle gaps agree to within 0.05 eV for all cases

tested.

Although the LDA HOMO/LUMO gap is known to reproduce qualitative trends of optical gaps correctly, the lack of a proper treatment of the self-energy correction and the exciton binding energy (Coulomb interaction between the excited electron and its resulting hole) calls for a more accurate tool to quantitatively calculate optical gaps. We have chosen to use quantum Monte Carlo (QMC) in order to calculate the optical gap using $E^{opt} = E_N^* - E_N$, where E_N^* (E_N) is the total energy of the cluster in its excited (ground) state. QMC is one of the most accurate methods for calculating total energies and gaps [29–31]. To date, most QMC calculations have been performed on small molecules or on periodic systems due to the computational workload of these calculations. Here, we use the linear scaling algorithm based on a maximally localized Wannier function basis [32] to perform QMC calculations on large clusters. Specifically, we perform QMC on all the hydrogenated silicon nanoclusters and a number of those containing oxygen. Through these representative clusters, we determine that the LDA can indeed qualitatively describe trends of optical gaps, both as a function of size, and with different passivants.

III. RESULTS

The role of contaminants on the surface of silicon nanoclusters, specifically oxygen, has generated some controversy. The school of thought advocating quantum confinement as the only mechanism responsible for visible PL would suggest that regardless of the passivating surface, the same results should be observed as long as all dangling bonds are saturated [20–22]. This line of thought contradicts results on porous silicon reported by Wolkin *et al.* [17] as well as the tight-binding calculations on various size nanoclusters reported in that work. In order to investigate the effect on the optical gap in silicon nanoclusters containing oxygen, we studied a single oxygen double bonded to the surface of clusters up to 1.8 nm in diameter. Fig. 1 shows our calculated LDA single-particle gaps and lowest QMC optical gaps of hydrogenated silicon nanoclusters, with and without oxygen, as

a function of cluster size. Our LDA results for fully hydrogenated nanoclusters show good agreement with previously published DFT values [13,14], and our QMC results agree with those of accurate GW calculations on small clusters [15]. Quantum confinement still plays a key role up to at least the sizes considered here as the single-particle (LDA) gap and the optical (QMC) gap of oxygenated clusters decreases with increasing size, albeit, at a much slower rate than for the perfectly hydrogenated clusters. Overall, the LDA gap *trends* as a function of size for both pure hydrogen and mixed hydrogen/oxygen passivated clusters are well reproduced by our QMC calculations. The shift in the gap from LDA to QMC in totally hydrogenated clusters is much greater (around 1.5 eV for clusters around 1 nm) than in those with oxygen contamination (around 0.6 eV). For the oxygen-contaminated clusters smaller than 2 – 2.5 nm, we find that the HOMO and the LUMO states are localized in the vicinity of the Si=O double bond. Fig. 2(a) shows that these HOMO and LUMO states are localized core states in $\text{Si}_{35}\text{H}_{36}$, while Fig. 2(b) shows that the HOMO and the LUMO are strongly localized near the surface oxygen in $\text{Si}_{35}\text{H}_{34}\text{O}$. We believe that the origin of the difference in shifts is predominantly due to this localization, as a much greater excitonic binding occurs in the oxygen contaminated clusters.

That double bonded oxygen atoms tend to lower the gap as shown in Fig. 1(a) are in qualitative agreement with results given by Wolkin *et al.* [17], although those semi-empirical tight binding calculations predicted that oxygen states should disappear from the gap above 3 nm instead of the 2-2.5 nm range we find. As shown in Fig. 1(b), a further significant reduction in the gap occurs when every double bond of the cluster surface (a total of six) is replaced by oxygen in Si_{10} and Si_{35} . This reduction is very significant (e.g. 25% of the total oxygen gap in $\text{Si}_{35}\text{H}_{34}\text{O}$) and is one possible explanation for the wide discrepancy among so many different experiments.

Our calculations involving silicon nanoclusters with oxygen may be summarized as follows: 1) quantum confinement is *not* the only mechanism responsible for visible PL, contrary to previous reports; 2) the oxygen states are not pinned, but also decrease with increasing size; 3) in the presence of one oxygen passivant, the oxygen gap will disappear at around

2 nm, smaller than the 3 nm critical size reported in tight-binding calculations [17]; and 4) multiple oxygen passivants can lower the gap even more significantly (an additional 0.6 eV) perhaps explaining the wide discrepancy between so many experiments in which either oxygen was present, or the impurities were unknown.

IV. DISCUSSION

In order to analyze the physical origin of the effect of oxygen on the single particle and the optical gap, we investigated the effect of other contaminants on the energy gap as well. In particular, we investigated whether the gap closing is related to the high electronegativity of the contaminant, the electronic levels of the passivant such as the lone pair state appearing in the middle of the gap, or the chemical environment, specifically, the existence of a double bond.

Oxygen is highly electronegative with a value (3.5) comparable to fluorine (4.0) and chlorine (3.5). We investigated the effect of the electronegativity of the passivants by calculating the gaps of $\text{Si}_{35}\text{H}_{35}\text{F}$ and $\text{Si}_{35}\text{H}_{35}\text{Cl}$. A comparison of the molecular energy levels for each of these clusters (see Fig. 3) reveals that F and Cl have relatively little effect on the gap, although the energy of the LUMO decreases slightly with respect to the fully hydrogenated cluster. As shown in Fig. 2(a), the HOMO and LUMO of $\text{Si}_{35}\text{H}_{36}$ are both confined to the core of the cluster. This confinement is similar to that seen in clusters with single bonded passivants. Using chlorine as an example, we see that the HOMO density is altered with respect to the fully hydrogenated cluster and the LUMO density is “pointing” towards the chlorine atom (see Fig. 2(c)). The principal effect of these passivants is to break the T_d symmetry and split the three degenerate HOMO states. Of course, due to symmetry breaking, the triple degeneracy of the HOMO found in a totally hydrogenated cluster with T_d symmetry is broken when a single contaminant is introduced, giving rise to a small splitting. Based on these observations, we conclude that most single bonded passivants will generate similar single-particle gaps, regardless of their electronegativity or individual atomic levels.

To further analyze whether there is some other characteristic of oxygen accounting for its closing the gap, such as the lone pair state of oxygen, we passivated $\text{Si}_{35}\text{H}_{35}$ with OH, which has a lone pair, and $\text{Si}_{35}\text{H}_{34}$ with CH_2 , a passivant with no lone pair. In the cluster containing an OH, we observed a slight decrease in the gap from the H-passivated silicon value, similar to the effect of the other single bonded elements (F and Cl). In the CH_2 case, we found instead a large reduction of the gap, down to 2.5 eV, similar to the gap observed in atomic oxygen, yet there is no lone pair in the CH_2 group. It appears, therefore, that neither the electronegativity of oxygen, nor its lone pair state is responsible for the significant gap closing. However, much as with oxygen and CH_2 , a large closing of the LDA gap from 3.4 eV to 1.8 eV occurs when a double bonded sulfur atom is used to passivate the surface. Similar to oxygen, the HOMO and LUMO are localized on the passivant. The effects of the double bonded passivants on the HOMO/LUMO gap are profound, with the gap decreasing from the completely hydrogenated case by an amount ranging from 0.9 eV (when CH_2 is added) to 1.6 eV (when sulfur is added).

Fig. 3 summarizes our LDA results for all the passivants considered here. The molecular energy levels of $\text{Si}_{35}\text{H}_{35}\text{X}$ where $\text{X} = \text{H}, \text{OH}, \text{Cl}, \text{and F}$ are nearly identical, with a 0.1 to 0.2 eV variation on the gap. Likewise, the three passivants forming double bonds with the surface (O, S, and CH_2), have similar energy levels (very different than the single bonded passivants).

The fluorine, chlorine, and OH results indicate that the electronegativity of a passivant does not play a key role in altering the gap. The fact that OH does not alter the gap indicates that lone pair states are also not responsible for the reduction observed by the presence of oxygen. This conclusion is further supported by the cluster passivated with CH_2 which has no lone pair, yet closes the gap more than all the single bonded passivants. We therefore believe that the presence of a double bond induces a considerable distortion of the tetrahedral sp^3 network of the cluster, which is responsible for a gap reduction. This conclusion is further verified by placing an oxygen in a bridged network (Si-O-Si). In $\text{Si}_{35}\text{H}_{34}\text{O}$, forming an Si-O-Si bridge distorts the network significantly (see Fig. 4). The resulting distortion is such

that a cluster with an Si-O-Si bond is actually almost 3 eV higher in energy than double bonded oxygen (in LDA), and the gap decreases by a significantly greater amount, similar to the reduction induced by double bonded oxygen. Thus we believe that any passivation process that significantly distorts the sp^3 network will also alter the gap.

In order to make contact with the wide range of experimental methods for ascertaining optical gaps, ranging from simple PL measurements [6] to XAS [22], the calculation of the strength of a given transition is of paramount importance. Despite its accuracy in calculating the energy gap of a given transition, QMC methods cannot routinely be used to generate absorption spectra since each excitation would have to be a separate calculation. Other methods, such as TD-LDA and GW-BSE, would be required to generate such spectra. However, we can estimate the relative strength of a given transition by calculating dipole matrix elements $f_{if} = \frac{2\pi}{\hbar} \left[\sum_{k=1}^3 \left[\int \psi_f^*(x_1, x_2, x_3) \hat{x}_k \psi_i(x_1, x_2, x_3) d^3r \right]^2 \right]^{\frac{1}{2}}$ where ψ_f^* is the LDA final state, ψ_i is the initial state, and the x_k 's are the three cartesian directions in real space. Because our adopted supercell size used is large, each ψ vanishes at the box edge. Thus, by integrating over the box in real space, we essentially integrate to ∞ and a reasonable estimate of transition (i.e. oscillator) strength may be obtained.

We examined whether the smallest gap in double bonded passivants can be observed. With this aim, we calculated the lowest transitions of the following clusters $\text{Si}_{35}\text{H}_{34}\text{O}$, $\text{Si}_{35}\text{H}_{24}\text{O}_6$, and $\text{Si}_{35}\text{H}_{34}\text{S}$. When a passivant is double bonded, such as oxygen and sulfur, the lowest lying transition is negligible; however, the HOMO-1/LUMO transition is strong, on the order of that of hydrogen passivation alone (over three times stronger in cluster with a sulfur impurity). GW-BSE calculations show this transition to be 0.2 eV larger than the HOMO/LUMO transition in clusters with one oxygen [33]. However, when six oxygen contaminate the surface, we obtain strong transitions, still smaller than the smallest, unobserved gap in a single double-bonded oxygen cluster. These LDA estimates of oscillator strengths agree with GW-BSE results [33] as well as TD-LDA results [34].

V. CONCLUSION

In conclusion, we have demonstrated that quantum confinement is just one mechanism responsible for optical transitions in silicon nanoclusters and that the specific surface chemistry must be considered to interpret experimental results. We have carried out an analysis of the densities associated with the HOMO and the LUMO of silicon nanoclusters passivated with hydrogen up to 1.8 nm in diameter as well as $\text{Si}_{35}\text{H}_{35}\text{X}$ and $\text{Si}_{35}\text{H}_{34}\text{Y}$ where $\text{X}=\text{H}, \text{F}, \text{Cl}, \text{or OH}$ and $\text{Y}=\text{O}, \text{S}, \text{or CH}_2$. Our calculations show that surface effects due to the different chemistry of single bonded passivants do not appreciably contribute to optical transitions, even in the case of highly electronegative passivants. In systems with double bonds (e.g. O as a passivant), we demonstrate that the local distortion of the sp^3 network at the surface is a mechanism responsible for PL. Disturbance of the sp^3 network induced by double bonded passivants closes the single-particle gap by at least 1 eV in the LDA and the optical gap by 2 eV in QMC for clusters 1 nm in diameter. Our results indicate that a range of absorption gaps could be seen using passivants such as O, S, and CH_2 and that even a single contaminant can have a large impact on experimental results. We also discover that multiple contaminants can further alter the gap giving a large (0.6 eV) range of observed results, perhaps partially accounting for wide discrepancies in experiments. We found that bridged oxygen may also alter the gap, especially if it distorts the network significantly as in $\text{Si}_{35}\text{H}_{34}\text{O}$. These results should help in interpreting experimental data for silicon nanoclusters.

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FIGURES

FIG. 1. a) Local density approximation and quantum Monte Carlo calculations for hydrogenated Si clusters with and without oxygen. The arrow indicates where the oxygen gap would no longer be seen if one oxygen is double bonded on successively larger clusters. b) Quantum Monte Carlo calculations compared with three experiments in which oxygen was present. The curve representing multiple oxygen contamination is shifted based on a local density approximation calculation in which six oxygens were placed on hydrogenated clusters (see text).

FIG. 2. The density (ψ_i^2) of the highest occupied molecular orbital and the lowest unoccupied molecular orbital for a) $\text{Si}_{35}\text{H}_{36}$, b) $\text{Si}_{35}\text{H}_{34}\text{O}$, and c) $\text{Si}_{35}\text{H}_{35}\text{Cl}$.

FIG. 3. Density of states of 1.1 nm silicon clusters with different passivants. Each curve is Lorentzian broadened by 0.06 eV.

FIG. 4. Double bonded and bridged oxygen in $\text{Si}_{29}\text{H}_{34}\text{O}$ and $\text{Si}_{35}\text{H}_{34}\text{O}$ clusters.

Fig. 1 Puzder *et al.*

Fig. 2 Puzder *et al.*

Fig. 3 Puzder *et al.*

Fig. 4 Puzder *et al.*

a) Bridged

b) Double Bonded

Accurate Prediction of Nonostructure Optical Gaps: Application to Silicon Quantum Dots

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Accurate Prediction of Nanostructure Optical Gaps: Application to Silicon Quantum Dots

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Quantum Monte Carlo (QMC) calculations of the optical gaps of silicon quantum dots ranging in size from 0 to 1.5 nm are presented. These QMC results are used to examine the accuracy of density functional (DFT) and empirical pseudopotential based calculations. The GW approximation combined with a solution of the Bethe-Salpeter equation performs well but is limited by its scaling with system size. Optical gaps predicted by DFT vary by 1-2 eV depending on choice of functional. Corrections introduced by the time dependent formalism are found to be minimal in these systems.

Accurate prediction of the optical gaps of semiconductors represents one of the outstanding problems in the rapidly growing field of nanoscience. A leading example is the challenge of predicting the size dependence of the optical gap of silicon quantum dots [1-9]. To date, producing samples of pure, crystalline, monodispersed silicon quantum dots has proved immensely difficult. Given this lack of consistent experimental data, it is highly desirable to develop accurate theoretical models to assist in the development of silicon based opto-electronic and biological nanotechnologies. The theoretical challenge is to develop a consistent description of the exchange and correlation between electrons in systems ranging from highly inhomogeneous molecules such as silane to large clusters approaching the bulk limit.

In the 0-2 nm size range, silicon nanoparticles offer a unique combination of technological applicability and dramatic quantum confinement effects. Unfortunately, it is precisely this size range where theoretical methods encounter the greatest difficulty: For larger clusters (>500 atoms), the optical gap can be approximated by calculating the quasiparticle gap using semi-empirical approaches and correcting for the relatively small (few meV) exciton binding energy. However, in the 0-2 nm size regime these approaches break down due to a poor descriptions of the cluster surface and excitonic binding energy. Accurate electronic structure approaches based on perturbation techniques such as coupled cluster (CC) and configuration interaction (CI), or the GW approximation combined with a solution to the Bethe-Salpeter equation (GW-BSE)[4] are unworkable as the system size increases due to unfavorable scaling with number of particles. Finally, mean-field methods such as density functional theory (DFT), which can be applied throughout this size regime, rely on approximate exchange-correlation functionals which are well known to yield accurate ground-state properties, but significantly underestimate optical gaps.

In this paper we demonstrate the ability of linear scaling quantum Monte Carlo (QMC) calculations[13] to accurately predict the optical gap of silicon nanostructures ranging in size from a few to several hundred atoms.

The QMC approach includes exchange and correlation interactions between all the electrons in the quantum dot in its groundstate and also the interaction between the electron and hole forming the exciton in an optically excited quantum dot. These calculations provide the first benchmark of the size dependence of the optical gap in silicon quantum dots and enable us to analyze the accuracy of previous calculation approaches. We examine the approximations present in a wide range of alternate approaches by additionally performing DFT calculations using both the local density (LDA) and hybrid B3LYP functionals, in both time independent and time dependent[14] (TD-LDA, TD-B3LYP) forms. We also perform empirical pseudopotential calculations of the quasiparticle gap, corrected by an empirical electron-hole Coulomb attraction[5]. We find significant differences between our QMC results and previous high-level *ab initio* calculations, with the previous calculations proving more or less accurate in different size regimes. Further, our calculations provide predictive data in experimentally accessible size ranges that can be directly compared with future optical measurements.

Our DFT-LDA calculations were performed using the JEEP[15] plane wave code with Hamman (silicon) and Gianozzi (hydrogen) pseudopotentials and a 35 Ry cutoff. The DFT calculations using the hybrid B3LYP functional were performed using the Gaussian 98 program[12]. The QMC calculations were performed using recent developments[13] to the CASINO QMC code[16]. We use the fixed node, diffusion Monte Carlo (DMC) implementation of QMC[17] for all calculations, with a trial wavefunction formed by a product of Slater determinants for up and down spin electrons and a Jastrow correlation function. The Slater determinants were formed from a set of truncated, maximally localized Wannier (MLW) functions[13, 18], obtained by applying a unitary transform to the single particle orbitals obtained from the initial DFT calculation.

We define the QMC optical gap, E^{opt} , as the difference in total energies, $E^{opt} = E^* - E^{GS}$, where E^{GS} and E^* are the total energies of the system in its ground and singlet excited state electronic configurations. IN our

QMC calculations E^* is formed by replacing the highest occupied molecular orbital (HOMO) with the lowest unoccupied molecular orbital (LUMO) in the Slater determinant of the up spin electrons[19]. The unitary transform used to obtain the MLW orbitals is performed on all the N occupied DFT orbitals except the HOMO and LUMO which remain as the original LDA orbitals. Using these same $N - 1$ transformed occupied orbitals to construct both the up and down spin determinants in both the groundstate and excited state calculations halves the memory requirements of the calculations. The DMC energy obtained from this trial wavefunction corresponds to the lowest energy of a system with the nodal symmetry of these Slater determinants[20]. This approach to calculating the optical gap has previously been shown to be an accurate predictor of the true optical gap in both the molecular[21–23] and bulk[24] silicon limits. The optical gap, E^{opt} , associated with this singlet excitation corresponds to the onset of optical absorption in the dot, or the photoluminescence (PL) energy. In multi-configuration language, it corresponds to the energy required to excite the dot from the groundstate into the state with a dominant contribution from the determinant representing a HOMO-LUMO singlet excitation. In all the dots studied here, the HOMO-LUMO dipole matrix elements indicate an allowed transition and therefore we believe this is the appropriate excitation to consider.

In Fig. 1 we compare our DMC calculated optical gaps with those obtained from a range of other theoretical approaches. Previous calculations have also chosen to compare optical gaps with a variety of experimentally measured values. However, due to the wide spread in measured values we choose to focus here on comparisons between different theoretical techniques. For consistency, the atomic geometries used for the DMC, LDA, B3LYP, TD-LDA, TD-B3LYP and EPM calculations performed in this work were identical and were obtained by relaxing the structure within LDA. Any differences with the structures used for the GW-BSE[4], LDA[3] and tight-binding[6] calculations are expected to be small.

In Fig. 1 we observe that in the large size regime (>2 nm, >250 atoms) semi-empirical tight binding and pseudopotential approaches agree well with one another. As expected, the semi-empirical methods underestimate the optical gap of small clusters where the surface plays a dominant role. Figure 1 also shows our LDA calculated gaps. Both the single particle HOMO-LUMO gap (LDA) and the optical gap calculated using the time dependent formalism[14] (TD-LDA) are shown. As one would expect the LDA gaps are too low compared with DMC for the entire size range. Interestingly, TD-LDA [see Fig. 2a] offers only a minimal improvement over single particle LDA.

In Fig. 2 we use our DMC results as a benchmark to investigate the predictive ability of a variety of state-of-the-art DFT approaches. Figure 2a plots the dif-

ference between the optical gap computed with DMC and calculations based on the LDA functional: (i) single particle gaps (our calculations), (ii) optical gaps constructed[3] by subtracting an empirical electron-hole exciton binding energy from the LDA quasiparticle gap and then corrected to include the electron-hole polarization energy[7, 25], (iii) TD-LDA calculations from Ref.[8], (iv) TD-LDA calculations to be published in Ref.[26] and (v) GW-BSE calculations which add a perturbative correction to an LDA calculation. Comparing DMC with curve (v) shows that the excellent agreement between the optical gaps calculated using GW-BSE and QMC for silane[21] extends to all the sizes that are accessible to GW-BSE (1-14 atoms). With the exception of GW techniques built upon tight-binding theory[7], GW-BSE is currently not applicable to systems containing more than a few atoms. Comparing curves (i) and (ii) we observe that the LDA gaps and the corrected quasiparticle gaps of Ref.[3] are in quite good agreement. This agreement is likely due to a fortuitous partial cancellation of the quasiparticle correction and exciton binding energy present in curve (ii) and omitted in curve (i) (both of which are several eV). Both methods however, underestimate the optical gap by 1-2 eV for these sizes of cluster.

We now consider the results of time dependent LDA calculations which are able to predict a portion of the absorption spectrum. When comparing QMC calculated optical gaps with the optical spectra predicted by TD-LDA it is important to use a consistent definition of the optical gap. Curves (iii) and (iv) in Fig. 2a are obtained from very similar TD-LDA calculations. However, while the calculations agree on the optical gap of silane, they disagree considerably for larger clusters. This disagreement is due to a difference in the definition of the optical gap in the two calculations. In Ref.[8] [curve (iii)] the optical gap is defined as the point at which the integrated oscillator strength exceeds a threshold of 10^{-4} . As stated above, for the purposes of this work [DMC and curve (iv)] we have chosen to define the optical gap as the value of the first non-zero (dipole allowed) transition as we believe this enables the closest comparison between different theoretical approaches. This definition corresponds to the emission (PL) energy[27]. In silane, the first excitation peak already exceeds the threshold required in Ref.[8] and so the optical gaps agree. For the larger clusters, the integration threshold of Ref.[8] is only exceeded after integrating over several small peaks in the absorption spectra, and therefore in Ref.[8] the optical gap is defined to be larger than our value based on the PL energy. When we compare the TD-LDA calculations in curve (iv) with our DMC calculations we observe a consistent underestimate of the optical gap of 1-2 eV within TD-LDA[26]. In fact, with the exception of silane the blue shift of the optical gap introduced by TD-LDA with respect to the LDA gap is typically only 0.2 eV. Previous works have demonstrated that in the bulk limit the

value of the optical gap predicted by LDA and TD-LDA approach the same value. Here, somewhat surprisingly, our results indicate that even for small clusters TD-LDA does not offer a significant improvement of LDA.

In Fig. 2b we plot the difference between the optical gap calculated in DMC with calculations based on the hybrid B3LYP functional[29]. Previous B3LYP calculations [curves (i) and (ii)][9] disagree with our results [curves (iii) and (iv)] for clusters < 1 nm due to the use of a smaller basis[30] in Ref.[9]. In our calculations, we employed a large 6-311++G(2d,2p) gaussian basis to ensure convergence of the gaps to within 0.05 eV. Comparing the results of our converged B3LYP calculations [curves (iii) and (iv)] with DMC results we observe that the single particle B3LYP gap is generally in good agreement with our DMC values for the optical gap. The size dependence of the B3LYP gap is stronger than that of the DMC results and hence the B3LYP gap tends to overestimate the optical gaps of the smallest and under estimate the optical gaps of the larger clusters. It is not surprising that the B3LYP gap is in reasonable agreement with the DMC values for the optical gap of silane and Si_2H_6 as these molecules were part of the original set of molecules used to parametrize the exact exchange component of the functional[29]. The B3LYP functional has also recently been shown to predict accurate values for the optical gaps of bulk silicon[31]. However, we believe that this is the first work to assess the accuracy of the B3LYP functional for clusters throughout the crossover size regime from small molecules to bulk solids.

In Ref.[9] the B3LYP functional is also used to perform time dependent density functional calculations (TD-B3LYP). Previous calculations for atoms and molecules[14] have shown that while TD-LDA calculations typically yield gaps that are slightly blue shifted with respect to the single particle gap, time dependent HF calculations yield gaps that are significantly red shifted with respect to the single particle gap. One might therefore expect that as the B3LYP functional contains a component of exact HF exchange that TD-B3LYP calculations of the optical gap would be red shifted with respect to the B3LYP gap. This is exactly what is observed in Ref.[9] and repeating the calculations with a larger basis we find the red shift is increased further for the smaller size clusters. For all sizes of cluster, the agreement between the TD-B3LYP optical gaps and the DMC optical gaps is *worse* than the agreement between B3LYP single particle gaps and DMC. This result is not surprising because one of the criteria used to fit the parametrization of this functional was that the *single particle* ionization potential (a quantity related to the quasiparticle gap) should reproduce the experimental value. The red shift of the gap introduced by the time dependent formalism was not accounted for in the original parametrization and therefore the optical gaps are too small.

When examining the density functional results from

Figs.2 (a) and (b) one should bear in mind that the optical gap is intrinsically a many-body quantity, including the interaction between all electrons in the system with the exciton created by the absorption of a photon. QMC calculations are, by construction, many-body calculations and can therefore capture these interactions. The Bethe-Salpeter equation, which describes the exciton as a linear combination of two-particle electron-hole pairs has been shown to accurately describe the binding energy of the exciton. In contrast, conventional DFT HOMO-LUMO gaps are purely single particle quantities. Of course, it is always possible to construct a functional which cancels the errors in the single particle LDA and HF gaps to yield a single particle gap in perfect agreement with the true optical gap for one particular size of cluster. However, the different size scalings of the quasiparticle gap and the exciton binding energy suggest that such a cancellation could not persist over a large size range. Such an argument underscores the surprising quality of the *optical* gaps predicted by the intrinsically *single particle* B3LYP gap. We do however, suggest using caution when applying the B3LYP functional for calculation of optical gaps in general.

While the present results for silicon quantum dots demonstrate surprisingly good agreement, we have also recently applied B3LYP to iso-electronic germanium clusters and found significantly larger discrepancies when compared to QMC calculations[32]. A deeper understanding of these results requires an analysis of the quasiparticle and exciton binding energies predicted by QMC, which we relegate to a future publication.

In conclusion, we have performed the first QMC calculations of the optical gap of silicon quantum dots ranging in size from 0 to 1.5 nm. This size range is large enough to connect small clusters at the molecular limit with those approaching the bulk limit. These calculations demonstrate the applicability of the QMC approach to this central problem in modern nanoscience. Further this QMC approach applies equally well to alternative material types such as germanium and cadmium selenide and to both crystalline and amorphous structures. By comparing with several alternative theoretical approaches we predict that for clusters > 3 nm in size, semi-empirical approaches are sufficient to accurately describe the size dependence of the optical gap. For clusters < 2 nm there is a wide spread in the optical gaps predicted by different approaches. The optical gaps predicted by DFT calculations, based on the LDA functional tend to underestimate the optical gap. Whereas, at least for silicon, the single particle gap predicted by DFT calculations using the B3LYP functional are in good agreement with our DMC optical gap calculations. However, time dependent corrections to this functional uniformly degrade the quality of the results.

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- FIG. 1: Size dependence of optical gaps of silicon nanoclusters, calculated using diffusion Monte Carlo (DMC), time independent (LDA) and dependent (TD-LDA) DFT, semi-empirical tight binding and pseudopotential approaches. DMC error bars are smaller than the symbols.
- FIG. 2: Deviation of the optical gap predicted by density functional calculations based on the (a) LDA functional and (b) B3LYP hybrid functional from the DMC optical gap.
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Fig. 1 Williamson *et. al.*

Fig. 2 Williamson et. al.

Synthesis Dynamics of Passivated Silicon Nanoclusters

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Synthesis dynamics of passivated silicon nanoclusters

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Quantum molecular dynamics and quantum Monte Carlo techniques are employed to gain insight into the effect of preparation conditions on the structural and optical properties of silicon nanoparticles. Our results demonstrate that (i) kinetically-limited nanostructures form different core structures than bulk-derived crystalline clusters, (ii) the type of core structure that forms depends on how the cluster is passivated during synthesis, and (iii) good agreement with measured optical gaps can be obtained for nanoparticles with core structures different from those derived from the bulk.

Silicon nanoclusters have been the focus of intense theoretical and experimental interest [1–4]. A combination of the unique optical properties of silicon quantum dots and their compatibility with existing silicon-based and nano-biological technologies demonstrates great promise for numerous applications. In the 1-3 nm size range, where Si quantum dots may exhibit visible luminescence, experimentally determined optical properties vary significantly depending on the synthesis technique [4–9]. For example, the optical gaps of silicon clusters formed by physical vapor deposition [10] were found to be several eV lower than those formed using inverse micelles [11]. Further, even quantum dots made via the same process have been found to exhibit widely-varying absorption and emission spectra, perhaps due to small differences in preparation conditions and limitations in the accuracy of characterization techniques. These discrepancies pose a significant challenge to the practical application of silicon quantum dots and demonstrate the need for accurate theoretical predictions to help guide experiments.

Previous theoretical studies of silicon nanoclusters have used either bulk crystalline [12] or quasi-amorphous structural templates [13] to generate atomic configurations. The highly curved surface is typically fully passivated with hydrogen to saturate dangling bonds. While these model structures allow for the study of a number of different properties (i.e., the effects of contamination and surface reconstruction), they do not allow one to examine the impact of the synthesis process itself. Investigating the synthesis process requires the use of computationally demanding quantum simulations in order to take into account the complex and subtle dynamical effects needed for accurate predictions.

In this Letter we employ a combination of quantum molecular dynamics (QMD) and quantum Monte Carlo (QMC) calculations to determine the impact of the experimental synthesis process on the structural and optical properties of 1 nm silicon dots. Our results indicate that when a finite-temperature synthesis and passivation process is emulated, the number of atoms in the core of the resulting cluster is larger than for ideal, bulk-derived structures. We observe a subtle interplay between the strain associated with high curvature and surface dangling bonds and the preference for silicon to form

tetrahedrally-symmetric cores. These two competing effects produce a class of structures defined by the core structure and the bonding of the core atoms to the surface. Rather than a search for low-energy structures, this classification results from a careful examination of the metastable, kinetically-limited nanostructures produced by QMD, and can be applied to other nanoscale systems. We also show that structures which are likely to form via a given synthesis method strongly depend on the mechanism by which the silicon surface is passivated and on the ability to satisfy surface strain during the growth sequence. Further, we present novel nanoscale reconstructions, unique to highly curved crystalline structures, that have lower energy and larger optical gaps than the bulk-inspired reconstruction.

Several experimental techniques for synthesizing silicon nanoparticles, such as physical vapor deposition [10] and laser ablation [14], generate a high temperature silicon vapor from which amorphous nanoclusters nucleate as the vapor cools. During or after cooling, there is typically exposure to some form of passivant (e.g., hydrogen, oxygen) which removes dangling bond states from the surface of the cluster. This synthesis process is simulated using QMD [15], starting from an amorphous cluster obtained by heating a bare cluster at 1500 K for ~ 2 ps. A new hydrogen atom is then added to an unpassivated surface atom every 0.3-0.5 ps until all silicon atoms are four-fold coordinated. Simple thermodynamic arguments, assuming atmospheric pressure and ideal gas vapor densities, predict an additional hydrogen will passivate the surface every 1-2 ps. By using a series of elevated temperatures ($T=600, 800$, and 1000 K), we were able to observe realistic passivation events on shorter time scales (0.3-0.5 ps) while confirming that the higher temperatures did not qualitatively alter the growth process. The combined total simulation time for all clusters investigated here was ~ 500 ps.

The present work considers the 1 nm size range where there are ~ 30 silicon atoms per quantum dot. We performed simulations starting from amorphous Si_{29} , Si_{30} , and Si_{31} . Surprisingly, in our simulations which started from Si_{29} , the single tetrahedral core structure predicted for 29 silicon atoms (see Fig. 1a) does not form. Instead, we found that the resulting passivated structures consist-

tently had a *double* tetrahedral core – two interior silicon atoms rather than one (see Fig. 1b). The formation of a double core was found to be completely independent of temperature and the order in which hydrogen atoms were added to the surface. The resulting structures were highly strained due to the lack of a symmetric arrangement of 21 surface silicon atoms around the 8-atom double core structure (i.e. 2 interior core atoms with 6 surrounding atoms).

FIG. 1. Results of QMD synthesis for Si_{29} and Si_{30} , compared with low-energy ideal structures. Interior core atoms are dark blue. (a) Ideal $\text{Si}_{29}\text{H}_{24}$ structure proposed by Mitas *et al.*; (b) Final $\text{Si}_{29}\text{H}_{21}$ structure from QMD synthesis at $T=1000$ K, relaxed at $T=0$ K; (c) Proposed ideal $\text{Si}_{30}\text{H}_{22}$ structure; (d) Final $\text{Si}_{30}\text{H}_{22}$ structure from QMD synthesis at $T=1000$ K, relaxed at $T=0$ K.

The explanation for the consistent formation of a double-core structure lies with the dynamics of bare silicon clusters. Above $T=300$ K, unpassivated crystalline nanoclusters become amorphous, with multiple atoms in the center of the cluster attempting to saturate the dangling bonds of the surface atoms. Clusters of amorphous Si_{29} typically have two to three such highly coordinated interior atoms. As hydrogens are added to the surface, the number of dangling bonds is reduced and the interior atoms develop stable bonds to the surface. Passivation has the effect of “freezing” that region of the cluster surface as atoms at the surface become four-fold coordinated. By the time enough hydrogens have been added to fully passivate the surface, the surface has frozen around two interior core atoms. A transition from this type of structure to a single-core structure would likely require a global reconstruction of the surface, with multiple events involving the simultaneous breaking of several

silicon bonds.

The competition between two silicon atoms in the central core region can be understood by examining the early stages of the passivation process. The core structure of a silicon cluster is defined by the number of atoms that occupy the interior region, completely surrounded by other silicon atoms. To quantify the degree to which a silicon atom is in the interior of the cluster, we estimate the fraction of the total solid angle around atom i that is not occupied by other silicon atoms. For simplicity, we approximate this solid angle by calculating the maximum base angle Ω of a cone whose apex is centered on atom i and whose volume does not intersect any other silicon atoms (see Fig. 2 inset). The quantity Ω is plotted as a function of time in Fig. 2 for a simulation of the synthesis of Si_{29} , starting from an unpassivated crystalline cluster. Within 0.5 ps, an atom has moved from the surface to become a second core atom in the cluster and remains there for the duration of the simulation.

FIG. 2. Interior parameter Ω_i vs. time for the silicon atoms in an Si_{29} QMD synthesis run at $T=1000$ K, with a hydrogen atom added to the surface of the cluster every 0.3 ps. The blue and red curves correspond to the two interior core atoms, and the grey curves are surface silicon atoms. The inset shows how Ω is defined, in this case for an interior atom (dark blue).

By symmetry, 30 silicon atoms are more favorable than 29 atoms for the formation of 1 nm double-core nanoclusters. $\text{Si}_{30}\text{H}_{22}$ has a symmetric construction which can be represented as a 28-atom cage (14 pentagons, 2 septagons) surrounding two interior atoms (Fig. 1c). This structure was stable to thermodynamic fluctuations at $T=1000$ K for 10 ps. Subsequent simulations of hydrogen passivation of amorphous Si_{30} at $T=600$ K and $T=1000$ K, using the same QMD synthesis calculations as for Si_{29} , again consistently produced double-core structures. Whereas for Si_{29} they were markedly different than

the ideal case, for Si_{30} QMD produced many low-energy structures (the example shown in Fig. 1d had a total energy which was only 0.1 eV higher than the ideal structure Fig. 1c) that are qualitatively similar to the ideal high-symmetry structure. Similar to Si_{29} , Si_{31} also produced double-core structures, although significantly more strained than those starting from Si_{30} .

As mentioned, a number of different experimental synthesis processes have been used to make silicon quantum dots. Recently, silicon nanoclusters with discrete cluster sizes have been produced by sonification of porous silicon [16]. In this process, silicon clusters are formed from larger pieces of hydrogenated silicon – a fundamentally different synthesis process to the silicon vapor based techniques described above, since the starting point is crystalline bulk, not amorphous vapor. If each fragment is passivated before amorphization takes place, the resulting nanoclusters may retain a crystalline core. The fact that the fragments are already partially passivated upon breakup likely plays a major role in slowing or preventing amorphization, and may allow only single-core 1 nm nanocrystals to form.

FIG. 3. Interior parameter Ω_i vs. time for the silicon atoms in (a) Si_{29}H_6 , (b) $\text{Si}_{29}\text{H}_{12}$, and (c) $\text{Si}_{29}\text{H}_{18}$ QMD simulations at $T=1000$ K. The colored curves correspond to atoms which are in the interior of the cluster at some point in the simulation, and the grey curves are surface atoms.

To determine the number of hydrogens required to maintain a single-core crystalline structure in a 29-

atom silicon cluster, we performed QMD simulations in which a number of neighboring hydrogen atoms were removed from a tetrahedrally symmetric $\text{Si}_{29}\text{H}_{24}$ nanocrystal, which was then heated to $T=600$ K and 1000 K. At $T=1000$ K, removal of only 6 hydrogen atoms ($\text{Si}_{29}\text{H}_{18}$) resulted in a persistently stable, single-core structure. When 12 hydrogen atoms were removed ($\text{Si}_{29}\text{H}_{12}$), the silicon cluster formed a double core within 0.5 ps. When 18 hydrogen atoms were removed (Si_{29}H_6), the cluster again formed a double core within 0.5 ps, but also exhibited dynamics consistent with an amorphous cluster, as shown by the exchange of interior core and surface atoms on a time scale of roughly 1 ps (Fig. 3c). We found that 14 neighboring hydrogen atoms ($\text{Si}_{29}\text{H}_{14}$) are required to maintain a single tetrahedral core. At $T=600$ K, similar behavior is observed, although the double-core formed more slowly than at $T=1000$ K. Based on these findings, it is possible that a 1 nm nanocluster exhibiting bulk-like crystallinity can be formed from the break-up of larger passivated clusters, as long as more than half the surface of the resulting nanocluster is passivated within picoseconds of break up.

FIG. 4. Two different reconstructions of a $\text{Si}_{29}\text{H}_{24}$ nanocluster: (a) $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$ (b) $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$.

Even if the 1 nm nanoclusters formed with porous sonification are in fact crystalline, the measured optical gaps are not in agreement with the lowest-energy crystalline $\text{Si}_{29}\text{H}_{24}$ structure. A bulk-like surface reconstruction of crystalline $\text{Si}_{29}\text{H}_{36}$ to $\text{Si}_{29}\text{H}_{24}$ was proposed [12] (see Fig. 1a) and found to have an optical gap in agreement with an experimentally-measured optical gap of 3.44 eV for 1 nm clusters synthesized using porous sonification [16]. Here we present two lower-energy reconstructions of $\text{Si}_{29}\text{H}_{24}$ with optical gaps significantly larger than 3.5 eV. The surface of a $\text{Si}_{29}\text{H}_{24}$ cluster can be represented as a 28-atom cage (12 pentagons, 4 hexagons) with a single silicon atom in the center, bonded to four surface atoms (related by T_d symmetry) to form a five-atom tetrahedral core. The remaining surface atoms are passivated with hydrogen. There are three unique ways to connect the interior core atom to the surface and maintain a tetrahedral core. The first ($\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$, Fig. 1a) was proposed

based on a bulk-like (2x1) reconstruction of dimer pairs on (001) facets. The other two (Fig. 4), $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$ and $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$, are *unique to a curved nanostructure*, and have no bulk analogue. Two similar reconstructions exist for ideal $\text{Si}_{30}\text{H}_{22}$ (Fig. 1d).

The total energies of $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$ and $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$ calculated with our QMC approach [17] are 0.6(1) eV and 1.0(1) eV lower than $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$, respectively, due to decreased strain around the surface dimers. In fact, a partial reconstruction from $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ to $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$, in which a single surface core atom takes the hydrogen from its neighbor which then bonds to the central core atom, also has lower energy than $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$. Therefore, even if $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ initially forms, it is highly likely that it would reconstruct to $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$, as the barrier only involves the breaking of a single silicon bond at a time.

TABLE I. Energy gaps for silicon nanoclusters, calculated using both LDA and QMC. For structures created with QMD, a range of LDA gap energies is given, with QMC gaps calculated only for the structure with the largest LDA gap.

	$E_{\text{gap}}^{\text{LDA}}$ (eV)	$E_{\text{gap}}^{\text{QMC}}$ (eV)
$\text{Si}_{29}\text{H}_{21}^{\text{QMD}}$	0.9-1.5	2.5(1)
$\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$	3.1	4.5(1)
$\text{Si}_{30}\text{H}_{22}^{\text{ideal}}$	2.2	3.2(1)
$\text{Si}_{30}\text{H}_{22}^{\text{QMD}}$	2.2-2.4	3.4(1)

In addition to energy differences, we also employ QMC to calculate optical gaps in the same manner as Ref. [18]. Our calculated QMC optical gaps for ideal $\text{Si}_{30}\text{H}_{22}$ and $\text{Si}_{29}\text{H}_{24}$ are 3.2(1) and 4.5(1) eV, respectively. The range of gaps for $\text{Si}_{30}\text{H}_{22}$ clusters generated by QMD synthesis is in better alignment with experiment [9,16] than the range of gaps for $\text{Si}_{29}\text{H}_{24}$ generated under the same synthesis conditions. Our calculations show that symmetric double-core (i.e. non-crystalline) structures not only have optical gaps similar to those measured experimentally, but form consistently from amorphous silicon nanoclusters in the first few picoseconds of synthesis.

Table I lists both LDA and QMC optical gaps for different structures considered here. While only the QMC results are expected to be directly comparable to experimental absorption data, note that the LDA gaps accurately reproduce the QMC trends. For $\text{Si}_{29}\text{H}_{24}$, the gaps for structures determined by QMD synthesis are significantly smaller than for the ideal, high-symmetry case. In addition, the optical gap calculated with QMC is 4.5(1) eV for $\text{Si}_{29}\text{H}_{24}^{\text{nanol}}$ and 4.1(1) eV for $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$, significantly larger than the 3.5(1) eV gap of $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ and current experimental measurements. In contrast, for $\text{Si}_{30}\text{H}_{22}$, the gaps produced by synthesis are roughly the same as the high-symmetry case. These differences are linked to the large variations in resulting structures described above; the double core is able to form with much less strain for Si_{30} while considerable strain was present

for the double core Si_{29} structures.

We find that during the formation process of 1 nm clusters, relaxation of the high strain induced by the curvature and dangling bond states at the surface is in direct competition with the preference of the interior atoms to be tetrahedrally coordinated. Our results show that the resulting structures consistently form with a non-crystalline, double tetrahedral core. For clusters with 30 silicon atoms, QMD produced structures with optical gaps in good agreement with both symmetric low-energy structures and experimental measurements. We find reconstructions unique to highly curved nanostructures which give evidence for larger optical gaps than previously predicted in 1 nm crystalline nanoclusters. In addition, we find that the stability of small, partially-passivated Si_{29} crystalline fragments strongly depends on the number of hydrogen atoms at the surface, with a crossover from double-core to single-core structures between 12 and 14 hydrogen atoms. This work suggests that the metastable nanostructures most likely to form via a given synthesis process should be classified in terms of both core structure and surface reconstruction.

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with a kinetic energy cutoff of 35 Ry.

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