Quantum Monte Carlo Calculations 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 optoelectronic 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 semiempirical 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 poor descriptions of the cluster surface and excitonic binding energy. Accurate electronic structure approaches based on perturbation techniques such as coupled cluster and configuration interaction, 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 near linear scaling quantum Monte Carlo (QMC) calculations [10] 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 ground state 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 performing both DFT and empirical pseudopotential calculations. 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 [11] 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 [10] to the CASINO QMC code [13]. We use the fixed node, diffusion Monte Carlo (DMC) implementation of QMC [14] for all calculations, with a trial wave function formed by a product of Slater determinants for up and down spin electrons and a Jastrow correlation function containing electron-electron and electron-nucleus terms. The Slater determinants were formed from a set of truncated, maximally localized Wannier (MLW) functions [10,15], obtained by applying a unitary transform to the single particle orbitals obtained from the initial DFT calculation. The MLW functions were truncated beyond a radius chosen to capture $> 99.7\%$ of the norm of the original function. A time step of 0.05 a.u. was used in all DMC calculations.

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 [16]. 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 ground state and excited state calculations halves the memory requirements of the calculations. The DMC energy obtained from this trial wave function corresponds to the lowest energy of a system with the nodes of these Slater determinants [17]. 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 [18–20] and bulk [21] 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 multiconfiguration language, it corresponds to the energy required to excite the dot from the ground state 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 empirical pseudopotential 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) semiempirical tight-binding and pseudopotential approaches agree well with one another. As expected, the semiempirical 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 [22] (TD-LDA) are shown. As one would expect, the LDA gaps are too low compared with DMC for the entire size range. Interestingly, TD-
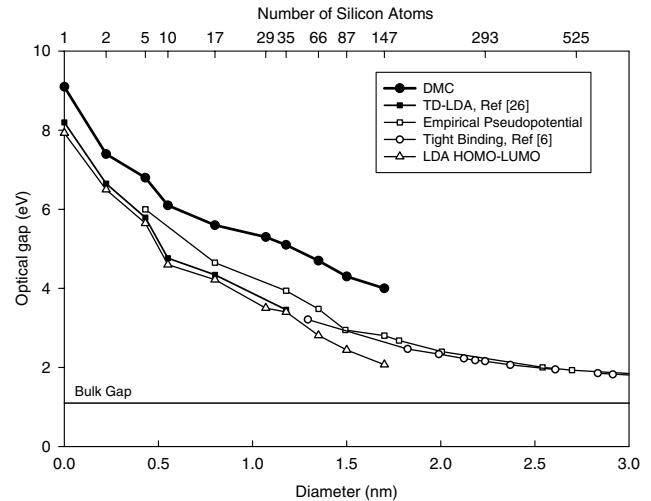

FIG. 1. Size dependence of optical gaps of silicon nanoclusters, calculated using diffusion Monte Carlo (DMC), time independent (LDA) and dependent (TD-LDA) DFT, semiempirical tight binding, and pseudopotential approaches. DMC statistical error bars are smaller than the symbols.

LDA [see Fig. 2(a)] offers only a minimal improvement over single particle LDA.

Figure 2(a) plots the difference 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 [7,23], (iii) TD-LDA calculations from Ref. [8], (iv) TD-LDA calculations to be published in Ref. [24], 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 [18] extends to all the sizes that are accessible to GW-BSE (1–14 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.

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. 2(a) 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 nonzero (dipole allowed) transition as we believe this enables the closest comparison between different theoretical approaches. This definition corresponds to the emission (PL) energy [25]. 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 exceeded only 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 [24]. 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 over LDA.
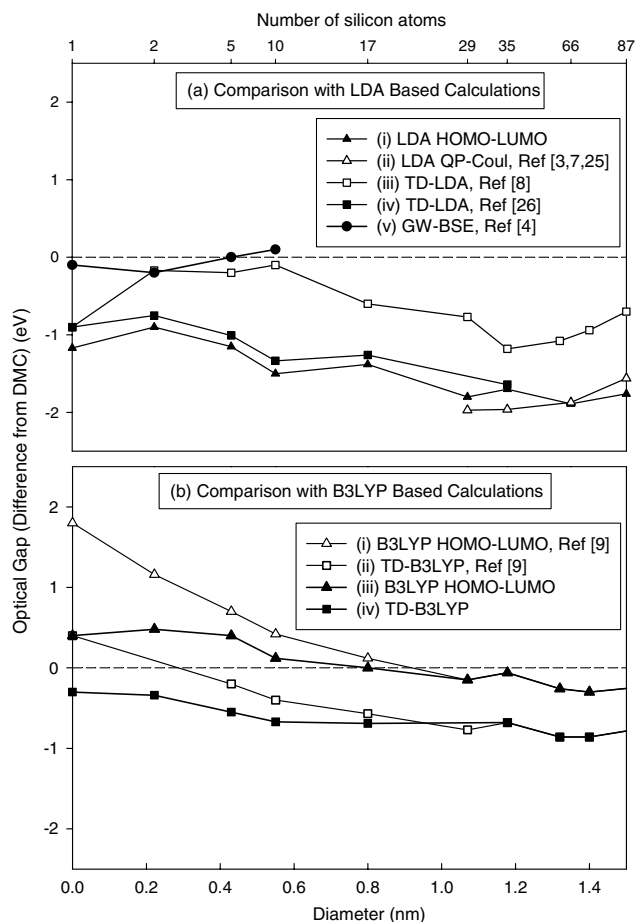

FIG. 2. Deviation of the optical gap predicted by density functional calculations based on the (a) LDA functional and (b) B3LYP hybrid functional from the DMC optical gap.

In Fig. 2(b) we plot the difference between the optical gap calculated in DMC with calculations based on the hybrid B3LYP functional [27]. 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 [28] in Ref. [9]. In our calculations, we employed a large $6\text{-}311++G(2d, 2p)$ 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 underestimate the optical gaps of the largest 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 [27]. The B3LYP functional has also recently been shown to predict accurate values for the optical gaps of bulk silicon [29]. 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 [22] have shown that while TD-LDA calculations typically yield gaps that are slightly blueshifted with respect to the single particle gap, time dependent HF calculations yield gaps that are significantly redshifted with respect to the single particle gap. One might therefore expect that, as the B3LYP functional contains a component of exact exchange, TD-B3LYP gaps would be redshifted with respect to the B3LYP gap, and this is confirmed both in Ref. [9] and by our calculations. For all sizes of clusters, 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 redshift 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 2(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.

However, we have also recently applied B3LYP to isoelectronic germanium clusters and silicon clusters with reconstructed surfaces and found significantly larger discrepancies when compared to QMC calculations [30]. 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, semiempirical 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 gaps 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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