High Level *Ab Initio* Calculations of the Optical Gap of Small Silicon Quantum Dots

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Using state of the art time-dependent density functional theory and multireference second-order perturbation theory, we have accurately calculated (within 0.3 eV) in real space the optical gap of small silicon quantum dots, with diameters up to 25 Å. Our results, which support the quantum confinement hypothesis, are in excellent agreement with recent and earlier experimental data on oxygen-free samples and the conclusions of Wilcoxon *et al.* [Phys. Rev. B **60**, 2704 (1999)]. We have found that the diameter of the smallest dot, which could emit photoluminescence in the visible region of the spectrum, is around 22 Å. Our work can resolve existing controversies and bridge diverse experimental and theoretical results.

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On top of the fundamental importance of Si quantum dots as nanoscale materials, the possibility of intense tunable photoluminescence (PL) from them has stimulated considerable efforts in this field [1–10]. By varying their diameter, intense PL across the visible spectrum can be obtained. Because of the large blueshift of the observed radiation with respect to the bulk Si band-gap energy (1.2 eV), it has been proposed that the luminescence in the visible is mainly due to quantum confinement. However, models involving siloxene derivates, polysilane, and hydrides on the surface of the dots have challenged this hypothesis [9].

On the experimental side, the majority of the experimental work thus far gives diverse results for the size of the Si dots responsible for visible PL. Recent experimental data suggest that the diameters of the dots able to emit in the visible are much less than 20 Å. For example, the results of Wolkin *et al.* [2] revealed optical gaps as small as 2.2 eV, for nanoclusters with a diameter of 18 Å. For nanoclusters of about the same size, Wilcoxon *et al.* [1] obtained a similar result (2.5 eV) together with a much larger gap of about 3.2 eV for highly purified samples of the same dot diameter. Furthermore, Schuppler *et al.* [4] have estimated the critical diameter for visible PL to be less than 15 Å.

Thus, there are two controversial issues in this field: (1) the mechanism responsible for the visible PL and (2) the variation of the optical gap with the dot diameter d. These issues are not independent of each other. A settlement of the second issue will settle at the same time the issue of the mechanism of the visible PL. The main source of error in the experimental results, besides the purity of the sample, is the determination of the diameter of the dot, which is very difficult for very small dots. As a result, the optical gap is a multivalued function of d, which is different in different works (see, for instance, Figs. 10, 4, and 5 in Refs. [1–3], respectively). As a matter of fact, in some cases [2], the diameter d of the dot is determined by comparison to theoretical calculations of the gap versus d. From the theoretical point of view, the *ab initio* investigation of the dot's optical properties demands an accurate account of electron correlation and involves a high computational cost, which scales at least with the fifth or sixth power of the cluster size, d. As a result, a large portion of the existing theoretical work is either semiempirical in nature, involving adjustable parameters, which are usually adjusted to appropriate bulk properties, or involves unrealistic assumptions and approximations for very small dots (see Ref. [8]). It is clear therefore that a high level accurate *ab initio* theoretical method, which could produce unbiased and realistic results for this size of nanoparticles, would be able to resolve the two controversial issues on this subject. With this aim, we present in this work for the first time accurate calculations of the optical gap based on time-dependent density functional theory (TDDFT) [11] and the multireference second-order perturbation theory (MR-MP2 [12]).

The size of the quantum dots considered here ranges from 1 to 281 Si atoms, with 4 to 172 H atoms (a total of about 453 atoms). The diameter of the larger clusters falls in the range of 12–25 Å for which visible photoluminescence has been reported [2,4,10,13–15]. All dots have T_d symmetry and their geometries have been fully optimized within this symmetry constrain using the hybrid nonlocal exchange-correlation functional of Becke and Lee, Yang and Parr (B3LYP) [16]. As it will be shown by comparison to MR-MP2 [12] calculations, the partially exact Hartree-Fock (HF) exchange that is included in the B3LYP method is very important for the correct description of the optical properties. The inclusion of exact HF exchange remedies the well-known deficiency of local-density approximation (LDA) to underestimate the band gap. To verify this, we have performed in addition TDDFT calculations using the well-known functional of Becke and Perdew (BP86) [17], which does not include exact (or partially exact) exchange. The calculated optical gaps in this

case are notably lower. The DFT and the TDDFT calculations were performed with the TURBOMOLE [18] suite of programs using Gaussian atomic orbital basis sets of split valence [SV(P)]: $[4s3p1d]/[2s]$ [19] quality which involves 5400 basis functions for the largest system studied. The TDDFT calculations have been performed as described in detail in Ref. [20] using the B3LYP functional consistently for both, the self-consistent solution of the Kohn-Sham equation for the ground state, and the solution of the linear response problem. The optical gap in TDDFT (and MR-MP2) is identified as the energy of the lowest allowed electronic transition (i.e., with nonzero oscillator strength).

The MR-MP2 calculations [12] were performed as described in Ref. [21]. In these calculations, ground state HF molecular orbitals were used and the RI (resolution of the identity) approximation for the two electron integrals (see Ref. [21]) was employed. Again, the SV(P) basis set was utilized. All valence electrons (32 for Si_5H_{36}, 104 for $Si_{17}H_{36}$, and 152 for $Si_{29}H_{36}$) were correlated. The zeroth-order wave functions in the MR-MP2 treatment were constructed from single excitation CI (configuration interaction) wave functions including about 30 of the frontier orbitals. With this choice, the largest amplitude in the first-order corrected MP2 wave functions is always smaller than 0.03, a point where MR-MP2 relative energies are usually converged to about 0.1 eV.

The MR-MP2 results practically coincide with the TDDFT/B3LYP results. Therefore, for computer time and space economy, the MR-MP2 calculations have been restricted here to nanoclusters containing up to 29 Si atoms (with 36 additional H atoms). The silicon nanoparticles considered here have a closed-shell electronic structure in the ground state with vanishing nondynamical electron correlation contributions. The lowest excited states of T_2 symmetry are dominated by a small number of single excitations between orbitals of pure valence character; the double excitation contributions are less than 8% in the MR-MP2 calculations. For states of this type, according to prior experience [20,21], MR-MP2 and TDDFT/B3LYP methods have an estimated accuracy of about 0.3 eV for the excitation energies. Test calculations at the MR-MP2 level using a larger triple-zeta atomic orbitals basis ($[5s4p1d]/[3s1p]$) for Si_5H_{12} give an excitation energy of 6.51 eV, smaller by only 0.25 eV, whereas for the largest clusters the basis set difference is expected to be negligible. Therefore, 0.3 eV is a conservative estimate of the error margin.

In Table I we have compiled the results for the first three pronounced transitions of SiH_4, which is a limiting case of the smallest quantum dot. For this stable system, there is a wealth of unambiguous experimental data (structural, optical, electronic) [22] taken under well-defined conditions, as well as other high level calculations based on the solution of the Bethe-Salpeter equation within the *GW* approximation [6].

TABLE I. Optical absorption energies of SiH_4 (in eV).

State	TDDFT/B3LYP	Experiment [22]	*GW* [6]
$4s$	8.8	8.8	9.0
$4p$	9.3	9.7	10.2
$4d$	10.7	10.7	11.2

As we can see, the agreement with experiment and, in part, with the *GW* results is very good. However, the electronic spectra of SiH_4 are dominated by Rydberg transitions, which are suppressed in the larger nanoclusters. For Si_5H_{12}, which is the next larger dot, the agreement of our results (6.66 eV with TDDFT/B3LYP and 6.76 with MR-MP2) with the experimental value of 6.5 eV, determined by optical absorption measurements [23], is excellent. The *GW* value is about 7.2 eV for the first allowed transition. In Table II we have summarized and compared the TDDFT/B3LYP results for the optical gap of nanoclusters from Si_5H_{12} up to $Si_{281}H_{172}$, together with some MR-MP2 results. The size of these nanoclusters ranges from about 7 Å up to 25 Å. This range includes the sizes of 15, 18, and 20 Å for which PL has been reported ([2,4,10]) with peaks between 2.1 and 2.5 eV. As we can see in Table II, our calculated optical gaps in this region range from about 3.4 to 6.7 eV, with a possible error of about 0.3 eV. The results from the two very different theoretical approaches agree to within 0.1 eV for the three smallest systems. These calculated values are clearly well above the observed limits of 2.1–2.5 eV. Therefore, since the observed PL could not have its origin on quantum dots of this type and/or size, we suggest that either the samples are contaminated with oxygen (mainly) or their size is not correctly determined. As will be illustrated below, this conclusion is not in conflict but, on the contrary, it is supported by recent experimental data from two different groups [1,2], which have demonstrated that these

TABLE II. Comparison of the optical gap for Si nanoclusters.

No. of Si atoms	Total No. of atoms	H-L[a] gap (eV)	TDDFT[b] (eV)	MR-MP2 (eV)	f[c]
5	17	7.6	6.66[d]	6.76[d]	0.0065
17	53	5.72	5.03	5.02	0.1507
29	65	5.15	4.53	4.45	0.0189
35	71	5.04	4.42	···	0.0052
47	107	4.64	4.04	···	0.1151
71	155	4.20	3.64	···	0.0124
99	199	3.89	3.39	···	0.0009
147	247	3.66	3.19	···	0.0007
281	453	3.11	···	···	···

[a]HOMO-LUMO gap from the Kohn-Sham eigenvalues of the ground state DFT/B3LYP calculation.
[b]TDDFT/B3LYP.
[c]Oscillator strength obtained by TDDFT/B3LYP.
[d]The experimental absorption value is 6.5 eV [23].

measured values refer to oxygen containing samples. Furthermore, as we have mentioned earlier, the experimental determination of the nanocluster sizes is difficult and rather ambiguous for very small nanoclusters (dots). It is very difficult to be certain, without large statistical samples, that the diameters obtained (usually) from TEM images are truly representative. In several cases in which statistical analysis was performed, it was found that nanocluster samples exhibit a broad distribution of sizes [1]. As a matter of fact, in order to avoid this ambiguity, Wolkin *et al.* [2] have determined the sizes of their Si dots by equating their measured peak PL energies with calculated excitonic band gaps, using a simple tight binding model. This model, which is similar to and produces almost identical results with those of Reboredo *et al.* [3], cannot match the accuracy of the present calculations. On the other hand, it is obvious that, if our calculations were used to determine the sizes of the Si dots, the agreement with the experimental results of Wolkin *et al.* [2] for oxygen-free samples, as is shown in Fig. 1, would be perfect by definition. This illustrates an alternative role our results could play; namely, the role of a well-defined reference "yardstick" for the actual size of the dots. Also, it is well known that surface oxidation of the samples in air could dramatically change their PL spectra. Wolkin *et al.* [2] have demonstrated that even a 3 min exposure of the samples in air produces a redshift as large as 1 eV, due to the formation of oxygen bonds on the surface. Thus, the great majority of experimental work deals with nanoclusters covered with few layers of silicon oxides and the dimensions of the inner crystalline core are not strictly defined. The last two observations can easily explain the discrepancy between our optical gap and some experimental measurements such us those of Schuppler *et al.* [4], Wilcoxon *et al.* [1], and Brus *et al.* [10].

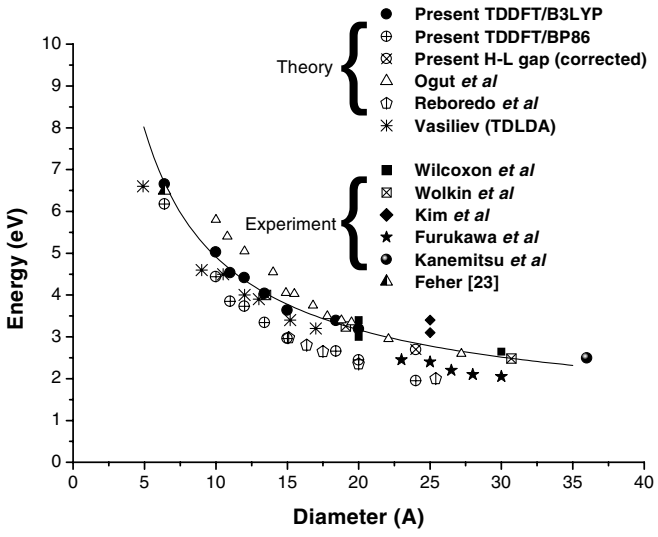

FIG. 1. Comparison of the calculated optical gap in this work with different experimental results and theoretical calculations. The solid line is a least-squares fit to the TDDFT/B3LYP results of Table II.

Looking at Fig. 10 of Wilcoxon *et al.,* which summarizes most of the existing experimental results for PL peak energies as a function of the diameter d of the nanoclusters, we can clearly see that all these measurements fall into the shaded region of the diagram. As explained by Wilcoxon *et al.,* all PL peaks of SiO_2 capped nanoclusters or nanoclusters embedded in glass matrices fall into this region. The central issue for this region [1], which contains a wide band of energies for each value of d, is the role of SiO_2 or glass and suboxide layer that almost certainly exists at the interface. As Wilcoxon *et al.* [1] point out, there are undoubtedly defects and surface states at this interface, which could play a significant role in the luminescence from these samples. The experimental data of Wilcoxon *et al.* [1] for the oxygen-free samples, for the same value of the diameter, fall above this shaded region. Obviously, this is the region on which we shall focus here to make contact with our calculations. This region corresponds to direct electron-hole recombination, as Wilcoxon *et al.* have suggested. For dots with diameters around 18–20 Å, which correspond to our Si dots with 99 and 147 Si atoms respectively, the experimental measurements of Wilcoxon *et al.* [1] on sized selected and purified samples give the energy of the major PL peak at 3.40 eV (365 nm). This is in excellent agreement with our results (3.2 eV, 3.4 eV). Wilcoxon *et al.* have attributed this peak to the direct $\Gamma_{25}-\Gamma_{15}$ transition, which in real space corresponds to the t_1-t_2 transition. This is also in agreement with our results, which verify the observation of this direct transition for the first time. The measured exciton binding energy, E_B, for the same sample is 0.4 eV, whereas the calculated value from the difference of the optical from the (HOMO-LUMO or H-L) gap is about 0.5 eV. As we can clearly see from Table II, this value of E_B varies from about 1 eV for Si_5H_{12} with $d = 7$ Å, to about half this value for nanoclusters in the range of 18–25 Å. The value of 0.45 eV for E_B remains practically constant over this large range of d. This can be used to calculate the optical gap of larger nanoclusters by performing simple ground state DFT/B3LYP calculations only. Actually, for the $Si_{281}H_{172}$ cluster we have used this correction of the H-L gap in order to estimate the optical gap. As we can see in Fig. 1, which shows the calculated optical gap as a function of d, the smallest possible dot diameter for visible PL (PL energy 3.0 eV) is about 22 Å.

In Fig. 1 we have included several diverse experimental results as well as two representative recent calculations (Öğüt *et al.* [8] and Reboredo *et al.* [3]). As we can see, the agreement with experimental data ranges from excellent, for oxygen-free or purified samples (such as those of Wilcoxon *et al.* [1], Wolkin *et al.,* [2] and Fehér [23]) to fair, for samples with no special precautions about purity or surface defects as, apparently, those of Furukawa *et al.* We can also see that the size adjustment of the

Wolkin *et al.* data, against our results, brings them into agreement with those of [1,8,13,15]. In the same Fig. 1, we have also included TDDFT results which we have performed using the BP86 [17] exchange and correlation functional, which, however, unlike B3LYP, does not include exact or partially exact exchange. As we can see, the BP86 results practically coincide with the results of Reboredo *et al.* [3], although on the average they are about 0.6–0.7 eV lower compared to the more accurate TDDFT/B3LYP results, which have been tested against our sophisticated *ab initio* MR-MP2 calculations. The similarity of our TDDFT/BP86 results with those of Reboredo *et al.* [3], which are based on tight-binding supercell calculations using empirical pseudopotentials, is rather surprising. This similarity is highly suggestive that, beside all technical differences between the two calculations, the real reason for the difference of their supercell results from our present real-space TDDFT/B3LYP results could be some kind of improper treatment, perhaps in the screening, of the exact exchange interaction in their calculations. On the other hand, the theoretical results of Öğüt *et al.* [8] for the excitonic energy gap overestimate the optical gap (with the meaning of the optical gap given here; namely, the energy of the lowest allowed excitation) especially for very small dots. This, according to Reboredo *et al.,* is due to underestimation of the screening function and overestimation of the quasiparticle energy gap in these calculations [8]. However, for dots larger than 17 Å in diameter, these discrepancies in their calculations seem to cancel out and have no real influence in the calculated optical gap, which is very close to our TDDFT/B3LYP results. After submission of the manuscript, we also became aware of the work of Vasiliev *et al.* [24] which employs pure time-dependent LDA theory, without partially exact exchange (hybrid B3LYP) and gradient corrections in the energy functional. We have now incorporated these results in our comparisons of Fig. 1 without further comments.

In conclusion, we have shown that (1) quantum confinement is responsible for the visible PL from oxygen-free samples of silicon nanoclusters (Si quantum dots). (2) The diameter of the smallest dots, which could emit PL in the visible (in the limits between violet and ultraviolet $\sim$3.0 eV), is around 22 Å. (3) The existing discrepancies in the experimental results are either due to oxygen contamination and/or size uncertainties. The discrepancies in the theoretical calculations are mainly due to the poor treatment of the exchange interaction.

Our calculations with an estimated error margin of 0.3 eV are in excellent agreement with existing experimental measurements on oxygen-free samples with well-defined size. Thus, our results provide a unique reference point for existing and future work on Si quantum dots.

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