Large-Scale First-Principles Electronic Structure Calculations for Nano-Meter Size Si Quantum Dots

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We have studied the system size dependence of the density of states, band gap, and the charging energy of the large size Si quantum dots of 2.2 to 7.6 nm diameters by first-principles electronic structure calculations. The largest model examined in this study consists of over 10,000 Si atoms, and we performed such large calculations by using recently developed real-space density-functional theory code suitable for massively parallel computers. The density of states of 6 nm-diameter Si quantum dot is almost the same as that of the bulk Si. The band gaps of the Si quantum dots have been calculated by the ∆SCF method with local-density approximation, and we have found that the difference between the ∆SCF band gap and the Kohn-Sham eigenvalue gap is equal to the inverse of the dot radius. Consequently the ∆SCF band gap converges to the Kohn-Sham eigenvalue gap in the infinitely large size limit with the local-density approximation. [DOI: 10.1380/ejssnt.2010.48]

Keywords: Density functional calculations; Silicon; Quantum dots

I. INTRODUCTION

Silicon quantum dots (QDs) have been attracted much attention because of the potential for several device applications, such as multi-valued memories [1], single-electron transistors [2], and optical emitting devices [3].

In order to understand the properties of QDs, it is important to clarify the relation between the electronic structure and the size of the QDs. First-principles calculations based on the density functional theory [4, 5] are often useful for such studies. However, the interesting sizes of the Si QDs are in a few-nano-meter diameter, in which thousands of atoms are contained, and therefore the first-principles calculations for such large systems are hard to be performed with traditional program codes.

In this study, we have performed first-principles electronic structure calculations for Si QDs in the sizes of 1 to 7 nm diameters by using a recently developed real-space finite-difference pseudopotential code suitable for massively parallel computers [6]. We have investigated the system size dependence of the density of states (DOS), the band gaps, and the charging energies of the Si QDs. We have calculated the band gaps by the ∆SCF method, which is based on the exact definition of the band gap, and compared them to the approximate Kohn-Sham (KS) eigenvalue gaps. Even in the local density approximation (LDA), the ∆SCF method is known to provide good quantitative ionization potentials for atoms and small molecules, while the highest-occupied KS eigenvalue is known to be poor approximation for the ionization potential. It is also known the difference between the highest-occupied and the lowest-unoccupied KS eigenvalues underestimate the band gaps of bulk materials. We have investigated the relation between the ∆SCF gaps and the KS eigenvalue gaps for Si QDs and found that there is a simple relation. Since we have performed the calculations for a wide range of QD sizes, we can easily deduce the infinitely large size limit of the band gap. We have also studied such infinitely large size limit of the QD band gaps comparing with the bulk Si band gap.

II. COMPUTATIONAL DETAILS

The computational model of a Si QD is constructed from a spherical crystalline Si cluster terminated with H atoms at the surface. We have not performed relaxation on the atomic structures. Instead, we have constructed the models by using the atomic positions of the bulk Si, and with Si-H bond length of 1.43 Å which is obtained by structure optimization for a small (1 nm diameter) cluster. The largest size of the Si QD examined here is of 7.6 nm diameter; it consists from 10,701 Si atoms and additional 1996 terminating H atoms.

In order to perform first-principles calculations for such large size systems, we have recently developed a program code suitable for massively parallel computers [6]. For ease of the parallelization, the code is based on the real-space finite-difference pseudopotential method [7], because it is free from the fast Fourier transform, which is unsuitable for parallel computations and inevitable for Hamiltonian operations in traditional plane-wave basis methods.

For the ionic potentials of Si and H, we used the Troullier-Martins type norm-conserving pseudopotential [8] with the Kleinman-Bylander’s separable approximation [9]. For the exchange-correlation functional, we used the local-density approximation [10].

The grid-spacing for finite-difference calculation was...
chosen as 0.45 Å, which corresponds to the cutoff energy of 14 Ry. We have confirmed that our results of the band gaps are changed less than 0.01 eV by reducing the grid-spacing to 0.38 Å. The total number of grid points for the largest model is 3,402,059. The parallelization is performed by dividing the 3-dimensional discrete space into the several sub-spaces in each of which the number of grid points is as nearly equal as possible.

All calculations were done with the PACS-CS, a massively-parallel cluster at University of Tsukuba [11]. For the largest size calculation, we employed 1024 nodes of the PACS-CS, which is of 5.6 TFLOPS theoretical peak performance, and took about 5 days for a case of the calculation.

III. RESULTS AND DISCUSSIONS

In Fig. 1(a), we show the DOS of the Si QDs of 5.7 nm and 6.0 nm diameters, in which 5011 and 6047 Si atoms are contained, respectively. For comparison, we also show the DOS of bulk Si in Fig. 1 (b). We have found there are no significant difference between the DOS of the Si QDs in those sizes, and they are almost the same as the DOS of bulk Si in Fig. 1 (b). We have found there are contained, respectively. For comparison, we also show the DOS of the Si QDs of 5.7 nm (Si5011H1267) and 6.0 nm (Si6047H1308) diameters (a) and bulk Si (b).

As seen in Fig. 2, the band gap decreases as the size of the Si QD increases. The band gaps from the KS eigenvalue difference seem to converge to the bulk band gap 0.53 eV rather than the experimental band gap 1.17 eV due to the well-known failure of the LDA. While the band gaps obtained from the ∆SCF calculations are larger than the KS eigenvalue gaps, and seem to be closer to the experimental bulk band gap. However, the ∆SCF gaps of QDs have not converged yet, even the size of 7.6 nm diameter, so we have to deduce true infinitely large size limit of the ∆SCF gaps of the Si QDs.

There are many theoretical investigations on the size dependence of the electronic structures of Si QDs [14–16]. Ferreyra and Proetto [14] calculated the size dependence of the band gap by using the effective-mass theory with finite confining potentials. The naive effective-mass theory with infinite confining potentials predicts that the size dependence of the band gap shows $1/D^2$ behavior. While the effective-mass calculation with finite barriers predicts softer power-law dependence $\sim 1/D^\gamma$ with $\gamma$ between 1 and 2. Zhou et al. [15] developed a novel first-principles computational method, called Chebyshev-filtered method, and applied it to the calculations of the ionization potential and the electron affinity of large-size Si nanocrystals. Zhou et al. also obtained softer power-law dependence $\sim 1/D^{1.4}$ and $\sim 1/D^{1.09}$ for the ionization potential and the electron affinity, respectively. König et al. [16] studied the effects of the surface termination of Si QDs by first-principles calculations, and they concluded that the quantum confinement is dominant rather than the surface effects for the Si QDs beyond 3.7 nm diameter.

There is a measurement with scanning tunneling spectroscopy for the band gap of Si QDs [13]. From the experiment, a curve of QD-size dependence of the band

\[ E_{\text{gap}}^{\Delta SCF} = E(N+1) + E(N-1) - 2E(N) = I(N) - A(N), \]
gap was obtained, and the fitting formula was given as
\[ 1.136 + 9.75/D^2 \text{ (eV)}, \]
where \( D \) was the diameter of a QD in nanometers [13]. The experimental curve is also shown in Fig. 2. At large diameter, the \( \Delta \text{SCFR} \) gaps become lower than the experimental curve and the bulk band gap.

In order to consider the origin of the deviation of the band gaps in the large systems, we show the KS eigenvalue shift by one-electron addition, namely \( \varepsilon_N(N+1) - \varepsilon_N(N) \), in Fig. 3. From Fig. 3, we have found that the KS eigenvalue shift in each size of the Si QDs is almost equal to the inverse of the radius \( R \) of the QDs, and the relation can be expressed as follows (in atomic unit):

\[ \varepsilon_N(N+1) - \varepsilon_N(N) \approx \frac{1}{R}. \]  

This is just the charging energy of the system with radius \( R \). Adding the charging energy Eq. (3) to the KS band gap Eq. (1), we have confirmed numerically that it is equal to the \( \Delta \text{SCFR} \) band gap:

\[ E_{\Delta \text{SCF}} = E_{\Delta \text{KS}} + \frac{1}{R}. \]  

The same relation can also be lead from the Janak’s theorem [17]. This result indicates that the band gaps are dominated by the KS eigenvalue gaps and the charging energies for Si QDs with small radius, while for the large radius QDs, the contribution of the charging energy becomes small and lack of the other contribution, namely the derivative discontinuity [18], becomes serious in the LDA calculations. Clearly, at the infinitely large size limit, the \( \Delta \text{SCF} \) gap converges to the KS band gap, which is known to underestimate the bulk band gap.

**IV. SUMMARY**

We have performed first-principles electronic structure calculations for large size Si QDs in nano-meter diameters by using recently developed real-space density-functional theory code suitable for massively parallel computers. We have studied the system size dependence of the DOS, band gap, and the charging energy of Si QDs. We have found that the DOS of the Si QD with 6 nm diameter (5,000-atom system) or larger is almost the same as that of the bulk. The band gaps of the Si QDs were obtained by the \( \Delta \text{SCF} \) method, and we have found that the difference between the \( \Delta \text{SCF} \) gap and the Kohn-Sham eigenvalue gap is almost equal to the energy of one-electron charging energy of the system. We have also found that the charging energy shows \( 1/R \) behavior with respect to the QD radius \( R \), and consequently the \( \Delta \text{SCF} \) band gap converges to the KS eigenvalue gap at the infinitely large size limit within the LDA calculations.

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