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Electron affinities and ionization energies in Si and Ge nanocrystals

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We present calculations for electron affinities, ionization potentials, and quasiparticle gaps for hydrogenated silicon and germanium nanocrystals (quantum dots) with radii up to 14 Å or about 800 atoms using real-space *ab initio* pseudopotentials constructed within the local-density approximation. We show that electron affinities and ionization energies exhibit a strong size dependence characteristic of quantum confinement, and remain significantly different from corresponding bulk values even for the largest nanocrystals studied. Both Si and Ge nanocrystals have very close values of ionization and affinity energies, while quasiparticle and single-particle gaps for silicon dots are slightly larger (~ 0.2 eV) than those computed for germanium nanocrystals. Our calculated affinities and ionization potentials scale with radius R of the nanocrystal as R^{-l}, where $l = 1.1 \pm 0.2$, in contrast to the scaling factor $l = 2$ predicted by simple effective-mass models.

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Owing to their potential applications in optoelectronics, the study of semiconductor nanocrystals (quantum dots) is a very active field of research. Optical properties of these confined systems are known to be quite different from their bulk counterparts. In particular, quantum confinement can change the optical characteristics of nanocrystals resulting in superior properties for device applications when compared to those of bulk materials.[1] As such, researchers have sought to develop accurate methods for computing excitation spectra and, specifically, the optical gaps of quantum dots. Often these methods first compute the energy necessary to create a noninteracting electron-hole pair, and then include the Coulomb energy of the pair (exciton energy). Examples of this procedure can be found in GW-Bethe-Salpeter[2] and in density-functional approaches.[3] In this paper, we focus on calculations of the energy to create a noninteracting electron-hole pair, also called the quasiparticle gap. This gap can also be defined as the difference between the *ionization energy* and the *electron affinity*.

At present, there exist several published calculations of ionization potentials and electron affinities for small hydrogenated semiconductor systems. For example, GW and quantum Monte Carlo (QMC) approaches have been used[2,4] to determine these quantities for hydrogenated silicon clusters $\mathrm{Si}_n\mathrm{H}_m$. While these methods can be very accurate, they are computationally intensive. Even with state of the art computational platforms, the total number of atoms is on the order of 100.[2,4] In contrast, the utilization of pseudopotentials constructed within the local-density approximation (LDA) of the density-functional theory is much less computationally demanding. When this procedure is implemented in real space, quantum dots with over 1 000 atoms have been explored.[3] Also, real-space methods allow charged states to be examined in a straightforward fashion. In contrast, supercell methods[5] must invoke an *ad hoc* compensating background for charged systems; otherwise, the Coulomb energy diverges.

While real-space methods have been used for $\mathrm{Si}_n\mathrm{H}_m$ nanocrystals,[3] the ionization and affinity energies were not presented for large dots. For small systems, these calculations agree quite well with results of a QMC approach, e.g., QMC (LDA) give 12.7–12.9 (12.1–12.5) and -0.2 (-0.3–0) eV for ionization and affinity in SiH_4.[4,5] For very large dots, one expects the quasiparticle gap to approach the bulk limit. In the case of silicon or germanium, this should be close to the optical gap as exciton effects are small, provided one uses an ‘‘exact’’ exchange-correlation functional within density-functional theory. Since LDA is not exact, the optical gap limit is not met. Rather one expects a quasiparticle gap to be equal to the LDA eigenvalue difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In both Si and Ge, the HOMO-LUMO gap calculated within LDA is known to be only about half of the optical gap.[6] However, how the bulk gap limit is reached within LDA is unknown and untested.

Here we perform explicit calculations of the electron affinity and ionization energy for ‘‘large’’ (with radius up to 14 Å or 800 atoms total) semiconductor nanocrystals using real-space *ab initio* pseudopotential calculations.[5,7] We consider Si and Ge nanocrystals, as they are two of the most widely studied types of the quantum dots. Our nanocrystals were modeled as spherical bulk-terminated Si or Ge clusters with surface dangling bonds saturated by hydrogen atoms. We employ Troullier-Martins pseudopotentials[8] for all elements. Details of the pseudopotential construction for both Si and Ge can be found elsewhere.[3,9] The real-space grid spacing was taken to be 0.9 a.u. (1 a.u. $= 0.529$ Å) as in previous work.[3] Convergence tests were made with grid spacing as small as 0.6 a.u. The domain containing the quantum dots was taken to be a sphere whose radius was chosen to be by about 10 a.u. larger than the radius of the quantum dot. The Kohn-Sham wave functions were required to vanish at the boundary of the domain. A generalized Davidson algorithm was used to diagonalize the resulting Hamiltonian matrix. The Hartree potential was obtained using a conjugate gradient method to solve the Poisson equation. We discretized the Poisson equation and matched the boundary potential with that of a multipole expansion of the charge density. Typically, six to ten diagonalizations were needed to obtain the self-consistent charge density from the solution of Schrödinger and Poisson equation.[5]

For an *n*-electron system, the electron affinity and ionization energies can be expressed in terms of the ground-state total energies E of the n, $(n+1)$, and $(n-1)$ electron systems as follows:[10]

$$I=E(n-1)-E(n), \tag{1}$$

$$A=E(n)-E(n+1). \tag{2}$$

It is straightforward within real space to compute the total energies as a function of the number of electrons. To calculate ionization energies and affinities, we need to know self-consistent solutions of three different charge configurations for each quantum dot. The computational demand for this approach can be reduced significantly by utilizing charge density of the neutral cluster to provide a good initial guess for self-consistent calculations for the charged systems.

The ionization energies I and electron affinities A for Si and Ge quantum dots as a function of the nanocrystal's radius R are shown in Figs. 1(a) and 1(b). At small values of R, the electron affinities are small in comparison with the ionization energies. Small affinity values are consistent with a weak localization of the lowest unoccupied state. As radius increases, the ionization energy gradually decreases whereas the affinity energy increases. We found ionization energies to be larger for Si than for Ge at small radii by about ~0.4 eV. For larger dots, the situation reverses; the ionization energy for Ge becomes larger. With respect to the electron affinities, they coincide at small sizes and become slightly larger in Ge nanocrystals with an increase of R.

We find that the ionization I and affinity A scale with the radius R of the nanocrystal as

$$I^{\mathrm{Si(Ge)}}(R)=I_{bulk}^{\mathrm{Si(Ge)}}+\frac{I_0^{\mathrm{Si(Ge)}}}{(R/a_B)^{l_I^{\mathrm{Si(Ge)}}}} \tag{3}$$

and

$$A^{\mathrm{Si(Ge)}}(R)=A_{bulk}^{\mathrm{Si(Ge)}}-\frac{A_0^{\mathrm{Si(Ge)}}}{(R/a_B)^{l_A^{\mathrm{Si(Ge)}}}}, \tag{4}$$

where a_B is Bohr radius (1 a.u.) and the scaling parameters I_0, A_0, l_I, and l_A are given in Table I. We used experimental values for the ionization energy to fix the bulk limit. The measured ionization energies I_{bulk} in bulk Si and Ge have similar values. Depending on the experimental conditions,[11] the bulk values for the ionization energy and work function range from 4.6 eV to 4.9 eV. We fixed values for $I_{bulk}^{\mathrm{Si(Ge)}}=4.8(4.8)$ eV. We assigned values of $A_{bulk}^{\mathrm{Si(Ge)}}=4.1(4.4)$ eV, as our pseudopotential calculations gave an indirect gap of 0.7 (0.4) eV for crystalline Si (Ge).

The scaling factors l_I and l_A in Eqs. (3) and (4) yield values <2, contrary to what one would have expected from the effective-mass approximation (EMA). Effective-mass theory predicts that both electron affinity and ionization energy should scale as $(MR)^{-2}$, where M is the effective electron or hole mass, respectively.[12,13] Large differences in electron and hole effective masses should result in a different scaling of the ionization energy and electron affinity. However, we found that the differences between the computed values of the ionization and affinity energies for Si and Ge to be small, typically 0.1–0.4 eV over the size range considered. The similar values of the ionization/affinity energies in Si and Ge quantum dots and their almost equal deviations from the respective bulk limits (indicated by straight dashed

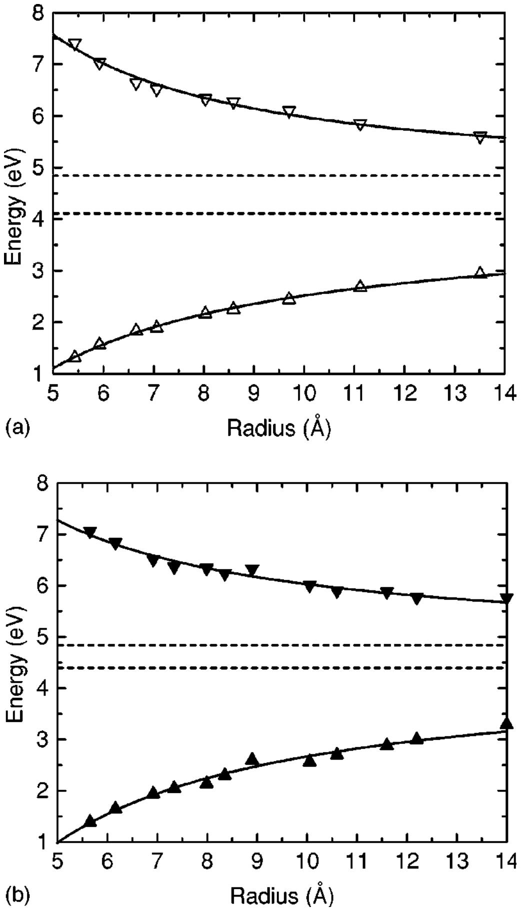

FIG. 1. (a) Ionization energy (▽) and electron affinity (△) of Si nanocrystals as functions of nanocrystal's radius R. Solid lines are the best fits to the calculated data. Straight dashed lines correspond to bulk values of ionization energy (4.8 eV) and affinity at 4.1 eV for Si. (b) Ionization energy (▼) and electron affinity (▲) of Ge nanocrystals. Solid lines are the best fits to the calculated data. Bulk values of Ge ionization energy and electron affinity are taken to be 4.8 and 4.4 eV, respectively.

TABLE I. Scaling parameters in fitting expressions for ionization energy I and electron affinity A [Eqs. (3) and (4)], quasiparticle E_{qp} and HOMO-LUMO gaps E_{HL}, and self-energy Σ for Si and Ge nanocrystals. Parameters A_0 and I_0 are in eV, all others are dimensionless.

	A_0	I_0	l_A	l_I	l_{qp}	l_{HL}	l_Σ
Si	23.5	44.4	0.9	1.2	1.1	1.3	0.9
Ge	30.8	24.2	1.0	1.0	1.0	1.1	0.9

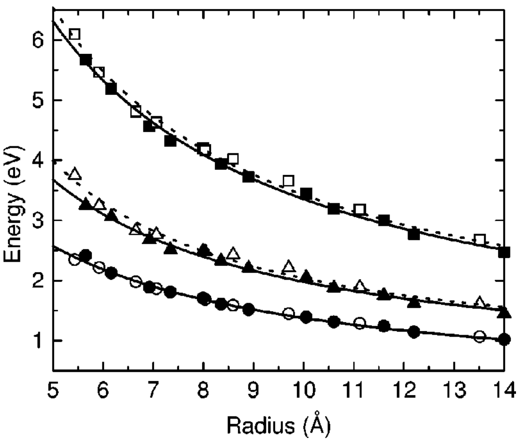

FIG. 2. Quasiparticle gaps (■), HOMO-LUMO gaps (▲), and self energy corrections (●) vs nanocrystal's radius *R*. Open symbols are for Si and closed are for Ge nanocrystals. Solid lines are the best fits to the data.

lines in Fig. 1) can be reconciled with EMA only by assuming equal values for both electron and hole effective masses in these systems. This would be inconsistent with the known differences between Si and Ge band masses in the bulk limit,[14] i.e., the band masses of Si are roughly twice as large as Ge. Of course, it is hard to justify the concept of the effective mass in the range of sizes (between 5 and 15 Å in radius) considered in the present work.

We note that ionization energy and affinity are about 1 eV removed from the bulk values even for the largest nanocrystal considered here. From the fitting functions (3) and (4), it is possible to deduce that both $I(R)$ and $A(R)$ will be within 10% from their bulk values at $R\approx 50$ Å corresponding to a quantum dot with $\approx 20\,000$ atoms. In the opposite limit of silane SiH_4 (or germane GeH_4) molecule, our calculations give ionization potential and electron affinity equal to 12.5 (12.3) and 0.0 eV, respectively. These numbers are only slightly different from those obtained earlier.[2] The differences are likely due to technical issues such as different pseudopotentials and/or a different basis set. The ionization potentials should be compared with experimental values of 12.6 (12.3) eV for silane (germane) determined from the photoelectron spectrum.[15,16] The results shown in Fig. 1 also indicate that at $R=5$ Å electron affinities are only about 1 eV larger than their values for germane / silane, while ionization energies are already 4 eV smaller than their corresponding limits for those molecules. This explains why the fitting function of the form given by Eqs. (3) and (4), which obviously diverges as $R\rightarrow 0$, works better for the ionization energy than for the affinity.

Within LDA, it is possible to relate the quasiparticle gap E_{qp} to the HOMO-LUMO gap E_{HL} by writing

$$E_{qp}=I-A=E_{HL}+\Sigma_{LDA}, \tag{5}$$

where Σ_{LDA} is the self-energy correction. The dependencies of E_{qp} together with the single-particle gap E_{HL} and Σ_{LDA} for Si and Ge nanocrystals are presented in Fig. 2. Owing to quantum confinement, all these quantities are enhanced substantially with respect to their bulk values $E_{qp}^{bulk}=E_{band}^{bulk}=0.7$ (0.4) eV, $\Sigma_{LDA}^{bulk}=0$ (within LDA, the bulk quasiparticle gap E_{qp}^{bulk} should be equal[6] to to the bulk value of the HOMO-LUMO gap, E_{HL}^{bulk}). The quasiparticle and HOMO-LUMO gaps have similar values in Si and Ge nanocrystals. In general, we find that Si gaps are larger by about 0.25 eV compared to those in Ge. This is consistent with the calculated bulk band gap differences of about 0.3 eV. The quantities $E_{qp}-E_{qp}^{bulk}$, $E_{HL}-E_{HL}^{bulk}$, and Σ_{LDA} scale with radius of the nanocrystal R as $R^{-l_{qp}}$, $R^{-l_{HL}}$ and $R^{-l_{\Sigma}}$ with the corresponding factors l_{qp}, l_{HL}, and l_{Σ} listed in Table I. Note that these factors are also less than $l=2$ predicted by the EMA.

Previous work on the optical gaps of Si and Ge nanocrystals[13,17] suggests that Si might not retain a larger gap at small nanocrystals size. In particular, effective-mass theory[13] and tight-binding calculations[17] predict that at small sizes the optical gaps in Si quantum dots are smaller than in Ge systems. In the EMA this is attributed to the differences between electron and hole effective masses in Si and Ge: the effective masses in Ge are smaller than in Si.[14] In contrast, recent pseudopotential calculations based on the delta-self-consistent approach gave optical gaps in Si dots larger than in Ge ones for systems with radius as large as ~ 10 Å.[18] Also, empirical pseudopotential calculations indicated the absence of crossing for the single-particle gaps for Si and Ge quantum dots which was interpreted in terms of an *L* to *X* transition in the germanium conduction band as the size of the dot decreased.[19]

It is hard to make direct comparisons with this body of work since we do not calculate the optical gaps directly. The optical gap E_{opt} can be related to the quasiparticle gap by a simple relationship

$$E_{opt}=E_{qp}+E_{coul}, \tag{6}$$

where E_{coul} is the Coulomb interaction between the electron-hole pair.[12] We note that unless the Coulomb contribution to the optical gap markedly changes for Si versus Ge dots, we would not expect the optical gaps in Si to fall below that of Ge as function of nanocrystal size based on our calculations for E_{qp}.

We have implicitly assumed in Eq. (6) that the optical transition is allowed. Owing to the indirect nature of bulk optical gaps Si and Ge, the oscillator strengths of the lowest-energy transitions have very small values. In the bulk limit of a perfect crystal, the transition is rigorously forbidden by wave-vector conservation. This is reflected in the oscillator strength of our nanocrystals considered as a function of size. For example, for the largest Ge nanocrystal that we examined, the oscillator strength of the lowest transition (as determined from E_{HL}) is about 10^{-5} of the total oscillator strength. This value decreases exponentially as the size of the nanocrystal increases.

In summary, we have performed calculations for electron affinities, ionization potentials, and quasiparticle gaps for hydrogenated Si and Ge nanocrystals up to systems containing about 800 atoms using real-space *ab initio* pseudopotentials constructed within the local-density approximation. We found that electron affinities and ionization energies exhibit a strong size dependence characteristic of quantum confinement, and remain significantly different from corresponding bulk values even for the largest nanocrystallites studied. Our estimations show that even for nanocrystals containing over 20 000 atoms that the quasiparticle gaps exceed the optical gap of the bulk material by more than 10%. It was also demonstrated that both Si and Ge nanocrystals have similar values of ionization and affinity energies: for Si, the quasiparticle and single-particle gaps for Si dots are slightly larger (~ 0.2 eV) than those computed for Ge. Our calculated affinities and ionization potentials scale with radius R of the nanocrystal as R^{-l}, where $l = 1.1 \pm 0.2$ in contrast to the scaling factor $l = 2$ predicted by simple effective-mass models.

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