Quasiparticle gaps and exciton Coulomb energies in Si nanoshells: First-principles calculations

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Quasiparticle gaps and exciton Coulomb energies of H-passivated spherical Si nanoshells are computed using first-principles ΔSCF method and selectively comparing to *GW* computations. We find that the quasiparticle gap of a nanoshell depends on both its inner radius R_1 (weakly) and outer radius R_2 (strongly). These dependences on R_1 and R_2 are mostly consistent with electrostatics of a metallic shell. We also find that the unscreened Coulomb energy E_{Coul} in Si nanoshells has a somewhat unexpected size dependence at fixed outer radius R_2: E_{Coul} *decreases* as the nanoshell becomes *more confining*, contrary to what one would expect from quantum confinement effects. We show that this is a consequence of an increase in the average electron-hole distance, giving rise to reduced exciton Coulomb energies in spite of the reduction in the confining nanoshell volume.

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It is well-known that quantum confinement (QC) and surface effects alter electronic and optical properties of nanoscale materials compared to their bulk form.[1] Increase in the quasiparticle or optical gaps by several eV's, reduction in effective medium screening, and one to two orders of magnitude increase in exciton binding energies are some of the many examples that confinement and surface effects bring out in nanostructured forms of matter.[2] In addition to these, geometrical or topological manipulation of nanoscaled materials can also lead to interesting physical and chemical properties, as evidenced for the case of carbon in its bucky-ball, nanotube, and graphene forms. Computational studies performed with state-of-the-art methods can be very useful in this respect, as they allow both prediction and microscopic understanding of novel properties in real and hypothetical material systems.

In this Brief Report, we examine electronic excitations and exciton Coulomb energies in Si "nanoshells" in order to understand the effects of finite cavities in confined nanostructures. The nanoshells we consider are formed from bulk-truncated spherical Si nanocrystals, which we will call "parent quantum dots," by creating concentric spherical cavities in them, and passivating the dangling Si bonds on the inner and outer surfaces by hydrogen atoms. Since the discovery of visible photoluminescence from porous Si,[3] the electronic and optical properties of Si quantum dots have been examined in great detail.[4] It is therefore surprising that these properties have not been investigated for Si nanoshells. In the present study, our primary goal is to examine how electronic and optical properties of spherical Si nanostructures evolve in going from the quantum dot to the nanoshell. A secondary motivation for this study is the recent interest in the electronic and optical properties of Si/Ge core-shell nanoparticles[5] and of metallic nanoshells, typically composed of noble-metal and transition metal elements in core-shell (or mixed-alloy) configurations over dielectric cores.[6,7] While bulk Si is obviously not a metal, Si clusters and nanocrystals have been shown to behave like metallic particles in response to both static[8] and time-varying electric fields.[9] Our results show that (i) Si nanoshells also have very interesting "metalliclike" electronic and optical properties, and (ii) the competition between geometrical or topological effects with QC can lead to peculiar size and shape dependences at the nanoscale.

Our computations for quasiparticle gaps were performed in real space using the higher-order finite difference pseudopotential method[10] using a uniform grid spacing of $h=0.6$ a.u. We used zero boundary conditions requiring the wave functions to vanish outside large spherical domains, the radii of which were adjusted from 34 to 50 a.u., depending on the size of the nanoshell. For a nanoshell of composition $\mathrm{Si}_{N-n}\mathrm{H}_{m_1+m_2}$, where N is the number of Si atoms in the parent quantum dot, n is the number of Si atoms taken out to create the cavity, and m_1 and m_2 are the numbers of H atoms passivating the inner and outer surfaces, respectively, we calculated the inner and outer radii as $R_1=[3(4n-m_1)/4\pi\rho_0]^{1/3}$, $R_2=[3(4N+m_2)/4\pi\rho_0]^{1/3}$, respectively, where $\rho_0=0.199\ 87$ Å^{-3} is the valence electron density in bulk Si. These expressions take into account the increase (decrease) of R_2 (R_1) due to passivating H atoms at the outer (inner) surfaces.[11]

The quasiparticle gap, E_{qp}, was computed from the vertical ionization potential (IP) and electron affinity (EA) within the ΔSCF approximation, in which $E_{qp}=\mathrm{IP}-\mathrm{EA}$.[12,13] It is well-known that in the bulk limit, the E_{qp} computed using local-density approximation (LDA) values for IP and EA converges to the bulk LDA band gap, which is underestimated by ~0.6 eV. For hydrogenated Si quantum dots the ΔSCF quasiparticle gaps are underestimated with respect to quasiparticle gaps obtained from *GW* calculations by a similar amount (0.6 to 0.9 eV), which is due, almost entirely, to underestimated IPs, as the calculated EAs were found to be within 0.1 eV of each other.[14] In order to assess the trend of *GW* versus ΔSCF quasiparticle gaps in Si nanoshells, we performed a *GW* calculation. Due to the large computational demand, the *GW* calculation was performed for the smallest nanoshell $\mathrm{Si}_{156}\mathrm{H}_{184}$ at a grid spacing of $h=0.8$ a.u. The self-energy was computed with a vertex correction using the polarizability obtained within the time-dependent LDA (the so-called G_0W_f approximation), which has been shown to improve IP and EA values.[14] We obtained IP and EA by diagonalizing the *GW* Hamiltonian in the space of Kohn-

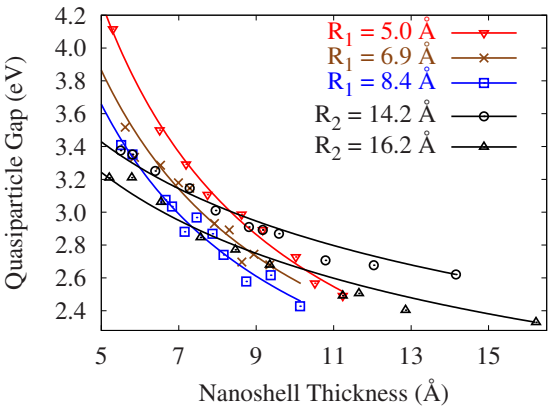

FIG. 1. (Color online) The computed ΔSCF quasiparticle gaps as a function of the nanoshell thickness at fixed inner radii of R_1 =5 Å (+), 6.9 Å (×), 8.4 Å (squares), and at fixed outer radii of R_2=14.2 Å (circles), and 16.2 Å (triangles). The solid lines are power-law fits (see the text), which are meant to serve as guides to the eye.

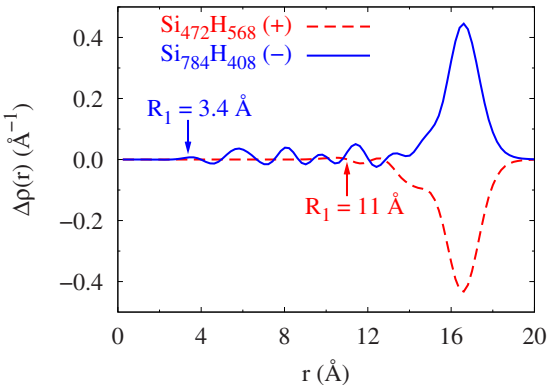

FIG. 2. (Color online) The computed differences between the radial charge density distributions of the anionic and neutral $Si_{784}H_{408}$ (blue solid line) and of the cationic and neutral $Si_{472}H_{568}$ (red dashed line) nanoshells, showing the localization of the added charge in the immediate vicinity of the outer radius R_2. Both nanoshells have the same R_2=16.2 Å. The arrows mark the positions of their inner radii.

Sham orbitals within the Tamm-Dancoff approximation (by ignoring all matrix elements between occupied and unoccupied orbitals). We used a total of 750 Kohn-Sham orbitals. Our computed *GW* and ΔSCF values for the IP of $Si_{156}H_{184}$ are 7.10 and 6.65 eV, respectively. The EAs, on the other hand, within *GW* and ΔSCF theories are practically the same, 2.56 and 2.62 eV, respectively. These suggest that the IP and EA values computed at the two levels of theory for Si nanoshells have a similar trend to those observed in Si quantum dots. While keeping this in mind, we note that the E_{qp} values reported in the rest of this Brief Report are the ΔSCF values without any scissors corrections.

The size dependence of the quasiparticle gaps in Si nanoshells is shown in Fig. 1, where we plot E_{qp} as a function of the nanoshell thickness $t=R_2-R_1$. We first focus on the t dependence of E_{qp} at fixed R_1. We considered three sets of nanoshells with Si_{35}, Si_{87}, and Si_{147} cores removed from the parent quantum dots, corresponding to inner radii of R_1 =5.0, 6.9, and 8.4 Å, respectively. The computed E_{qp} as a function of t show two trends: first, the gap is inversely proportional to the nanoshell thickness, which is expected due to QC effects. Fitting the computed gaps for each R_1 in this size range with a power-law t dependence as $E_{qp}(t)-E_{qp}^{\text{bulk}}=At^{-\alpha}$, we find $\alpha\sim 0.9-1.0$, with small variations due to different R_1 for the three sets of nanoshells. Second and more interestingly, we find that E_{qp} does not just depend on the thickness of the nanoshell. For a given thickness, E_{qp} depends also on R_1, and increases as R_1 decreases. For example, at $t\sim 5.5$ Å, E_{qp} increases by more than 0.7 eV in going from a nanoshell with a Si_{147} cavity to one with a Si_{35} cavity.

Next, we focus on the thickness dependence of the quasiparticle gaps at fixed R_2. We considered two sets of nanoshells with parent quantum dots of 525 and 801 Si atoms, corresponding to R_2=14.2 and 16.2 Å, respectively. At each fixed R_2, we increased R_1 from zero to a maximum value chosen such that there is at least one shell of Si atoms fully coordinated with only Si atoms in the nanoshell. The results, also displayed in Fig. 1, show the inverse correlation of E_{qp} with thickness, but with a much weaker dependence on t compared to the dependence at fixed R_1. Fitting the computed quasiparticle gaps for each fixed R_2 in this size range with a power-law t dependence as $E_{qp}(t)=E_{qp}^{\text{dot}}(R_2/t)^{\beta}$, where E_{qp}^{dot} is the quasiparticle gap for the parent quantum dot (R_1=0), we find $\beta\sim 0.25$. These sets of findings at fixed R_1 and R_2 suggest that the quasiparticle gaps of spherical quantum nanoshells can be adjusted by different amounts by appropriately varying either the inner and outer radius.

The first-principles results presented so far are different from predictions based on the simplest form of the effective mass approximation (EMA) corresponding to infinite barriers at the inner and outer boundaries. The $n_r=l=0$ solution of the single particle potential $V(r)=0$ for $R_1<r<R_2$ and ∞ elsewhere, is given by

$$\psi(\mathbf{r})=\frac{1}{\sqrt{2\pi r^2(R_2-R_1)}}\sin\left[\frac{\pi(R_2-r)}{R_2-R_1}\right]. \quad (1)$$

The resulting eigenvalue spectrum is inversely proportional to the square of the thickness, which would imply that the gap for a nanoshell in the infinite potential EMA should scale as $E_{\text{gap}}^{\text{EMA}}\propto t^{-2}$. Our first-principles computations show that E_{qp} depends on both R_1 and R_2 with a stronger dependence on R_2 compared to that on R_1. It is, however, important to note that more sophisticated EMA treatments taking into account charging energies, anisotropic effective masses, intervalley couplings, and finite barriers at the boundaries will most likely bring EMA predictions into better agreement with first-principles results.[15]

The size dependence of quasiparticle gaps can be explained qualitatively using classical electrostatics by examining the spatial distribution of the positive and negative charges added to a nanoshell. In Fig. 2, we display the radially averaged charge density differences $[\Delta\rho(r)]$ between the negatively (and positively) charged nanoshell and the neutral nanoshell with a Si_{801} parent quantum dot (R_2=16.2 Å). The results show that most of the extra charge is concentrated within a few Å of R_2. For a macroscopic *metallic* shell of

inner and outer radii R_1 and R_2, respectively, the work done to charge the shell and bring the charge to (and from) infinity is proportional to $1/R_2$ irrespective of R_1, since any extra charge on a metallic shell resides entirely at the outer radius. If the Si nanoshells behaved exactly like metallic macroscopic objects and all the extra charge were to accumulate at R_2, we would expect IP and EA to scale as $1/R_2$ and not depend on R_1. The strong and nearly t^{-1} dependence of the quasiparticle gap when R_2 is varied at fixed R_1 is, therefore, qualitatively consistent with predictions from classical electrostatics. In addition, the dependence on R_1 is found to be very weak, especially for nanoshells of thickness more than 1 nm, where quantum effects are expected to be less important, as shown by the last three data points at fixed R_2 in Fig. 1. The small but somewhat appreciable magnitude of $\Delta\rho(r)$ away from $r=R_2$ is, therefore, also consistent with the weak R_1 dependence of the quasiparticle gaps.

Another quantity of interest that plays an important role in determining optical gaps E_{opt} is the exciton Coulomb energy E_{Coul}. Neglecting the small contribution from the exchange interaction, the optical gap is given by $E_{\text{opt}}=E_{qp}-E_{\text{Coul}}$. First-principles computation of the screened E_{Coul} for confined systems is extremely demanding. It was shown, however, that screening in Si quantum dots is quite inefficient, with average dielectric constants being approximately one order of magnitude smaller than the bulk dielectric constant.[2] Therefore, here we focus on the computationally less demanding unscreened E_{Coul} to estimate exciton binding energies in Si nanoshells. Although even the computation of the unscreened E_{Coul} would require the solution of coupled equations for the interacting electron-hole pairs, using first-order perturbation theory, the unscreened E_{Coul} can be expressed rather accurately in terms of the hole ψ_h and electron ψ_e wave functions as[17]

$$E_{\text{Coul}} = \int \int \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{2}$$

Earlier studies[12,16,17] in Si quantum dots showed that QC increases the magnitude of E_{Coul} significantly. It was also shown, using first-principles[12] and semiempirical pseudopotential calculations,[17] that the EMA overestimates the magnitude of E_{Coul}. In order to understand the size dependence of E_{Coul} in Si nanoshells, we first analytically calculated the unscreened E_{Coul} within the EMA using the envelope wave functions $\psi(\mathbf{r})$ in Eq. (1) for both the electron and the hole. The resulting expression (in a.u.) is given by

$$E_{\text{Coul}}^{\text{EMA}}(R_1,R_2) = \frac{2}{\pi(R_2-R_1)} \int_0^{\pi} dx \frac{\sin^2 x(2x-\sin 2x)}{x + \dfrac{\pi R_1}{R_2-R_1}}. \tag{3}$$

In the limit $R_1 \to 0$, the definite integral can be expressed in terms of sine integral functions and gives the familiar result $E_{\text{Coul}}^{\text{EMA}}(R_1 \to 0) = 1.786/R_2$. The above expression for E_{Coul} shows that even at the EMA level, the exciton Coulomb energy in spherical nanoshells depends on both R_1 and R_2. In addition to EMA, we computed E_{Coul} using first-principles wave functions for the electron and the hole. As in the quasiparticle computations, we first computed E_{Coul} as a function of nanoshell thickness at fixed R_1, which are plotted in Fig. 3(a). We observe that EMA overestimates E_{Coul} compared to first-principles results, which is similar to the trend observed in Si quantum dots. The main reason for this behavior is that an oversimplified infinite potential in the EMA approach constrains the electron and hole wave functions to vanish abruptly at R_1 and R_2 rather than allow them to decay smoothly into the vacuum.[12,15,17] We also observe that both the EMA and *ab initio* results predict an inverse correlation of E_{Coul} with the nanoshell thickness, as expected from a QC model.

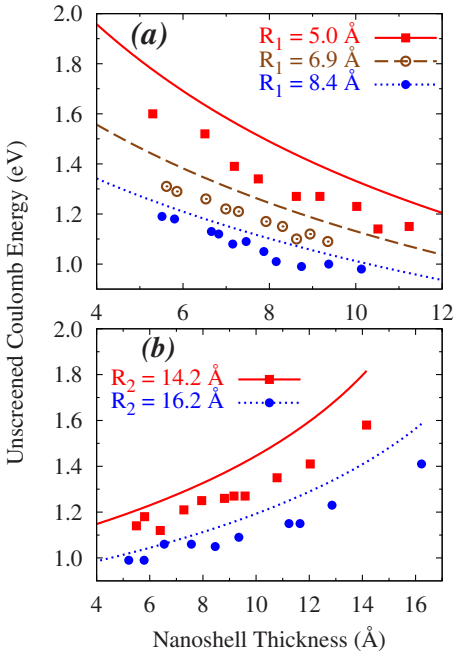

FIG. 3. (Color online) The unscreened exciton Coulomb energies computed from first-principles wave functions directly from Eq. (2) (discrete data points shown by solid or hollow circles and squares) and using the EMA expression in Eq. (3) (continuous, dotted, or dashed lines) as a function of the nanoshell thickness for (a) fixed R_1 and (b) fixed R_2.

The thickness dependence of E_{Coul} for nanoshells with a fixed R_2, on the other hand, is quite unexpected, and is shown in Fig. 3(b). While EMA still overestimates E_{Coul} with respect to *ab initio* results, at both levels of theory E_{Coul} is directly proportional to the nanoshell thickness. In other words, E_{Coul} *decreases* as the nanoshell becomes more *confining*, which is not in accord with expectations from a QC model. This finding, which is peculiar at first sight, can be explained using an argument based on a competition between quantum confinement and geometrical (or topological) effects, as follows: in going from a quantum dot (with no cavity) to a nanoshell of the same outer radius, two main changes occur that affect E_{Coul}. First, the electron and the hole wave function amplitudes increase, since ψ_e and ψ_h are confined to smaller volumes. Second, due to the cavity in the interior portion of the nanoshell, the "average distance" between the electron and the hole increases compared to that in the dot. While the effect of the confinement is to increase

E_{Coul}, the effect of the relative increase in the electron-hole separation is to lower it. Our computations show that for a spherical nanoshell, the "distance effect" is more dominant, resulting in a decrease in E_{Coul} in spite of the increased confinement. One way of seeing this more explicitly is to assume constant wave functions $\psi_e(\mathbf{r})=\psi_h(\mathbf{r})=V^{-1/2}$ (where V is the volume of the nanoshell). Though somewhat unrealistic due to discontinuities at the boundaries, the simple form of the wave functions allows direct calculation of the integral in Eq. (2), which results in $E_{\mathrm{Coul}}=3(2R_2^5-5R_1^3R_2^2+3R_1^5)/5(R_2^3-R_1^3)^2$. One can now show that E_{Coul} obtained with $R_1=0$ is always larger than $E_{\mathrm{Coul}}(R_1,R_2)$ for any nonzero value of R_1, given that $R_2>R_1$.

Our unexpected finding of smaller exciton Coulomb energies in spherical nanoshells raises an interesting question regarding the role that geometry or topology plays in various properties of nanostructures. In particular, a spherical nanoshell is neither convex, which is a *geometrical* property, nor simply connected, which is a *topological* property. An intriguing question is which of these actually plays a more important role in dominating over QC effects. For example, in an attempt to figure out the possible roles played by geometry and topology and their competition with QC, it would be interesting to consider the case of a solid nanostructure in the shape of a star, which is simply connected, yet nonconvex.

In summary, we calculated the quasiparticle gaps E_{qp} and exciton Coulomb energies E_{Coul} of spherical Si nanoshells passivated by H at the inner and outer surfaces using first-principles ΔSCF method and selectively comparing to *GW* computations. We found that the quasiparticle gaps depend on both R_1 (weakly) and R_2 (strongly), which might be important in tailoring the optical properties of nanostructures with cavities in them. These findings differ from predictions based on the simplest version of the EMA with infinite potentials at the boundaries, in which E_{qp} depends only on the thickness of the nanoshell. These dependences of E_{qp} on R_1 and R_2 can be qualitatively explained using classical electrostatics of a metallic shell. We also found somewhat unexpectedly that the exciton Coulomb energy in Si nanoshells of fixed outer radius decreases as the nanoshell becomes more confining via the creation of spherical cavities, contrary to what one would expect from QC effects. We argued that this is due to the increase in the average distance between the electron and the hole, which gives rise to reduced E_{Coul} in spite of the reduction in the confining nanoshell volume. This finding highlights the potentially useful roles geometry and/or topology could play (in competition with QC effects) in bringing out novel properties of nanostructures.

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