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Universal optical response of Si-Si bonds and its evolution from nanoparticles to bulk crystals

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We use quantum-mechanical calculations and classical theories of the optical absorption of free and embedded nanoparticles to demonstrate a universality of the optical response of Si-Si bonds, independent of bonding configurations. We also demonstrate that the classical theory remains valid down to atomic-scale nanoparticles and that the evolution of the optical spectrum of a free nanoparticle would evolve to the bulk spectrum when the particle contains hundreds of thousands of Si atoms.

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I. INTRODUCTION

The optical response of small particles as a function of their size, shape, and surrounding environment has a long history, dating back to Maxwell.[1] According to a well-known theory by Mie[2] based on Maxwell's equations, the optical absorption of a spherical particle in vacuum can be expressed in terms of the dielectric function of the constituent material and scales linearly with the volume (for radii that are smaller than the wavelength of light). Slightly more complicated formulas can be derived for ellipsoidal particles and other shapes.[3] For embedded particles, the dielectric function of the matrix also enters.[4] These macroscopic theories have been used widely with success.[5] The obvious question is when does the theory break down as the particle volume is decreased through the nanoscale? The question can be answered by either quantum calculations or measurements of the optical-absorption constant as a function of particle size. A related but different question is when does the optical response of a solid fragment approach that of the bulk material without dependence on size and shape?

Silicon nanoparticles (NPs) are an excellent vehicle to address the above questions. Silicon NPs have been studied by both experiments and theory. One well-known result is the optical gap, which has been found by theory to increase gradually from the bulk value of 1.2 eV to as much as 4 eV for nanoparticles.[6] The minimum gap in a crystal, however, is determined by the details of the energy bands. In the case of Si, because of the indirect nature of the gap, absorption at threshold is very weak and gradually rises to a main peak at 4–5 eV. For the purposes of this paper, we will focus on this main peak as the optical signature of crystalline Si. In experimental and theoretical works so far, several puzzles have emerged. Experimental absorption spectra of Si NPs containing 18–41 atoms have been found to be nearly identical in the accessible range of 1–6 eV.[7] The data show no scaling with NP volume. Additional partial data further indicate that the common spectrum starts at about 15 atoms and persists to at least 70 atoms. The authors argued that the common spectrum is similar to that of crystalline Si. Small particles, however, do not have *diamondlike* bonding[8] and the connection with the bulk spectrum has been disputed.[9] Somewhat later, explicit calculations of the spectra of small spherical Si nanoparticles with diamondlike bonding were reported.[10] The spectra have a main peak at about 4–5 eV and do not scale with NP volume, leading the authors to conclude that the spectrum converges to the bulklike spectrum even for particles as small as 41–137 atoms. More recent theory, however, based on higher-order approximations for calculating optical spectra found that the peak at 4–5 eV is shifted to higher energies.[11,12] More specifically, in Ref. 12, it was found that the Si particles containing 21–28 atoms in their lowest-energy non-diamond-like configuration have identical spectra, rising slowly to a main peak at ∼10 eV and scaling with NP volume. These spectra are clearly different from the bulk-Si spectrum. However, the authors found that using the measured dielectric function of bulk diamond-structure Si, the classical Mie theory reproduces the calculated spectra very well, including the scaling with volume. It is clear that so far no definitive picture has emerged about the evolution of the spectrum from nanoparticles to bulk Si and the range of applicability of Mie theory in the nanoscale.

In this study, we combine the theoretical results of Ref. 12 with present calculations and resolve the above quandaries. We focus on the dominant peaks of the spectra, from which we can draw broad-based conclusions. We will demonstrate that if the spectrum of NPs were measured in the range 1–15 eV, the main peak would indeed be at ∼10 eV and that this feature would persist for particles containing hundreds of thousands of atoms and would only gradually evolve toward the bulklike peak at 4–5 eV for particles containing millions of atoms and beyond. We call, therefore, for different experimental data of optical absorption of Si NPs in the range 5–15 eV to test the prediction. This predicted shift is singularly large and comparable to the shifts of the minimum optical gap.[6] We will also account for the misleading similarity of the theoretical spectra of Ref. 10 with the spectrum of bulk Si. In the process we will uncover a surprising *universality of the optical response of Si-Si bonds* that applies to Si NPs in vacuum, independent of their bonding configurations, to Si NPs embedded in an insulating matrix and to bulk forms of Si. This universality is of course manifest in the behavior of the dominant spectral peak, whereas other features (minor peaks and minimum optical gaps) are expected to vary with structure.

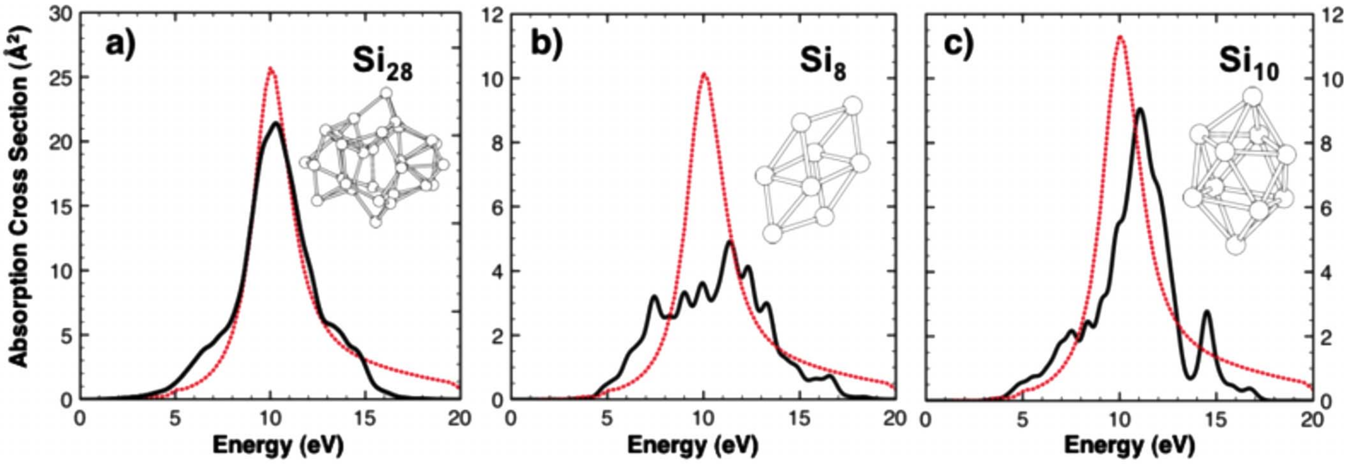

FIG. 1. (Color online) TDLDA absorption cross section per atom (black, solid lines) and Mie theory predictions (red, dashed lines) as a function of energy for (a) Si_{28} (from Ref. 12), (b) Si_8, and (c) Si_{10}. The structures of the Si nanoparticles shown in the insets (b) and (c) were obtained from Refs. 14 and 15.

II. SILICON NANOPARTICLES IN VACUUM

We start with a brief summary of the results presented in Ref. 12. In that paper, the spectra of spherical Si NPs containing 20–28 atoms in vacuum were calculated using a real-space frequency-domain implementation of the time-dependent local-density approximation (TDLDA).[13] The corresponding classical spectra based on Mie theory were also calculated according to the formula[2]

$$\sigma_{\mathrm{abs}}(\omega) = \frac{9\omega V}{c} \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega)+2]^2+\epsilon_2(\omega)^2}, \qquad (1)$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real and imaginary parts of the dielectric function of the constituent material, c is the speed of light, and V is the volume of the Si NPs. The resonance condition (Mie peak) occurs when $\epsilon_1(\omega)=-2$ and $\epsilon_2(\omega)$ is small. This Mie peak cannot be related to a specific class of excitation in a bulk material since both parts of the dielectric function ϵ_1 and ϵ_2 play a role in the resonance condition. The experimental dielectric function of crystalline Si in the diamond structure was used even though the nanoparticles have a non-diamond-like structure. The Mie condition is reached at $\omega \sim 10$. Despite the fact that the Si nanoparticles have a non-diamond-like structure, the agreement between the quantum and classical spectra is excellent. A typical case is shown in Fig. 1(a).

One can argue that the agreement between the quantum spectra and Mie theory is fortuitous because the "constituent material" of the nanoparticles is not really a diamond-structure crystalline Si. In order to probe into this issue we performed different calculations for "spherical" NPs with diamondlike bonding using the same method as in Ref. 12. We started with a central atom plus its four tetrahedral neighbors (total of five atoms) and then added another set of tetrahedral neighbors for a total of 17 Si atoms. Since these structures have manifest "dangling bonds" we calculated the TDLDA absorption spectra for both bare and hydrogenated NPs. The results are shown in Fig. 2. It is clear that by the time we have 17 atoms and tied-off dangling bonds, the agreement with Mie theory is very real. The agreement for the smaller NPs even for NPs with dangling bonds is not as good, but one can clearly say that, apart from the fine structure, the spectrum is centered about 10 eV.

We pushed the theory further to very small Si NPs, eight and ten atoms, with totally relaxed structures and found that the agreement with Mie theory still holds [Figs. 1(b) and 1(c)]. We tested even the ultimate single Si-Si bond (disilane, H_3-Si-Si-H_3); its absorption spectrum, which has been measured,[16] has a broad peak centered at ~ 10 eV [see Fig. 3(a)]. The inevitable conclusions are the following: (a) there exists a certain universality of the optical response of Si-Si bonds that persists even in nontetrahedral configurations, and (b) Mie theory, with the dielectric function of bulk diamond-like Si, applies to the ultimate nanoscale. The only exception appears to be ultrasmall noncompact particles of planar configuration.[17]

The ultimate origin of the universal behavior is the fact that occupied states are always bonding combinations of hybridized Si 3*s* and 3*p* orbitals (sp^3 orbitals in the case of Si atoms in tetrahedral environments). The finals states are the corresponding antibonding combinations. Thus, there are generic average initial and general average final states that give rise to the universal features in the optical spectra.

One might of course ask why diamondlike Si is the standard. If we were to make a large Si particle out of hypothetical fcc Si, Mie theory would in principle demand that we use the dielectric function of fcc bulk Si. We calculated the dielectric function of ffc bulk Si within a simple LDA application of Fermi's golden rule (independent-particle picture) where only interband transitions were taken into account. 120 points in k space and a lattice parameter of 3.02 Å were used for the calculation. If we examine the dielectric functions of diamondlike and fcc bulk Si [Fig. 3(b)] we find that on the scale of interest here, they have virtually the same optical behavior—a slow rise to a main Si fcc peak that is only about 1.3 eV lower than the main peak of Si diamond-like. Furthermore, calculations of the density of states of Si in several other structures[18] suggest strongly that the optical

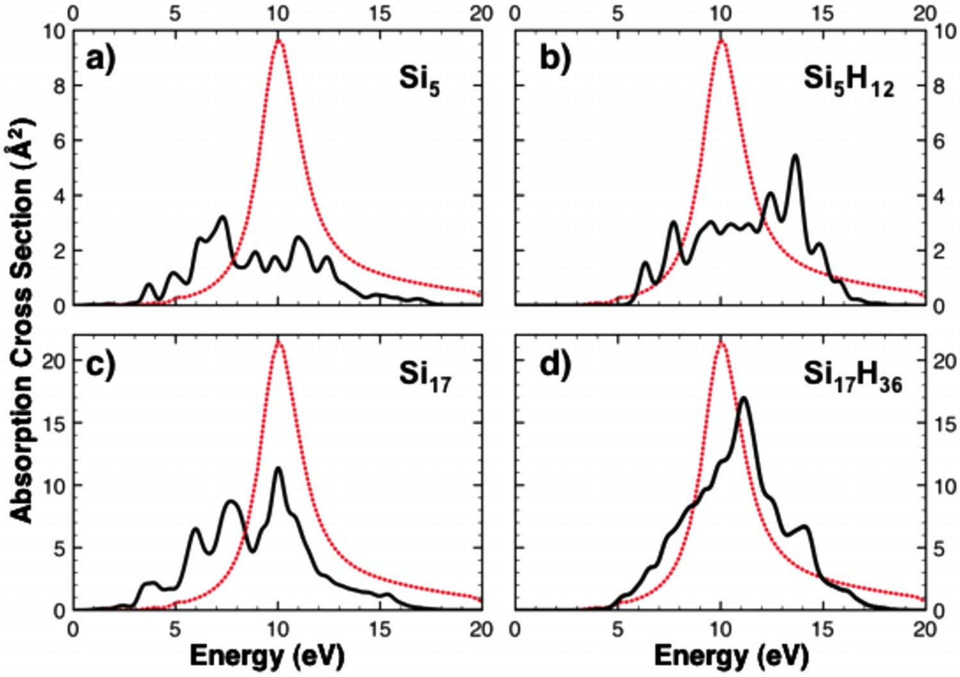

FIG. 2. (Color online) TDLDA absorption cross section (black, solid lines) and Mie theory predictions (red, dashed lines) as a function of energy for (a) Si_5, (b) Si_5H_{12}, (c) Si_{17}, and (d) $Si_{17}H_{36}$.

spectra remain essentially the same. Thus, the universality that we uncovered with the above analysis has truly deep roots. Later in the paper, we show that this universality persists for embedded nanoparticles in a striking way. For now, however, we continue with Si NPs in vacuum.

It would be very valuable to have experimental spectra in the range beyond 6 eV to test the above theoretical results. There are solid grounds, however, to believe their validity. First, TDLDA has been tested for other NPs for which experimental spectra are available and agreement between experiment and theory is excellent.[13] On the other hand, it is well-known that Mie theory is excellent for large nanoparticles with all kinds of constituent materials.[19] In the case of Si, Mie theory tells us that the spectrum of spherical Si NPs with diamondlike bonding and radii that are much smaller than the wavelength of light has a definitive peak at ~10 eV as shown in Figs. 1 and 2. Only the intensity should scale with the NP volume. Since TDLDA finds a peak at ~10 eV for Si NPs of various sizes and diverse bonding, we have a confirmation of our main result; Mie theory gives correct absorption spectra for Si NPs down to the atomic scale even for NPs whose bonding is not diamondlike. We have, therefore, an initial confirmation of the concept of universality of the optical response of Si-Si bonds.

The next obvious question is when does the absorption spectrum of a nanoparticle approach that of bulk Si? We note that Eq. (1) of Mie theory is naturally valid for relatively large particles as long as the radius is smaller than the wavelength. Equation (1) is actually the first term in an expansion and higher-order terms become important as the radius approaches the wavelength [the first term in the expansion, Eq. (1), is linear in R/λ, where R is the particle radius and λ is the wavelength of light]. For 10 eV light, the wavelength is 120 nm. A particle with radius equal to half this value contains several million atoms. Clearly, we expect the Mie signature spectrum with the 10 eV peak to persist to particles containing hundreds of thousands of atoms, with the intensity always scaling with the volume. Only for larger particles higher-order terms in the Mie expansion become important. They are expected to gradually shift the 10 eV peak to lower

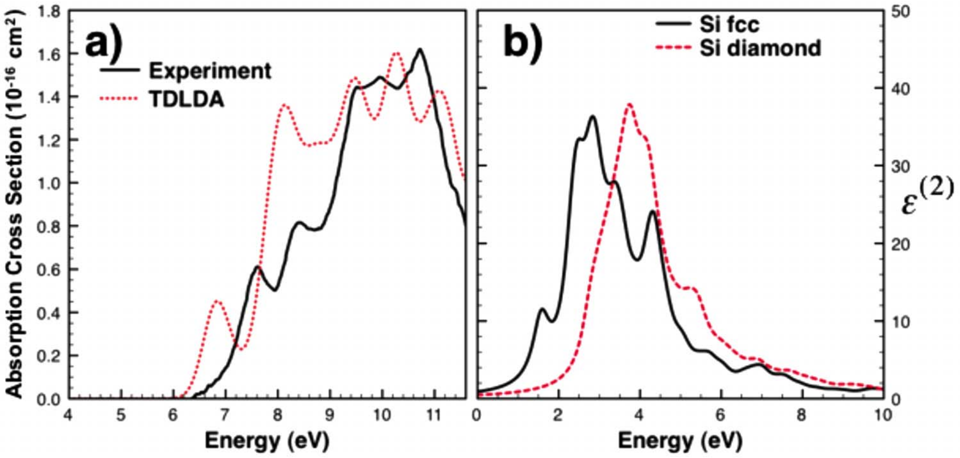

FIG. 3. (Color online) (a) Absorption cross section of Si_2H_6 (black, solid lines) and TDLDA calculations (red, dashed lines). Si_2H_6 experimental data were taken from Ref. 16. (b) Imaginary part of the dielectric function of fcc and diamondlike bulk Si calculated by first-principles methods within the local-density approximation (LDA) shown as solid and dashed lines, respectively.

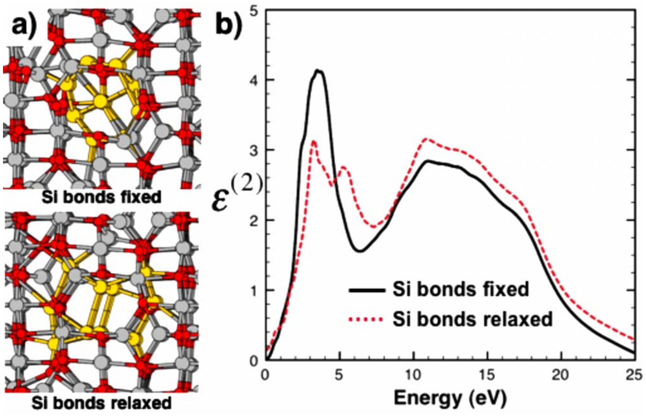

FIG. 4. (Color online) (a) Imaginary part of the dielectric function, $\epsilon_{(2)}(\omega)$, calculated by first-principles methods of the Si_8 and Si_{10} nanoparticles embedded in a $1\times2\times2$ supercell γ-Al_2O_3 matrix (160 atoms) with 2 f.u. of Al_2O_3 removed. Numbers within parentheses show the volume fraction between the Si nanoparticles and the matrix. (b) Imaginary part of the effective dielectric function, $\epsilon^{(2)}_{\text{eff}}$, calculated with different volume fractions, f, using the Maxwell-Garnett theory given by Eq. (2).

energies. The higher-order terms contain effects of scattering that are added to the basic absorption effects of the first term. For even larger particles ($R/\lambda \gg 1$), diffraction effects are also present, the Mie theory breaks down, and different models need to be used, i.e., Fresnel equations. The net conclusion is that it takes hundred of thousands of atoms, perhaps millions of atoms, to obtain bulk-Si optical response.

The above conclusion is of course at sharp variance with the conclusion of Ref. 10. The calculated optical spectra of small Si NPs reported in that paper have a main peak at 4–5 eV, i.e., they are already similar to the spectra of bulk Si. The resolution of this quandary is that the calculations of Ref. 10 are based on a simple (LDA) application of Fermi's golden rule for transitions between the calculated energy levels. TDLDA, on the other hand, is a far more sophisticated formulation of the optical excitation problem that incorporates the dictums of time-dependent density-functional theory with a suitable exchange-correlation kernel.[21] The origin of the differences in the LDA and TDLDA spectra is the Coulomb and the exchange-correlation kernels. Prior calculations on small NPs independently demonstrated that TDLDA spectra are shifted to higher energies relative to simple LDA spectra. In the case of Na NPs for which experimental spectra are available, the calculated TDLDA spectra are in good agreement,[13] confirming the suitability of the theory to calculate optical excitations. Thus, it is the inaccurate approximation used in Ref. 10 that produced the misleading result that small NPs already have optical spectra that converge rapidly to the bulk-Si spectrum. The present conclusion that it would take hundreds of thousands of atoms to converge to the bulk-Si spectrum holds true.

III. SILICON NANOPARTICLES IN A DIELECTRIC MEDIUM

We now turn to examine the optical response of embedded Si NPs. We chose the γ alumina as the matrix because of its large energy gap and an interest in exploring the possibility of imparting color to alumina by embedded NPs (the natural oxide that forms on aluminum is a form of the γ alumina). We are hampered in this pursuit by the fact that it is not practical to use the TDLDA formalism applied for particles in vacuum. In fact TDLDA per se gives the same spectrum for a perfect bulk crystal as the simple (LDA) application of Fermi's golden rule for transitions between eigenstates. In the case of a crystal, one must use the so-called GW scheme for self-energies and the Bethe-Salpeter equation (BSE) to include electron-hole interactions.[22] These schemes are also impractical for the large supercells needed to calculate spectra of embedded NPs. In fact, even for LDA calculations, which we performed for the embedded Si NPs, it is practical to do calculations only for very small embedded NPs, namely, eight and ten atoms. The results nevertheless give a powerful confirmation of the concept of the universal optical response of Si-Si bonds.

We modeled the γ-Al_2O_3 crystalline structure using the lowest-energy defect-spinel structure obtained by Cai *et al.*[23] In the defect-spinel structure, one out of nine Al sites are vacant.[24] The NPs were located at the center of an O_h vacancy in a $1\times2\times2$ γ-Al_2O_3 triclinic supercell of dimensions $12.5\times11.3\times11.3$ Å^3 approximately and 32 Al_2O_3 f.u. We removed 2–3 f.u. of Al_2O_3 nearest to the O_h vacancy in order to give enough space to locate the Si

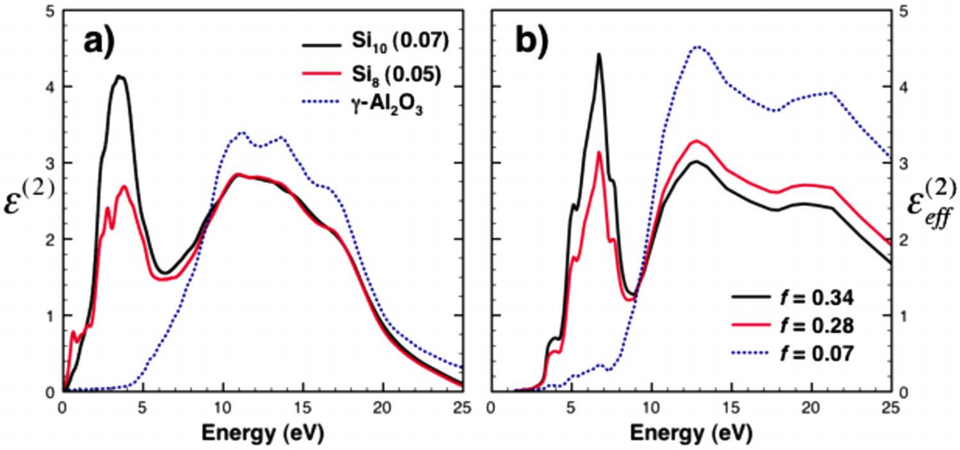

FIG. 5. (Color online) (a) Structural geometry of the Si_{10} NP and the surrounding γ-Al_2O_3 matrix system while keeping the Si bonds fixed as if the Si NP was in vacuum and after allowing them to relax. Red, gray, and yellow circles correspond to O, Al, and Si atoms, respectively. (b) Imaginary part of the dielectric function, $\epsilon^{(2)}(\omega)$, calculated by first-principles methods of the Si_{10} NPs embedded in the γ-Al_2O_3 matrix shown in Fig. 3(a).

NPs. We used the eight-atom and ten-atom NPs of Figs. 1(b) and 1(c) in two sets of calculations. First, we kept the embedded Si NP frozen and relaxed only the alumina matrix around it. The calculations were performed using the VASP code.[20] We calculated the imaginary part of the dielectric function, $\epsilon_2(\omega)$,[25] of the Si NPs/γ-Al_2O_3 system with 850 bands and a Monkhorst-Pack scheme with 12 **k** points. Calculations with larger number of **k** points and bands were also performed for all cases but we did not find any appreciable difference in their spectra for energies below 30 eV. In a second set of calculations, we allowed all the Si and the matrix to relax to the lowest-energy configuration and recalculated $\epsilon_2(\omega)$. The results for the ten-atom NPs are shown in Fig. 3. The astounding result is that despite the extensive rebonding that occurs, the spectrum of the embedded NP, the peak at 4–5 eV, remains essentially the same, confirming the universality of the optical response of Si-Si bonds. A similar result is found for eight-atom embedded NPs.

The analog of Mie theory for embedded particles is due to Maxwell-Garnett[4] and is known as the effective-medium theory. The absorption spectrum of the composite can be expressed in terms of the volume fraction occupied by the NPs and the dielectric functions of the matrix and the NP constituent material. More specifically the dielectric function of the composite is given by

$$\epsilon_{\mathrm{eff}} = \epsilon_m \frac{(1+2f)\epsilon_{\mathrm{NP}} + 2(1-f)\epsilon_m}{(1-f)\epsilon_{\mathrm{NP}} + (2+f)\epsilon_m}, \qquad (2)$$

where f is the volume fraction of the particle in the matrix and ϵ_{NP} and ϵ_m are the bulk dielectric functions of the materials forming the NP and the matrix, respectively.

Using the measured dielectric functions of alumina[26] and silicon[27] and the nominal volume fractions of the NPs in our supercells, we obtain the spectra shown in Fig. 4(b). The Maxwell-Garnett spectra clearly do not match the spectra calculated using LDA. The key difference is that the LDA spectrum has a peak at 4–5 eV, which is redshifted and has an enhanced oscillator strength with respect to the classical spectra. The shift can be understood as a typical result of using the Fermi golden rule within a LDA framework. As we saw earlier, TDLDA shifts the Si peak to $\sim$10 eV for Si NPs in vacuum, in agreement with the Mie theory. Even though it is not practical to perform a TDLDA calculation for the embedded NPs, it is clearly safe to infer that such a calculation would again shift the absorption peak of Si-Si bonds to higher energies, precisely as found by the Maxwell-Garnett theory. The only intriguing question is whether a hypothetical TDLDA, or even a GW/BSE, calculation would also lead to a diminished oscillator strength for the Si-Si peak as in the Maxwell-Garnett spectrum or whether its intensity will persist as in Fig. 5(a). If the latter is true, the experimentally measured spectrum would look like the solid (red and black for Si_8 and Si_{10}, respectively) curves in Fig. 5(b), where we rescaled the volume of the NP to produce a Maxwell-Garnett spectrum that matches the intensity of the Si-Si peak to that of the quantum calculation. Clearly, it would be very worthwhile to check this possibility by experiments because it would signify a “quantum enhancement” of the absorption of embedded NPs relative to the predictions of the Maxwell-Garnett theory.

IV. SUMMARY AND CONCLUSIONS

In summary, we have demonstrated that Si-Si bonds have a universal optical-absorption response, independent of bonding configurations. For Si particles, the classical Mie theory applies all the way down to the atomic-scale particles, yielding an optical-absorption coefficient with a main peak at $\sim$10 eV. This signature persists to particles containing hundreds of thousands of Si atoms when it gradually converges to the optical signature of bulk Si, with a main peak at $\sim$4–5 eV. Other experimental data to test the prediction of a dominant 10 eV peak in the absorption spectra of Si NPs are needed. For embedded NPs, again we have a universal response, independent of bonding configurations. The position of the main peak arising from Si-Si bonds is affected by the matrix. Accurate calculations are not practical, but there exists a possibility that very small NPs exhibit a “quantum-enhanced” absorption relative to that predicted by the classical theory for embedded NPs. This possibility can be tested by experiments and future calculations when they become practical.

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