

Calculation of optical absorption spectra of hydrogenated Si clusters: Bethe-Salpeter equation versus time-dependent local-density approximation

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We present calculations of the optical absorption spectra of clusters SiH_4 , $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$, as determined from two different methods: the Bethe-Salpeter equation (BSE) with a model dielectric function, and the time-dependent density-functional theory within the adiabatic local-density approximation (TDLDA). Single-particle states are obtained from local-density approximation (LDA) calculations and, for the BSE calculation, a quasiparticle gap correction is provided by quantum Monte Carlo calculations. We find that the exchange-correlation kernel of the TDLDA has almost no effect on the calculated spectra, while the corresponding attractive part of the electron-hole interaction of the BSE produces enhanced absorptive features at low energies. For the smallest cluster SiH_4 , the two methods produce markedly different results, with the TDLDA spectra appearing closer to the experimental result. The gross features of the TDLDA and BSE spectra for larger clusters are however similar, due to the strong repulsive Coulomb kernel present in both treatments.

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I. INTRODUCTION

During the past few years, there has been much interest in the optical properties of hydrogen-terminated Si nanoclusters, in part because of their connection to porous Si and in part because they are viewed increasingly as prototypical quantum confined semiconductor systems. Experimental measurements of the optical gap as a function of cluster size have yielded widely differing results,¹ and absorption spectra on monodispersed samples over a broad frequency range are practically nonexistent on all but the smallest of these clusters.² Theoretical treatments of optical properties have included many-body perturbation theory, based on tight-binding³ and density-functional⁴ single-particle descriptions, and time-dependent density-functional-theory (TDDFT) calculations within the adiabatic local-density approximation (TDLDA) (Refs. 5 and 6) and beyond.⁷ The major goal of these theoretical works has been to predict the dependence of optical properties (e.g., the optical gap) on cluster size. Viewed from a semiconductor physics perspective, there are two distinct components of the optical gap: the quasiparticle (or band) gap, which is the difference between the ionization energy and the electron affinity, and the exciton binding energy, which arises from the electron-hole attraction. Both are radically different from their bulk values in small nanoclusters due to quantum confinement. As cluster size decreases, the increase in the quasiparticle gap blue shifts the absorption edge, while the increase in exciton binding energy partially redresses this and red shifts the edge. In addition, inclusion of the electron-hole attraction greatly enhances oscillator strength near the absorption edge.^{4,8} The extent to which these various effects control the behavior of optical properties in these systems is not well understood at

present. This is a result of the lack of direct comparisons of spectra between different calculational methods performed on identical systems, as well as a general lack of experimental data.

In this work, we compute the optical absorption spectra of several hydrogenated Si clusters up to 1 nm in diameter using two related approaches: the Bethe-Salpeter equation (BSE), with a quasiparticle self-energy inferred from quantum Monte Carlo calculations,⁹ and the TDLDA. We find that the results of both approaches are similar in certain respects for clusters in the 1-nm-size range, though there are also important differences in the magnitudes of the optical gaps and in the intensities of spectral features near the absorption edge. For SiH_4 however, there are drastic differences in the intensity profile over a wide range in energy. Comparisons to gas-phase transmission measurements² favor the TDLDA SiH_4 result over that of our approximate BSE treatment, although the TDLDA optical gap is less accurate than the one provided by the Monte Carlo calculation.⁴ We discuss the manner in which these similarities and differences may arise from the particulars of the underlying equations and comment on the validity of these and other closely related approaches.

II. THEORY AND COMPUTATION

In order to include the effects of the electron-hole interaction on the absorption spectrum, it is necessary to appeal to a theory which mixes single-particle configurations. Two such theories are the TDDFT and the many-body perturbation theory involving the BSE. Both describe *particle-hole pair* states, $\sum_{eh}\psi(e,h)|e,h\rangle$, where $|e,h\rangle$ denotes a (properly antisymmetrized) product state containing an electron in

TABLE I. LDA HOMO-LUMO gaps $E_{\text{HOMO-LUMO}}$, time-dependent LDA (TDLDA) and diffusion quantum Monte Carlo (DMC) optical gaps E_{opt} , and DMC and Bethe-Salpeter equation (BSE) (with Hybertsen-Levine-Louie model screening) exciton binding energies E_{ex} . All energies are in eV.

Cluster	LDA $E_{\text{HOMO-LUMO}}$	TDLDA E_{opt}	DMC E_{opt}	DMC E_{ex}	BSE E_{ex}
SiH ₄	7.9	8.2	9.2	3.8	3.8
Si ₅ H ₁₂	5.7	5.8	6.8	4.3	3.9
Si ₁₀ H ₁₆	4.6	4.8	6.0	3.6	3.1
Si ₁₇ H ₃₆	4.1	4.3	5.6	3.0	2.4
Si ₂₉ H ₂₄	2.8	2.9	3.6	2.6	2.4
Si ₃₅ H ₃₆	3.4	3.5	5.1	2.6	1.5

band e and a hole in band h . For an excited state with energy E , the relative admixture [given by the $\psi(e, h)$] of each configuration can be determined by solving the equation of motion for the particle-hole pair,^{8,10,11}

$$[(E_e - E_h) - E]\psi(e, h) + \sum_{e'h'} K(eh; e'h')\psi(e', h') = 0, \quad (1)$$

where E_e and E_h are single-particle energies for the electron and the hole, respectively, and K is the electron-hole interaction kernel. In the BSE treatment, $K(eh; e'h') = K_{\text{Coul}}(eh; e'h') + K_{\text{dir}}(eh; e'h')$, where

$$K_{\text{Coul}}(eh; e'h')$$

$$= 2 \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_e^*(\mathbf{r}_1) \phi_h(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{e'}(\mathbf{r}_2) \phi_{h'}^*(\mathbf{r}_2)$$

is the repulsive Coulomb kernel (also known as the exchange kernel^{8,10}) and

$$K_{\text{dir}}(eh; e'h') = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_e^*(\mathbf{r}_1) \phi_h(\mathbf{r}_2) \times \frac{-e^2}{\epsilon(\mathbf{r}_1, \mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{e'}(\mathbf{r}_1) \phi_{h'}^*(\mathbf{r}_2)$$

is the attractive screened direct kernel. The $\phi(\mathbf{r})$ are single-particle wave functions. Note that the roles of \mathbf{r}_1 and \mathbf{r}_2 are different in K_{Coul} and K_{dir} . In the TDLDA, $K(eh; e'h') = K_{\text{Coul}}(eh; e'h') + K_{\text{xc}}(eh; e'h')$, where

$$K_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2; t, t') = \delta(t - t') \frac{\delta^2 E_{\text{xc}}}{\delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2)}$$

is the exchange-correlation kernel,¹² $\rho(\mathbf{r})$ is the ground state charge density, and E_{xc} is the LDA exchange-correlation energy functional. The locality of E_{xc} in space causes K_{xc} to be a single integral over \mathbf{r} . After E and ψ of Eq. (1) have been determined, the absorption spectrum can be calculated with either a sum-over-states expression⁴ or an equivalent iterative approach.⁸

In addition to the different choice of K , the TDLDA and BSE methods differ in their choice of single-particle states. In the TDLDA, the E_e, E_h and ϕ_e, ϕ_h , which enter Eq. (1) refer to LDA single-particle states, while for the BSE they should refer to *quasiparticle* states, as determined from, say,

a *GW* calculation.¹³ Thus, the BSE determines excitations of the N -electron system by first making reference to the $(N + 1)$ and $(N - 1)$ -electron systems, while the TDLDA deals directly with the N -electron system. Because the single-particle gap of the LDA is known to be small relative to both the quasiparticle gap and the optical gap of semiconductors, the TDLDA interaction kernel K must contain both the physics of quasiparticle self-energies and electron-hole binding if the resulting absorption spectrum is to agree with experiment. In the BSE approach, the single-particle states are corrected first to include the quasiparticle self-energies and the interaction kernel then serves to couple the quasielectron and quasihole together to form an exciton. We will show that these methodological differences have important practical consequences when computing the spectra of hydrogenated Si clusters.

In our BSE calculations for Si clusters, we take the quasiparticle wave functions to be equal to the LDA wave functions, as is often done in quasiparticle calculations using a LDA+*GW* approach.^{4,13} Due to the demanding nature of the *GW* self-energy calculation, we apply a simple scissors correction^{14,15} to the conduction state energies to shift the absorption edge to the correct optical gap energy.¹⁶ While this works well for bulk Si, we expect the quasiparticle self-energy corrections to be quite state dependent in small clusters. This may undermine the accuracy of our approach somewhat, yet it will be shown that this added approximation facilitates the comparison between the BSE and the TDLDA. Application of the scissors correction requires that the optical gap be known. We determine both the optical and quasiparticle gaps of each cluster with a highly efficient diffusion quantum Monte Carlo (DMC) technique reported elsewhere.^{17,18} Our results for the optical gaps of SiH₄-Si₁₀H₁₆ (see the third column of Table I) agree to within a few tenths of an eV of the values obtained by an *ab initio GW*+BSE approach.⁴ In addition, we obtain the optical gap of bulk Si to within the statistical error of the method,^{17,19} so we expect our gap calculations to be accurate for a cluster of any size.

One remaining ingredient to the BSE calculation is the dielectric function $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$ used in the evaluation of K_{dir} . The proper dielectric function to use for this level of theory is the one determined by the random-phase approximation (RPA).²⁰ Unfortunately, the poor scaling of the RPA computation with a number of atoms prevents us from doing this

calculation for these systems. Instead, we use a model that approximates the behavior of the RPA dielectric function, namely, the Hybertsen-Levine-Louie model (HLL).²¹ There are two inputs to this model: the position-dependent electron charge density $\rho(\mathbf{r})$ and the (position-dependent) dielectric constant ϵ_∞ . We determine $\rho(\mathbf{r})$ from the LDA calculation. For the dielectric constant, we define a sphere of radius R around the cluster center, and take $\epsilon_\infty(\mathbf{r}) = \epsilon_{dot}$ if $\mathbf{r} < R$ and $\epsilon_\infty(\mathbf{r}) = 1$ if $\mathbf{r} > R$. ϵ_{dot} is computed from a Penn-like model,

$$\epsilon_{dot} = 1 + (\epsilon_{bulk} - 1) \left[\frac{E_{bulk}^{OP} + \Delta}{E_{dot}^{OP} + \Delta} \right]^2,$$

where E_{bulk}^{OP} and E_{dot}^{OP} are the quasiparticle gaps of bulk Si and the Si dot, respectively, and Δ is the difference between the energy of the E_2 peak of the bulk Si absorption spectrum and the *direct* gap ($=4.2 \text{ eV} - 2.5 \text{ eV} = 1.7 \text{ eV}$).²² We take the radius of the cluster, R , to be the distance from the cluster center to the outermost Si atoms.²³ While the HLL model's approximate inclusion of local-field effects may not fully account for the polarization terms discussed by previous authors,²⁴ we show below that exciton binding energies obtained by solving the BSE with this screening model reproduce the qualitative trends in DMC binding energies of the Si clusters quite well.

It should be noted that our BSE approach [LDA plus scissors shift of conduction states computed by DMC plus solution of Eq. (1) with HLL screening model] reproduces the absorption spectrum of bulk Si remarkably well, producing results essentially indistinguishable from those of the fully *ab initio* GW+BSE calculation.⁸ This can be seen in Fig. 1(a), where the imaginary part of the long-wavelength dielectric function $\epsilon_2(\mathbf{q} \rightarrow 0, \omega)$ is compared to the experimental result.²⁵ Though accurate treatment of the bulk is not the goal of the present study, it should be noted that this agreement is *not* achieved in the case of the TDLDA. It has been shown that the absorption spectrum of a bulk system computed within the TDLDA is essentially equal to that determined with the LDA alone,²⁶ so the optical gap of bulk Si is underestimated by $\sim 0.5 \text{ eV}$. Comparison of the TDLDA Si spectrum to the experimental result appears in Fig. 1(b). Note that the intensity well above the absorption edge is rather more discrepant than in the BSE case.²⁷

In our work, pseudopotential LDA calculations were performed with the GP and ABINIT codes.^{28,29} The GP quantum molecular-dynamics code was used to relax the geometries of the ideal structures.³⁰ ABINIT was used to calculate single-particle states at a fixed geometry. A 35-Ry-energy cutoff was used for all LDA calculations and between 100 and 200 conduction states were computed, depending on the cluster size. The clusters were placed at the center of a cubic unit cell with periodic boundary conditions. For SiH_4 , Si_5H_{12} , and $\text{Si}_{10}\text{H}_{16}$ clusters the side length of the cube was 29 a.u., while for $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$ it was taken to be 35 a.u. TDLDA calculations were performed with the ABINIT code (which follows the prescription outlined in Ref. 29). BSE calculations were performed with the method described in Ref. 8, in which matrix elements of K_{dir} are computed by transforming particle-hole pair states from a single-particle

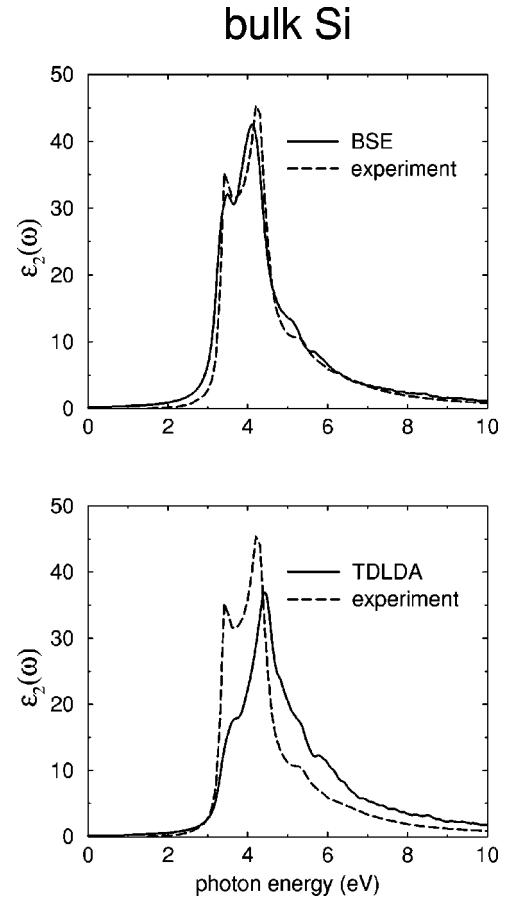


FIG. 1. (a) Solid line: our BSE result for bulk Si [including a scissors shift of conduction states as determined from performing a GW calculation (Ref. 8) and screening of the direct term provided by the HLL model]. Dashed line: experimental result of Ref. 25. (b) Solid line: our TDLDA result (without K_{xc} , see text) for bulk Si. Dashed line: experiment.

eigenstate basis (e, h) to real space ($\mathbf{r}_1, \mathbf{r}_2$): $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{eh} \phi_e(\mathbf{r}_1) \phi_h^*(\mathbf{r}_2) \psi(e, h)$. The \mathbf{r} points were chosen to lie on a uniform cubic mesh of spacing 1.5 a.u. (which we deemed to be the sufficient resolution for obtaining a converged spectrum).³¹ By transforming first from (e, h) $\rightarrow (\mathbf{r}_1, h)$ and then from $(\mathbf{r}_1, h) \rightarrow (\mathbf{r}_1, \mathbf{r}_2)$, the number of operations in the transformation can be made to scale as $N_r^2 N_{\text{bands}} \propto N_{\text{atom}}^3$. Since this is the dominant time consumer in the calculation of the spectrum,⁸ our BSE calculations as outlined above are made to scale as N_{atom}^3 .

III. RESULTS AND DISCUSSION

Figure 2 shows the results of the TDLDA calculation of the absorption spectrum of $\text{Si}_{10}\text{H}_{16}$.³² The solid line indicates the LDA result, obtained by setting the interaction kernel $K=0$. After a small peak at 4.6 eV [the LDA HOMO-LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap], the LDA result exhibits a number of prominent peaks between 5 eV and 9 eV. The TDLDA result shows peaks with much smaller oscillator strength in this energy range. This is a result of the repulsive

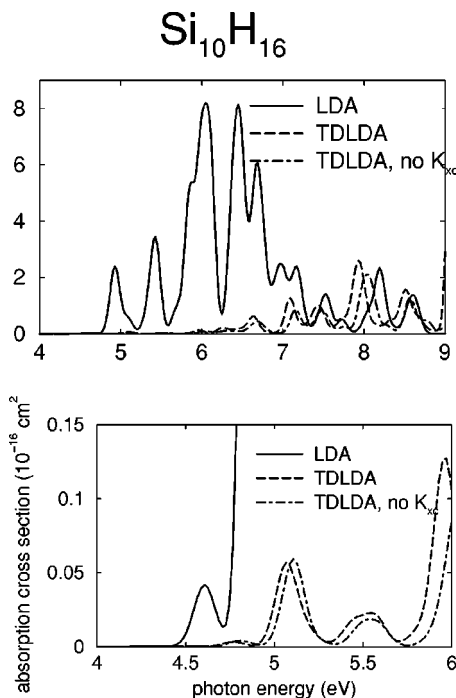


FIG. 2. (a) Absorption cross section (in units of 10^{-16} cm^2) of $\text{Si}_{10}\text{H}_{16}$ calculated with LDA (solid line), TDLDA (dashed line), and TDLDA *without* the exchange-correlation kernel K_{xc} (dot-dashed line). (b) Same spectra near the optical gap region.

Coulomb kernel, which enhances the oscillator strength of higher-energy excitations, leaving less strength near the edge. Note that we obtain almost the same result by neglecting the exchange-correlation kernel in the TDLDA calculation (see dot-dashed curve). Thus, the TDLDA computation appears to be practically identical to a time-dependent Hartree calculation³³ in that the time-dependent many-body effects going beyond mean-field are absent, or at least unimportant in this treatment. Though it seems from Fig. 2(a) that the TDLDA absorption edge has been pushed to higher energy by K_{Coul} , Fig. 2(b) shows that the edge, though greatly reduced in intensity, is at roughly *the same energy* as the LDA edge (which is fixed at the LDA HOMO-LUMO gap). These same statements apply to all of the hydrogenated Si clusters we have studied (see the first and second columns of Table I).

Before proceeding to the BSE results for the absorption spectra, we discuss the validity of the HLL screening approach. The proper way to assess validity or lack thereof is to compare the results of our BSE calculations to those using the full RPA dielectric function. Though calculations of this type have not yet been performed for the three largest clusters in our study, they have been carried out for SiH_4 - $\text{Si}_{14}\text{H}_{20}$ by Rohlfing *et al.*⁴ Unfortunately, the use of different single-particle energies (state-dependent GW self-energy calculation versus our scissors shift of conduction states) makes a detailed comparison with these results difficult. While we do obtain a qualitative agreement with the Rohlfing *et al.* results, it is not possible to draw quantitative conclusions regarding the extent to which the local-field effects are properly accounted for in the HLL model. However, we are able

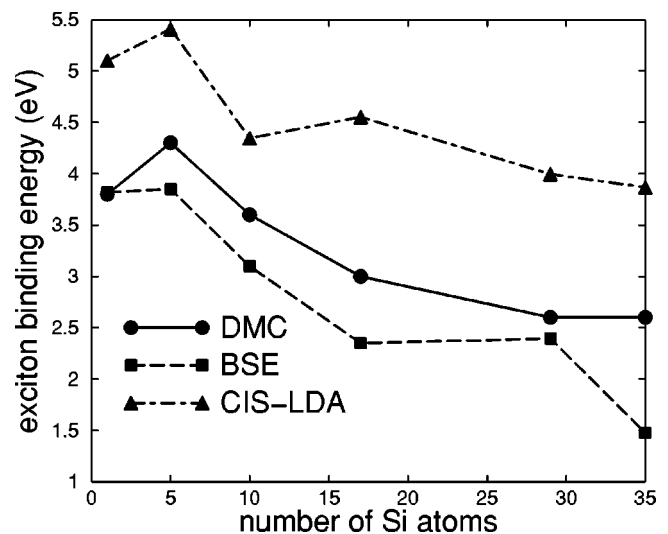


FIG. 3. Exciton binding energies of hydrogenated Si clusters computed with DMC (solid line), BSE with the HLL screening model (dashed line), and CIS-LDA (dot-dashed line) as a function of the number of Si atoms. Clusters included are SiH_4 , Si_5H_{12} , $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$.

to compare our *exciton binding energy* to that computed within the DMC (see the fourth and fifth columns of Table I). We define the binding energy to be the difference between the quasiparticle gap and the lowest optical excitation for which there is a *nonzero* transition dipole matrix element. This binding energy is independent of the scissors shift provided by the DMC, because adding a constant to the quantity in the square brackets of Eq. (1) does not change the form of the solution. Figure 3 shows our computed exciton binding energies as a function of cluster size, indicated by the number of Si atoms. The solid lines connect DMC results, which we view to be correct to within an error (statistical plus nodal) of 0.5 eV. The dashed lines connect our BSE results with the HLL screening. Differences are typically no more than ~ 0.5 eV for binding energies of a few eV,³⁴ though there is a deviation of ~ 1.0 eV for $\text{Si}_{35}\text{H}_{36}$. The dot-dashed lines connect BSE results with *no* screening or $\epsilon=1$. Such a calculation is equivalent to performing a singles-excitation configuration-interaction calculation with LDA single-particle states (CIS-LDA). Note that these binding energies are considerably higher than those for which screening is included, *even for SiH_4* . Thus, we argue that screening of K_{dir} is important even for the smallest Si clusters, and that the HLL model is at least sufficient for reproducing the qualitative trends in exciton binding energies.

While our primary interest is in clusters of ~ 1 nm diameter, accurate experimental absorption spectra are currently available only for the smallest clusters.² Thus, we consider SiH_4 in some detail. Figure 4 shows the results of our calculations for the photoabsorption cross section of SiH_4 as a function of photon wavelength, together with the experimental result of Itoh *et al.*² Three calculational results are shown: the BSE (with a scissors shift gap correction from Monte Carlo and screening of the direct term provided by the HLL model), the TDLDA, and the LDA. Note that the TDLDA

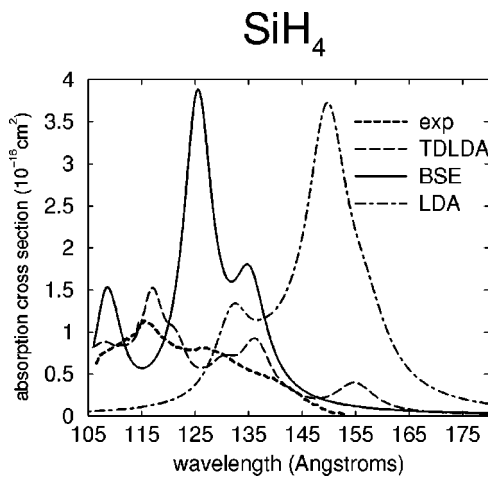


FIG. 4. Absorption cross section (in units of 10^{-16} cm^2) for the SiH_4 cluster as a function of wavelength. Experimental data (bold, short-dashed curve) as taken from Ref. 2.

result is quite close to the measured spectrum, both in overall magnitude and in the relative intensities of spectral features.³² In particular, the experimental curve possesses three prominent peaks in this region with intensities which decrease with wavelength. The TDLDA result also has this structure, though the low-energy peaks are too low in energy relative to experiment, a manifestation of the fact that the TDLDA underpredicts the optical gap of this system. While the BSE result exhibits a low-energy (high-wavelength) onset which is closer to experiment (simply a result of having shifted the spectrum to agree with the DMC optical gap), the distribution of intensity is considerably more different from the experiment than that of the TDLDA. The bare LDA result is similarly discrepant, though now with the same incorrect onset as that of the TDLDA calculation.

Since our BSE calculations were performed using a number of approximations beyond just the use of the BSE itself, it is possible that some or all of these approximations are responsible for the rather poor agreement with experiment. First, our use of a state-independent scissors correction to the LDA energies may be insufficient for such a small cluster. Also, the HLL screening model, meant for inhomogeneous but extended systems, may be inaccurate for treating SiH_4 . However, it can be seen that our approximate BSE results are grossly similar to those of Rohlffing and Louie,⁴ who used the BSE without these approximations. Although there are differences between our results and theirs, the experimental signature of the three main peaks with intensities that increase with energy is missing in both BSE results. Because our BSE result possesses too much oscillator strength at low energy relative to experiment, it is natural to assume that the screening of the direct term of the interaction is not sufficient. Indeed, if the direct term were screened out completely, the result would be almost identical to that of the TDLDA (recall that the TDLDA does not have a direct term and the K_{xc} term present instead is of little consequence for these systems). However, recent work by Ogut *et al.*³⁵ suggests that for SiH_4 , the dielectric function is rather small. Furthermore, if we take an unphysically large ϵ_∞ of 3.0 and an $R=0$

(thereby filling all space with a dielectric medium of $\epsilon=3$), the disagreement with experiment still persists.

One remaining possibility is that the LDA states are inaccurate in some sense. It has been shown that the LDA LUMO for SiH_4 is localized quite close to the molecule, in contradiction to the more accurate theoretical results which suggest it to be rather delocalized,⁴ a finding borne out by the experimental observation that SiH_4 has a negative electron affinity. Two fixes have been proposed to remedy this problem: Grossman *et al.*⁴ computed the quasiparticle wave functions in the *GW* approximation when calculating the self-energy correction, rather than simply taking them to be equal to the LDA wave functions (this amounts to considering the off-diagonal elements of the self-energy operator). They found that the SiH_4 LUMO was then considerably less bound and demonstrated better agreement with the DMC optical gap. Corrections to the resulting absorption spectrum were not reported, however. Vasiliev³⁶ took a density-functional-based approach in which the exchange-correlation potential was systematically corrected to produce the correct long-range behavior for a finite system. He demonstrated that the SiH_4 HOMO-LUMO transition energy was then above the ionization threshold, and the resulting spectrum seemed to be in an even better agreement with experiment than the standard TDLDA provides. It was also shown that the effect of this modified exchange-correlation potential on the TDLDA absorption spectrum is smaller for the larger clusters, and is practically negligible for clusters in the 1-nm-size range. As we will demonstrate below, this is the range in which our BSE and TDLDA results produce grossly similar spectra. Thus, while a good description of the SiH_4 spectrum within our BSE treatment is still lacking, we suspect that larger clusters will be better described by the method, though accurate experimental data for these clusters is not yet available (recall that for the case of bulk Si, our BSE treatment works very well, producing results in far better agreement with the experiment than does the TDLDA).

Figure 5 shows our calculated BSE absorption spectra (solid curves) together with the TDLDA spectra (dashed curves) for $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$ clusters. Note that gross features, such as the rates of increase of intensity with energy, are very similar for the results of the two methods. This can be understood as follows: since K_{xc} has little or no effect on the TDLDA results, K_{Coul} is responsible for the redistribution of oscillator strength resulting in the slow rise of intensity with energy (compare the $\text{Si}_{10}\text{H}_{16}$ results here with the LDA result of Fig. 2). This kernel is present in both TDLDA and BSE, so it affects both. The additional electron-hole interaction term of the BSE, K_{dir} , has the effect of moving oscillator strength to lower energy without changing the shape of the spectrum dramatically.³⁷ This movement is partly canceled, however, by the (scissors) self-energy correction which widens the gap, and is not present in the TDLDA (recall that our TDLDA optical gaps are very close to the LDA band gaps). Thus, we can say that the TDLDA benefits from a partial cancellation between the quasiparticle self-energy correction and the electron-hole attraction. Two points must be stressed however: (1) With the exception of $\text{Si}_{29}\text{H}_{24}$, the TDLDA optical gaps are still an eV

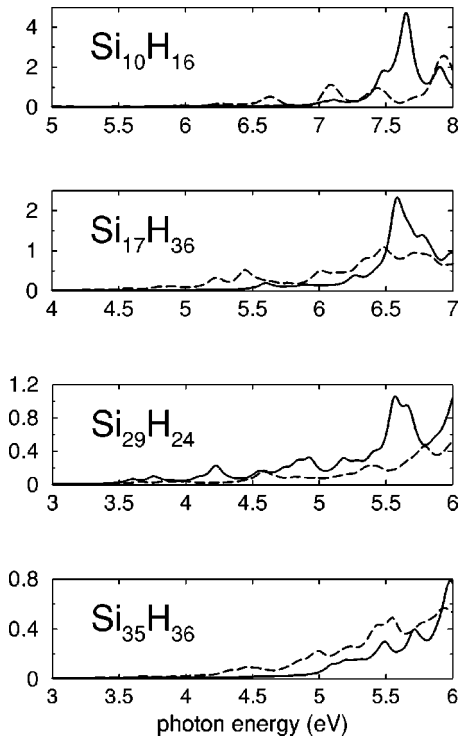


FIG. 5. Absorption cross sections (in units of 10^{-16} cm^2) for $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$ computed with our BSE method (solid lines), and TDLDA (dashed lines).

or more lower than the optical gaps computed with DMC (see the second and third columns in Table I). While this is hardly apparent in Fig. 5, due to the small oscillator strength of these low-energy peaks, it is expected that these differences could be observed in photoluminescence experiments. (2) The BSE results exhibit considerably stronger features in this energy range as compared to the TDLDA results. See, e.g., the large peak at 7.6 eV for $\text{Si}_{10}\text{H}_{16}$ and the peaks between 5 eV and 6 eV for $\text{Si}_{29}\text{H}_{24}$. While we know of no experimental results on the absorption spectra of these specific clusters in the energy ranges of interest at present, we submit that measurements should be able to distinguish differences of this magnitude. Finally, we point out that the partial cancellation in the TDLDA calculation mentioned above cannot persist to larger cluster sizes; in the bulk limit, the quasiparticle self-energy correction is ~ 0.5 eV, while the exciton binding energy is a mere ~ 20 meV.

In the BSE approach, the attractive term of the electron-hole interaction (K_{dir}) involves the screened Coulomb interaction, but the repulsive term K_{Coul} involves the bare interaction. While we have adopted this strategy here, there are other approaches that treat screening differently. In the work of Franceschetti *et al.*²⁴ on quantum dots containing in excess of 10^4 atoms, both direct and Coulomb terms are screened with the same dielectric function. This approach can be shown to be appropriate for their study, in which only absorption within the first few tenths of an eV of the edge is studied.³⁸ In another work,³⁹ the absorption spectrum of $\text{Si}_{29}\text{H}_{24}$ is computed with a singles-only configuration-interaction (CIS) approach. In CIS, neither direct nor Coulomb terms are screened, and the single-particle states are

those of Hartree-Fock⁴⁰. We argue that the lack of screening in that calculation is insufficient, in that the exciton binding energy would be greatly overpredicted.⁴¹ Consequently, our CIS-LDA calculation for $\text{Si}_{29}\text{H}_{24}$, in which we take $\epsilon=1$, produces markedly different results from our BSE calculation.⁴² As mentioned above in connection with the exciton binding energies, we find that screening of the attractive part of the electron-hole interaction is crucial for all the clusters of our study.

Our results for the clusters of this study reinforce the view (expressed variously by many researchers¹¹) that the TDLDA works better for smaller systems. The absorption spectrum of SiH_4 determined with the TDLDA is in reasonably good agreement with experiment, even in the absolute magnitude of intensities (see Fig. 4). As mentioned above, this agreement would likely improve even further if the theory is corrected in a way such as to bring the ionization threshold below the HOMO-LUMO transition energy.³⁶ It must be emphasized that at least in the simplest approach we present, the TDLDA is essentially equivalent to a time-dependent Hartree calculation for these systems, since the K_{xc} term is practically negligible here. The more involved BSE calculation yields notably worse results for SiH_4 , though we know it to be a far better theory for the description of bulk optical properties.⁸ It remains to be seen if a description in the BSE framework can yield an absorption spectrum for SiH_4 of accuracy comparable to that of the TDLDA as far as the overall distribution of intensity is concerned (as stated above, our hybrid BSE-DMC approach does produce an optical gap which is in better agreement with the experiment than does the TDLDA). The main deficiency may indeed be an improper description of the localization, or lack thereof, of the low-lying single-particle states.⁴³ The fact that our TDLDA and BSE calculations of the absorption spectra of the ~ 1 -nm-sized clusters produce broadly similar features suggests that this size range may be better described. It bears repeating, however, that even in this regime, the BSE produces more dramatic absorptive features at low energies. We await accurate measurements on monodispersed samples to support or deny these claims.

IV. CONCLUSIONS

We have computed the optical absorption spectra of clusters SiH_4 , $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{17}\text{H}_{36}$, $\text{Si}_{29}\text{H}_{24}$, and $\text{Si}_{35}\text{H}_{36}$ with two different, but related, computational approaches: The Bethe-Salpeter equation with screening determined from the Hybertsen-Levine-Louie model and an optical gap computed with diffusion quantum Monte Carlo, and time-dependent density-functional theory in the adiabatic local-density approximation. When comparing the results of the two methods, we find that gross features are similar for the larger clusters, due to the important role played by the Coulomb kernel in both treatments, but there are notable differences in the optical gaps and in the intensities of peaks within several eV of the absorption edge. For SiH_4 , we find that TDLDA produces a spectrum in remarkably good agreement with experiment, while our BSE approach concentrates oscillator strength too low in energy. Finally, when adopting an approach that involves mixing of configurations (such as those

presented here), we find that screening of the direct term is crucial if only singly-excited configurations are considered.

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