

Excitonic Effects and the Optical Absorption Spectrum of Hydrogenated Si Clusters

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We calculate the optical absorption spectrum of hydrogen-terminated silicon clusters by solving the Bethe-Salpeter equation for the two-particle Green's function using an *ab initio* approach. The one-particle Green's function and the electron-hole interaction kernel are calculated within the *GW* approximation for the electron self-energy operator. Very large exciton binding energies are observed. Our results for the one-particle properties and the optical absorption spectra of the clusters are in very good agreement with available experimental data. [S0031-9007(98)05792-5]

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Optical excitations of hydrogen-terminated Si clusters have been investigated extensively both in experiment [1,2] and theory [3,4]. Theoretical studies of Si_mH_n include many different approaches ranging from empirical tight-binding schemes to *ab initio* local-density approximation (LDA) investigations and quantum chemistry methods. Most of these approaches focus on the dependence of band edges and gap energies on the size and shape of the clusters. A calculation of the entire excitation spectrum of small semiconductor clusters including excitonic effects has not yet been presented. Therefore, only limited information on the optical properties of such systems is available, so far.

In this paper, we present a detailed study of the excitations of the electronic system of several small semiconductor clusters, fully including all relevant electronic correlation effects using state-of-the-art *ab initio* approaches. We employ the usual many-body concept of defining Green's functions of increasing order for the N -electron system and evaluating the equations-of-motion for them. Such approaches have been applied to extended systems with excellent success (see Refs. [5,6] for the one-particle, and Ref. [7] for the two-particle Green's function results), but their application to nanostructures is extremely demanding. The clusters we study in this paper can be regarded as the molecular limit of semiconductor nanostructures. The analysis of many-body effects in these systems, together with respective data on extended crystals, will allow for a more detailed understanding of electronic correlation in the entire range of semiconductor systems from the molecular to the nanoscale and macroscopic regime.

As a starting point, we perform an LDA pseudopotential calculation for each cluster relaxing the geometric structure. Based on the LDA results, we construct the electron self-energy operator within the *GW* approximation [8] and calculate the one-particle Green's function, which yields quasiparticle (QP) energies that correspond to single-electron ionization and affinity energies. Details of these calculations are given elsewhere [9]. From these results, we finally construct the two-particle interac-

tion kernel and solve the Bethe-Salpeter equation for the two-particle Green's function [10–12], which yields the optical absorption spectrum.

The only previous study of this kind is a recent calculation by Onida *et al.* [13] on the alkali-metal cluster Na_4 , employing plane-wave representation techniques. Because of the much larger energy cutoff required for *GW* calculations on Si-H systems as compared to Na and because of the larger size systems studied here, a plane-wave expansion would be very demanding. Instead, we employ a Gaussian-orbital representation technique [9] that allows for an efficient expansion of all quantities with basis sets of very moderate size, using 30 to 50 basis functions per atom. Such basis sets have been shown to yield highly accurate results for a wide range of systems, including Si and Si surfaces [9]. Using this approach, we have studied five different Si-H clusters (i.e., SiH_4 , Si_2H_6 , Si_5H_{12} , $\text{Si}_{10}\text{H}_{16}$, and $\text{Si}_{14}\text{H}_{20}$) with diameters ranging from about 3 to 9 Å, allowing for a systematic investigation of quantum confinement effects as well as the effects of dynamical screening and mixing of electron-hole configurations on the exciton spectra as a function of cluster size.

We have carefully checked the LDA energy spectrum, which is in excellent agreement with LDA results available in the literature [14], as well as the QP energies of single electrons and holes. For the highest occupied molecular orbit (HOMO) of SiH_4 (Si_2H_6), e.g., we obtain an LDA energy of -8.4 eV (-7.3 eV) and *GW* QP energy of -12.7 eV (-10.6 eV), respectively. The latter is in excellent agreement with the measured ionization energy of -12.6 eV (-10.7 eV) [2]. Taking into account the excellent QP results for bulk Si [5] and for free and H-covered Si surfaces [6,9], the GWA can thus be considered to be valid for the entire range of Si and Si-H systems from the molecular to the macroscopic scale.

To discuss optical excitations that do not change the number of electrons, one has to go beyond the one-particle Green's function and solve the Bethe-Salpeter equation (BSE) for the two-particle Green's function G_2 , fully

including the electron-hole interaction kernel K :

$$G_2(\omega) = G_2^{(0)}(\omega) + G_2^{(0)}(\omega)K(\omega)G_2(\omega). \quad (1)$$

A fundamental analysis and systematic formal development of this kind of approach can be found, e.g., in Refs. [10–12]. $G_2^{(0)} = G_1G_1$ is constructed from the one-particle Green's function G_1 . We obtain it from the QP amplitudes ψ_m^{QP} and energies ϵ_m^{QP} resulting from the GWA calculation as discussed above [15]. Another crucial quantity is the electron self-energy contribution to the electron-hole interaction kernel K which we obtain using the GWA. K is finally given as a sum of an unscreened exchange term K^x and a direct, screened Coulomb interaction term K^d if one makes the standard approximation that the functional derivative of W with respect to G_1 is negligible [12].

The excitation energies Ω_S of the N -particle system are given by the frequency poles of $G_2(\omega)$. At Ω_S , the operator $[1 - G_2^{(0)}(\omega)K(\omega)]$ must have an eigenvector

$$(\epsilon_n^{\text{QP}} - \epsilon_m^{\text{QP}})A_S(mn) + \sum_{m',n'} (2K_{mn,m'n'}^x \delta_{M,0} + K_{mn,m'n'}^d(\Omega_S))A_S(m'n') = \Omega_S A_S(mn). \quad (3)$$

The exchange term K^x is nonzero only for spin-singlet excitations, having spin multiplicity $M = 0$. The direct interaction term [12]

$$K_{mn,m'n'}^d(\Omega_S) = \int d^3r d^3r' \psi_n^*(\mathbf{r})\psi_{n'}(\mathbf{r})\psi_m(\mathbf{r}')\psi_{m'}^*(\mathbf{r}') \\ \times \frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} W(\mathbf{r}, \mathbf{r}', \omega) \\ \times \left[\frac{1}{\Omega_S - \omega - (\epsilon_{n'}^{\text{QP}} - \epsilon_m^{\text{QP}}) + i0^+} + \frac{1}{\Omega_S + \omega - (\epsilon_n^{\text{QP}} - \epsilon_{m'}^{\text{QP}}) + i0^+} \right] \quad (4)$$

requires a frequency integration which we evaluate analytically within the plasmon-pole model for the dynamical behavior of $W(\omega)$. Since K^d depends on the excitation energy Ω_S , Eqs. (3) and (4) have to be solved self-consistently for each excitation S . In the calculation, we start from assuming static screening in Eq. (4) and solve Eq. (3) accordingly. For each excitation S , we then again calculate K^d employing Ω_S . The difference to the former K^d constitutes a perturbation to Eq. (3) which is evaluated to first order for each S , yielding converged excitation energies Ω_S after a few iterations of Eqs. (3) and (4). The final excitation energies are lower than those resulting from static screening by several tenths of eV.

In Fig. 1 we display the calculated optical spectra of SiH_4 , Si_2H_6 , Si_5H_{12} , $\text{Si}_{10}\text{H}_{16}$, and $\text{Si}_{14}\text{H}_{20}$ (solid lines). They are given by the spin-singlet transitions [17], weighted by the respective electric dipole oscillator strength $M_S \sim 1/\Omega_S^2 |\sum_{m,n} A_S(mn) \langle m|\hat{\mathbf{p}}|n\rangle|^2$. The dotted lines show the respective absorption spectrum resulting from the QP energies only, i.e., completely neglecting the electron-hole interaction. The inclusion of the interaction modifies the shape of the spectrum significantly due

to mixing of different electron-hole configurations. Most importantly, the entire spectrum is shifted to lower energies by several eV. In Table I we compare our results for the pronounced transitions of SiH_4 and Si_2H_6 with measured absorption energies by Itoh *et al.* [2]. The optical spectra of the two clusters consist of several well-defined peaks. For both systems, the lowest transition energy is in very good agreement with the measured data. The higher transitions also agree with experiment to within 0.5 eV, i.e., within an accuracy of 5%. For the larger systems, the optical spectra become more complex due to the increasing number of QP states and of electron-hole excitations. It should be noted that, since we are interested in only low-energy excitations, we have restricted ourselves to including no more than 30 unoccupied electron states n in the solution of Eq. (3). This limits the number of resulting excitations. Figure 1 does not show excitations above 11.9 eV (11.5 eV) for $\text{Si}_{10}\text{H}_{16}$ ($\text{Si}_{14}\text{H}_{20}$), as indicated by the vertical dashed lines.

The excitonic binding energy (i.e., the negative expectation value of K) amounts to several eV, up to 7.7 eV for the lowest spin-triplet excitation in SiH_4 . It is thus

$$|N, S\rangle = \sum_m^{\text{hole}} \sum_n^{\text{elec}} A_S(mn) \hat{a}_m^\dagger \hat{b}_n^\dagger |N, 0\rangle, \quad (2)$$

where $|N, 0\rangle$ is the ground state of the system, \hat{a}_m^\dagger creates a quasihole m , and \hat{b}_n^\dagger creates a quasidelectron n . Four-particle or higher processes are neglected. The BSE finally yields the following equation for the electron-hole amplitudes $A_S(mn)$ and the excitation energies Ω_S [12]:

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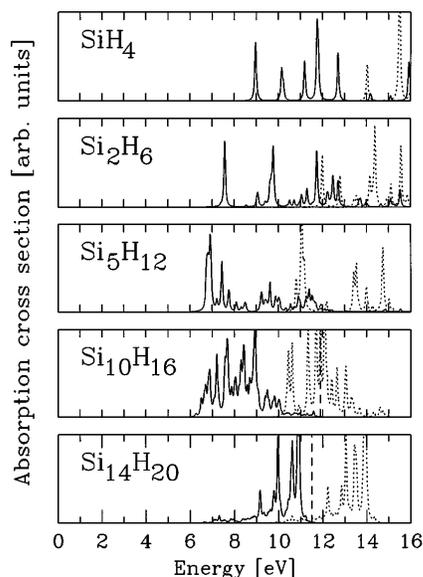


FIG. 1. Calculated optical absorption spectrum of Si_mH_n clusters. The spectra include an artificial broadening of 0.04 eV. The dotted lines show the spectra without electron-hole interaction.

more than two orders of magnitude larger than in bulk Si (15 meV). This large binding energy is caused by two effects. First, the spatial confinement of electrons and holes increases the overlap and thus the attractive interaction between them. Second, the dielectric screening in such small systems is much weaker than in extended bulk systems. Therefore, the electron-hole interaction is much less efficiently screened than in the bulk, increasing the exciton binding energy even further. In all cases, the binding energies for the triplet states are larger than for the singlet states by 0.5–1 eV since the triplet states do not observe the repulsive exchange interaction term K^x .

It has sometimes been presumed that at least the lowest-energy excitation of a semiconductor cluster might be given by a single transition from the HOMO to the lowest unoccupied molecular orbital (LUMO) state, i.e., it might be represented by a single “basis excitation” $\hat{a}_m^\dagger \hat{b}_n^\dagger |N, 0\rangle$ in Eq. (2). From our calculations, we observe that this is not the case. Even for the smallest clusters, the excited states involve a complicated mixing of a large number of electron-hole pairs (m, n) , as a result of the nondiagonal elements of the electron-hole interaction $K_{mn, m'n'}$. Neglecting these elements results in errors of

TABLE I. Optical absorption energies of SiH_4 and Si_2H_6 (in eV). The experimental data are from Itoh *et al.* [2].

SiH_4		Si_2H_6	
This work	Expt.	This work	Expt.
9.0	8.8	7.6	7.6
10.2	9.7	9.0	8.4
11.2	10.7	9.6–9.8	9.5, 9.9

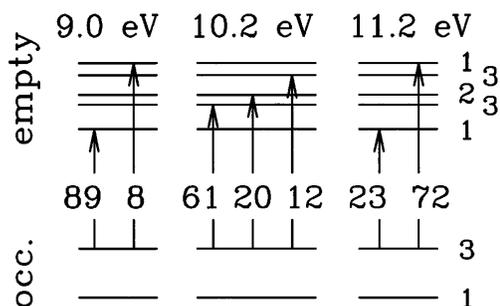


FIG. 2. Contribution (in percent) of different electron-hole pair configurations to three spin-singlet transitions in SiH_4 (labeled by their transition energy Ω_S on the top). Note that the positions of the levels are not drawn to scale. The degeneracies of the one-particle levels are given on the right-hand side. Contributions smaller than 1% are not shown.

the excitation energies of as much as 1 eV. In Fig. 2 we depict the contribution $|A_S(mn)|^2$ of different electron-hole pairs (denoted by arrows from occupied to empty levels) to the three transitions in SiH_4 discussed in Table I. Note that the one-particle levels consist of up to three different states that are degenerate due to the symmetry of SiH_4 , which further increases the complexity of the composition of the transitions. The contributions shown in Fig. 2 have been added up to account for these degeneracies. Similarly complex compositions are found for the spin-triplet transitions. As the size of the systems increases, the composition becomes even more complex due to the increasing number of states per energy interval. Roughly speaking, the energy interval involved in the formation of an exciton is of the same order of magnitude as its binding energy.

In Fig. 3 we compile the lowest excitation energies for spin-triplet and spin-singlet excitations. As the size of the clusters increases, these excitation thresholds are reduced. The splitting between triplet and singlet excitations is reduced, as well, resulting from the decreasing overlap between the electron and hole, and the respectively decreasing exchange interaction K^x . In most cases, the calculated lowest spin-singlet excitation, although optically allowed in principle, is not observable in optical absorption due to a vanishing electric dipole oscillator strength. Therefore we include the lowest dipole-allowed spin-singlet excitations in Fig. 3, as well. Baierle *et al.* [4] have recently obtained the lowest excitation energy of Si_5H_{12} and $\text{Si}_{10}\text{H}_{16}$ within configuration-interaction calculations with single-excitations (CIS) and within correlated Hartree-Fock calculations (included in Fig. 3). It is unclear from Ref. [4] whether the quoted transitions refer to spin-triplet or spin-singlet excitations. Our transition energies are higher than those results. We have also included the measured lowest optical absorption energy of SiH_4 and Si_2H_6 in Fig. 3 [2]. Our results for the lowest dipole-allowed spin-singlet excitation are in excellent agreement with the data. This demonstrates that our approach of calculating electron-hole

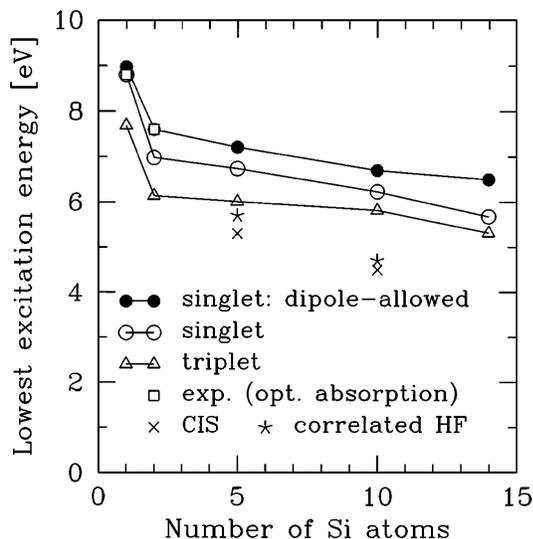


FIG. 3. Excitation energies of the lowest spin-triplet, spin-singlet, and dipole-allowed spin-singlet excitations. We include theoretical results from CIS calculations (\times) and from correlated Hartree-Fock calculations (\star) by Baierle *et al.* [4], as well as experimental data (\square) by Itoh *et al.* [2].

excitations in confined systems includes the important physical aspects, and the involved assumptions are valid. Furthermore, the employment of localized Gaussian orbital basis functions provides an efficient, accurate, and reliable computational scheme. The scaling of our method is roughly $O(N^3)$ (N being the number of atoms), which is better than the scaling of most *ab initio* quantum chemistry approaches. Application of this approach to the absorption spectra of bulk insulators and semiconductors has yielded equally excellent agreement with experiment [7].

In summary, we have developed a method for studying the electron-hole excitations in small semiconductor clusters. The quasiparticle spectrum of electrons and holes is evaluated in the *GW* approximation and the electron-hole excitations are obtained by solving the Bethe-Salpeter equation for the two-particle Green's function. We have evaluated the excitation energies and optical absorption spectra of five different Si_mH_n clusters. Very large excitonic binding energies are observed for these small clusters. A large number of electron-hole configurations is involved in the excitonic transitions. Our calculated optical absorption spectra are in very good agreement with available experimental data.

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