



Size dependence of the optical properties of silicon clusters

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Ab initio calculations of the optical properties of silicon clusters of 20, 60, and 70 atoms are presented. Quantum molecular dynamics using a minimal sp^3 basis set are performed to find metastable and equilibrium atomic configurations. The optical properties of these clusters are calculated using an extended sp^3d^5 basis. We discuss the dependence of the optical properties on the number of atoms as well as on the geometric configuration of these clusters.

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1. Introduction

The continuing development of nanostructure technology makes more demanding the theoretical understanding of these unique systems. Silicon clusters of small and intermediate size have received a great deal of attention [1, 2]. One of their more interesting characteristics is perhaps that silicon clusters do not show equilibrium symmetric fullerene structures like in carbon. This behavior has been attributed to the different competition between structure (strains) and electronic properties (bonding) involved in the equilibration process. Some theoretical efforts have been made in understanding this behavior, and a number of equilibrium structures of these systems have been studied [2]. Complete experimental characterization using traditional techniques, such as X-ray diffraction, has been hampered due to the small size of these systems, suggesting the use of optical techniques. However, the determination of the optical properties of these clusters from a first-principles method that could help one compare with experiments is still lacking.

We present a new first-principles computational scheme to calculate the optical properties of clusters and crystalline systems. Up to now, the microscopic study of the optical properties has been limited in part by the intensive computer work required. Our method employs a localized basis set that is more convenient and efficient to study clusters than other *ab initio* methods based on plane-wave basis sets [3]. The use of localized wave functions reduces the number of calculations needed to compute various quantities, such as the dielectric function, $\epsilon(\omega)$. Typically, plane-waves *ab initio* calculations require thousands of wave functions

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to compute correctly the valence and conduction bands. A localized basis set like ours employs a number of wave functions equal to the local basis set size times the total number of atoms of the system. For the largest cluster studied here, we employed $sp^3d^5 = 9$ (localized orbitals) \times 70 (atoms) = 630 wave functions. We applied this scheme to calculate the electronic and optical properties of silicon clusters consisting of 20, 60, and 70 atoms.

2. Atomic models and computational procedure

The approach used here is a quantum molecular dynamics (QMD) based in a first-principles method developed by Sankey and Niklewski [4]. This scheme is based on density functional theory in the local density approximation (LDA), using the Hamann–Schlüter–Chiang pseudopotentials, and a minimal sp^3 basis representation. A comprehensive discussion of this scheme, approximations used, and a description of various tests can be found in Ref. [4]. In particular, this method has been shown to be very useful in the description of small [5] and large silicon systems [2, 6]. Notice that this technique does not involve fitting parameters like semiempirical approaches, and it is more convenient to study clusters than other *ab initio* methods using plane-wave basis sets.

Our starting point are the ideal cluster structures that resemble the corresponding carbon fullerenes C_n ($n = 20, 60,$ and 70), but properly scaled to the Si–Si bonding environment. We study the metastable and equilibrium geometries of silicon clusters that are obtained using annealing and quenching computational techniques [2, 4]. A detailed discussion of this procedure and of the calculated Si_n atomic configurations used here, was presented by Song *et al.* [2].

Once the metastable and equilibrium atomic configurations of the Si_{20} , Si_{60} , and Si_{70} clusters are found, we calculate their electronic and optical properties. In the calculation of $\epsilon(\omega)$, electron transitions between filled and empty electronic states must be taken into account, valence (v) and conduction (c) bands have to be described as well as possible. Therefore, we perform first-principles calculations using an extended basis, where the d atomiclike localized orbitals are included. This extended basis has shown to be very accurate, comparing very well to conventional plane-wave *ab initio* methods in describing valence and conduction bands of a variety of systems [7].

The imaginary part of $\epsilon(\omega)$ is calculated according to the well known relation

$$\epsilon_2^{jj}(\omega) = \frac{e^2 \hbar^2}{\pi m^2 \omega^2} \sum_{v,c} |\langle \psi_c | \hat{\mathbf{e}}_j \cdot \mathbf{p} | \psi_v \rangle|^2 \delta(E_c - E_v - \hbar\omega), \quad (1)$$

where $\hat{\mathbf{e}}_j$ is a unitary vector along the direction of the external electromagnetic field of energy $\hbar\omega$, and \mathbf{p} is the momentum operator. To calculate the optical matrix elements $\langle \psi_c | \hat{\mathbf{e}}_j \cdot \mathbf{p} | \psi_v \rangle$ of eqn (1), we use the commutation relation between Hamiltonian and position operator, $\mathbf{p} = (im/\hbar)[H, \mathbf{r}]$. The matrix elements of the momentum operator between eigenstates are obtained in terms of those between localized orbitals $\phi_n(\mathbf{r})$ as [8, 9]

$$\begin{aligned} \langle \phi_n(\mathbf{R}) | p_j | \phi_{n'}(\mathbf{R}') \rangle &= \frac{im}{\hbar} \sum_{n''} \{ \langle \phi_n(\mathbf{R}) | H | \phi_{n''}(\mathbf{R}'') \rangle \langle \phi_{n''}(\mathbf{R}'') | r_j | \phi_{n'}(\mathbf{R}') \rangle \\ &\quad - \langle \phi_n(\mathbf{R}) | r_j | \phi_{n''}(\mathbf{R}'') \rangle \langle \phi_{n''}(\mathbf{R}'') | H | \phi_{n'}(\mathbf{R}') \rangle \}. \end{aligned} \quad (2)$$

Here, $p_j \equiv \hat{\mathbf{e}}_j \cdot \mathbf{p}$ and $r_j \equiv \hat{\mathbf{e}}_j \cdot \mathbf{r}$, and n denotes the angular momentum index. The matrix elements of the position operator can be written as

$$\langle \phi_n(\mathbf{R}) | r_j | \phi_{n'}(\mathbf{R}') \rangle = \frac{1}{2}(R_j + R'_j) \langle \phi_n(\mathbf{R}) | \phi_{n'}(\mathbf{R}') \rangle + \langle \phi_n(\mathbf{R}) | \left[r_j - \frac{1}{2}(R_j + R'_j) \right] | \phi_{n'}(\mathbf{R}') \rangle. \quad (3)$$

Usually, the second term on the right side of eqn (3) is assumed small and neglected, and the nonorthogonality

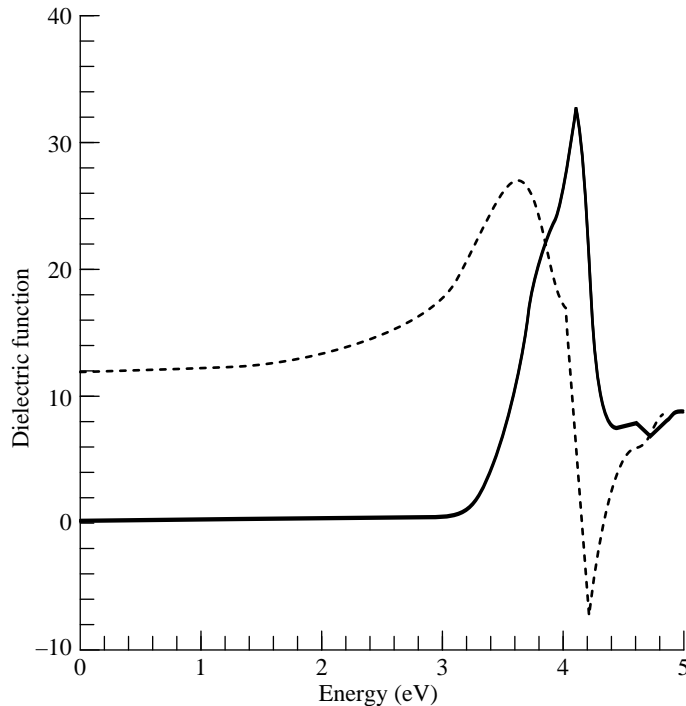


Fig. 1. Real (---) and imaginary (—) parts of $\epsilon(\omega)$ for bulk silicon as a function of energy.

of the basis is ignored. Here, we perform calculations taking into account the nonorthogonality of the basis, and the second term on the right side of eqn (3) is approximated by considering only intra-atomic transitions.

3. Calculated electronic and optical properties

We first calculate $\epsilon(\omega)$ for bulk silicon. In Fig. 1, we show the real (dashed line) and imaginary (solid) parts of $\epsilon(\omega)$ as a function of energy. We employ the scissors operator to rigidly open the underestimated LDA gap, leaving the wave functions unchanged [10]. The imaginary part is calculated using a relation similar to eqn (1), where the sum over valence and conduction states was averaged over 4648 special points in the irreducible part of the Brillouin zone and electron transitions up to 10 eV are included. The calculated value of the static dielectric constant $\epsilon(0) = 11.76$, is in excellent agreement with the experimental result of 11.8. The imaginary part of $\epsilon(\omega)$ in Fig. 1, shows that electron transitions start at about 3 eV, and two main peaks appear at 3.6 and 4.2 eV. These transitions correspond to those observed at 3.4 and 4.5 eV, respectively. The intensity of the calculated peak at 3.6 eV does not correspond to the experimental value. This is expected, since exciton effects are not included in the present calculation. The calculated real part of $\epsilon(\omega)$ also resembles the experimental one, where a maximum is found at 3.3 eV and a minimum at 4.3 eV [11].

We now calculate the electronic and optical properties of silicon clusters of 20, 60, and 70 atoms, with geometry configurations calculated in Ref. [2]. It is found that metastable configurations of Si_{60} , and Si_{70} are fullerenelike, while equilibrium geometries are of the network type [2]. The Si_{60} (Si_{70}) equilibrium network is 0.33 (0.27) eV/atom more stable than the metastable fullerenelike configuration. In Fig. 2, we show (A) metastable and (B) equilibrium configurations of Si_{60} , as well as their corresponding electronic density of states (EDOS). In Fig. 2A, we can see that the metastable structure shows atomic coordinations similar to the

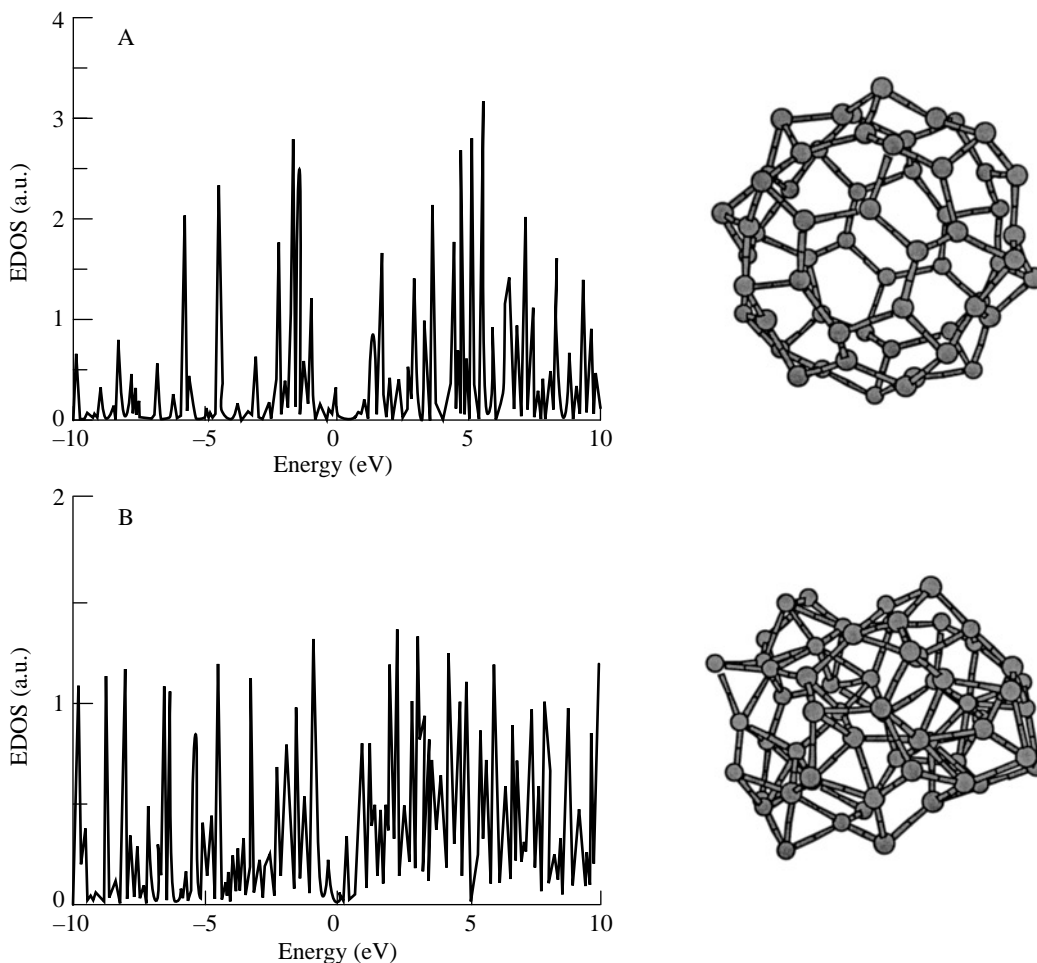


Fig. 2. Atomic structure and EDOS of (A) metastable and (B) equilibrium configurations of Si_{60} . The zero of the EDOS corresponds to the calculated Fermi level. A level broadening of 0.08 eV was used.

ideal Si_{60} clusters, composed by hexagons and pentagons, although the ideal geometry is strongly distorted. Figure 2B shows the equilibrium Si_{60} cluster. Here one can see the change on atomic coordination resulting in part from stabilization of the dangling bonds introduced by the surface strains. The Si_{20} cluster does not have a fullerene-like metastable structure, and the equilibrium configuration is also of the network type, which is 0.46 eV/atom more stable than the ideal fullerene geometry.

The differences between these clusters are directly reflected in their optical response. We show in Fig. 3 the imaginary part of $\epsilon(\omega)$ of Si_{60} for the (A) metastable and (B) equilibrium configurations. The optical gap of 0.55 eV corresponding to the equilibrium structure is almost half of that of the metastable configuration of 0.91 eV [12]. This is also shown in the EDOS in Fig. 2. The $\epsilon(\omega)$ spectrum of the network structure is more intense than the metastable one, in general both spectra in Fig. 3 show similar line shape. The same electron transitions at about 0.9 eV are present in both spectra, while the network cluster shows additional structure at 0.55 eV. These latter electron transitions could be easily associated with the different atomic coordination and geometry of the cluster. Notice that another important characteristic of these optical spectra is that the

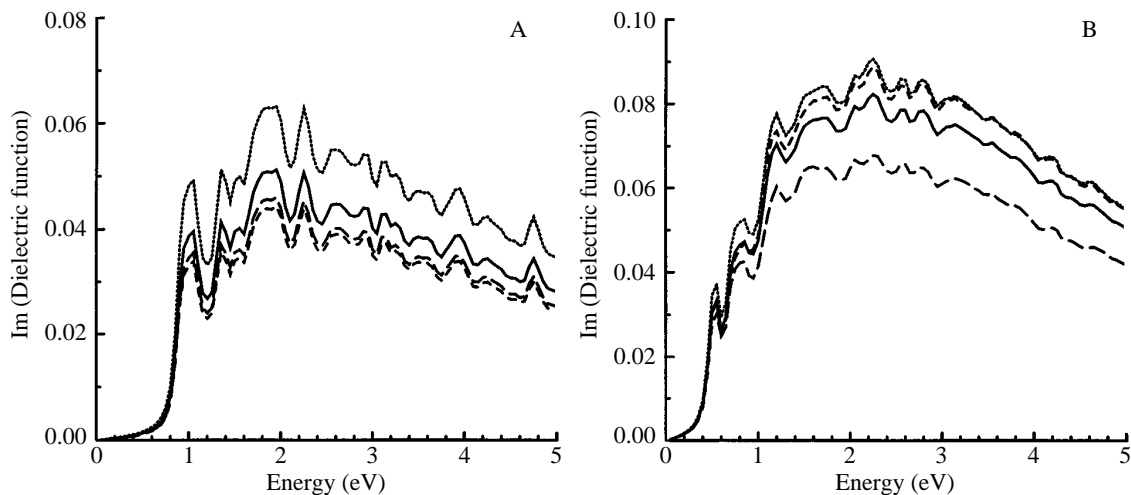


Fig. 3. Imaginary part of $\epsilon(\omega)$ for (A) metastable and (B) equilibrium configurations of Si_{60} . The solid line represents the average over three different light polarizations along x (.....), y (-----), and z (-.-.-) directions.

response along three different orthogonal directions is very similar, varying only in intensity, and related to their overall isotropic geometry.

The energetic, as well as the electronic and optical properties of metastable and equilibrium configurations of Si_{70} are similar to those described above for Si_{60} [9]. The gap of the metastable and equilibrium configurations are 0.44 eV and 0.40 eV, respectively [12]. The large geometric difference between equilibrium and ideal configurations of Si_{20} is dramatically reflected in $\epsilon(\omega)$ (not shown). While the ideal structure shows a metalliclike behavior with a large value of ϵ_2 for small frequencies, the equilibrium configuration has an optical gap of about 1.13 eV. The EDOS of ideal Si_{20} is more sparse than the one in the equilibrium structure. We also observe in $\epsilon(\omega)$, that the spectrum for the ideal configuration shows more peaks compared with the soft curve of the network structure. We can conclude that the equilibration process of Si_{20} is accompanied by a breaking of degeneracies in the levels near the Fermi level. A more detailed discussion of the geometrical configurations, the electronic and optical properties, will be presented elsewhere [9].

The results presented here are in general agreement with experimental [13] and theoretical [14] observations of optical spectra for chains of silicon atoms. It has been found that light absorption on chains consisting of small number of Si atoms ($n \leq 20$) occurs at higher energies than in longer structures. When the number of atoms in the chains increases, the energy absorption tends to a constant value ($n \geq 80$) [13]. Here, we find the same qualitative behavior in ϵ_2 . The optical gap of the equilibrium Si_{20} cluster is about 0.6 eV larger than that of Si_{60} , while this is only 0.1 eV larger than the gap of the equilibrium Si_{70} cluster [12].

In summary, we have developed a first-principles method to calculate the optical properties of clusters, surfaces and crystalline systems. This method is based on a localized orbitals basis set. We calculated the electronic and optical properties of the Si_{20} , Si_{60} , and Si_{70} clusters with different atomic configurations depending on their total energy. We found that ideal, metastable and equilibrium geometries have different optical response that strongly depend on the atomic size and configuration of the cluster. The results are in general agreement with experimental and theoretical observations.

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