Ab initio Calculations for the Polarizabilities of Small Semiconductor Clusters

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Polarizabilities of small Si_n, Ge_n ($n \leq 10$), and $\mathrm{Ga}_n\mathrm{As}_m$ ($n + m \leq 8$) clusters are calculated using the higher-order finite-difference pseudopotential method in real space. We find the polarizabilities of the clusters considered to be higher than the value estimated from the "hard sphere" model using the bulk static dielectric constant. The computed polarizabilities per atom tend to decrease with increasing the cluster size. This trend resembles the case of metallic clusters, for which the bulk limit is approached from above, and confirms the "metalliclike" nature of small semiconductor clusters. [S0031-9007(97)03429-7]

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Despite the fact that the electronic and structural properties of semiconductor clusters have been intensively investigated over the last decade, only two attempts to calculate the polarizabilities of some selected clusters have been reported [1,2]. The first approach was based on an empirical tight-binding method [1], and the second implemented an *ab initio* pseudopotential plane-wave technique [2]. Unfortunately, the available calculations exhibit rather strong diversity. The tight-binding calculations yield polarizabilities which overestimate the measured values. The plane-wave method also has some disadvantages. The conventional supercell approach introduces an artificial periodicity for localized systems. Since the position operator is not uniquely defined in a periodic environment, evaluating the polarizability is not trivial. In order to describe the polarizability in momentum space, the plane-wave method employs perturbation theory and evaluates the dielectric function on a spatial grid [3], which requires a large number of bands to be included in the calculations, and significantly increases computing time. On the other hand, our calculations are performed in real space, where polarizability can be defined in a very straightforward fashion, and the associated computational work requires minimal effort.

Our calculation technique is based on the higher-order finite-difference method [4]. We used Troullier-Martins nonlocal pseudopotentials [5] in Kleinman-Bylander form [6]. The exchange-correlation term was approximated by the Ceperley-Alder functional with the Perdew-Zunger parametrization [7]. With this approach, the Schrödinger equation for electronic states of a cluster was solved self-consistently on a three-dimensional Cartesian grid within a spherical domain. Boundary conditions were imposed on the system by requiring wave functions to vanish outside the sphere. This method has proved its efficiency for localized systems and has allowed us to determine the minimum-energy structures for the clusters of interest [8–10].

We implemented a finite-field method [11,12] to calculate the polarizability. In real space, we can include an external electric field into the Hamiltonian simply by adding one extra term to the effective potential:

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{\mathrm{eff}}(\mathbf{r}) - e\mathbf{F}\cdot\mathbf{r}\right)\phi_i(\mathbf{r}) = E\phi_i(\mathbf{r}), \qquad (1)$$

where the effective potential $V_{\mathrm{eff}}(\mathbf{r})$ includes ionic, Hartree, and exchange-correlation terms, $\phi_i(\mathbf{r})$ is the one-electron pseudowave function, and $\mathbf{F}$ is the applied uniform electric field. From the solution of Eq. (1), we can determine the dipole moment and the total ground-state energy as functions of the applied electric field.

The polarizability is defined by

$$\alpha_{ij} = \frac{\partial\mu_i(\mathbf{F})}{\partial F_j} = -\frac{\partial^2 E(\mathbf{F})}{\partial F_i \partial F_j}; \qquad i,j = \{x,y,z\}. \qquad (2)$$

Using the finite difference expressions for the first and second derivatives, we can find the diagonal elements of the polarizability tensor α_{ii} from the dipole moment $\boldsymbol{\mu}(\mathbf{F})$, or from the total energy $E(\mathbf{F})$ at $\mathbf{F} = 0$, and $\mathbf{F} = \pm\delta F_i$ applied along the ith axis. The value normally measured in experiments is the average polarizability given by $\langle\alpha\rangle = \frac{1}{3}\,\mathrm{tr}(\alpha_{ij}) = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$. Because of rotational invariance of the trace of the polarizability tensor, this value does not depend on the choice of the coordinate system.

To determine the ground-state structures, we proceeded as described in a previous work [8]. We used a grid spacing $h = 0.7$ a.u., and required at least an 8 a.u. separation between the position of any atom and the spherical boundary. The choice of these parameters was justified by the fact that no significant changes in the value of the total energy and the interatomic forces were detected with a further increase of the radius of the boundary sphere or decrease of the grid spacing. The resulting geometries of Si_n and Ge_n clusters with $n \leq 10$ are shown in Fig. 1(a). In all cases, the configurations of Ge_n clusters were found to be similar to those of Si_n with an average increase of interatomic distances by about 4%. Because of the large number of possible stoichiometries, the minimum-energy structures for $\mathrm{Ga}_n\mathrm{As}_m$ were determined only for clusters

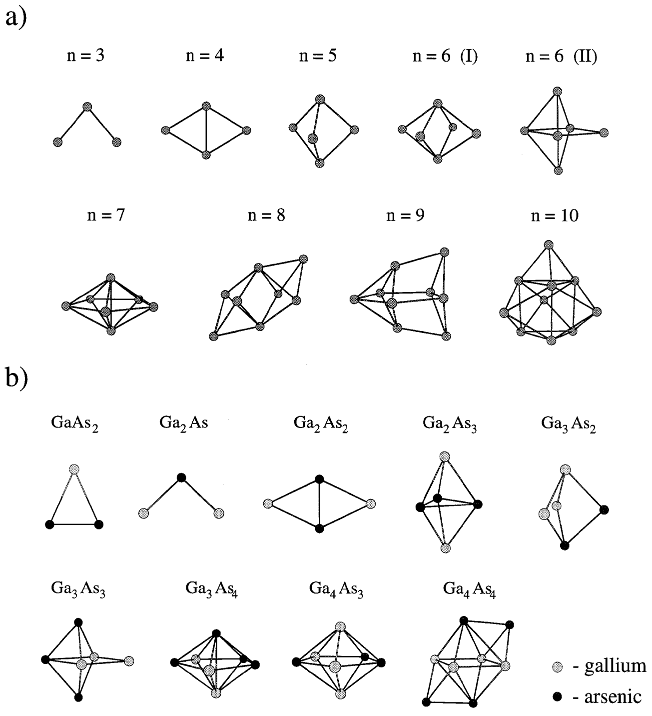

FIG. 1. (a) Structures of Si_n and Ge_n clusters. Two quasidegenerate isomers are shown for $n = 6$. (b) Structures of $\mathrm{Ga}_n\mathrm{As}_m$ clusters.

with the ratio n/m close to unity, and the total number of atoms ≤ 8. The calculated structures are shown in Fig. 1(b), and their geometries often resemble those of Si_n or Ge_n clusters with alternating Ga and As atoms. These results agree with recent calculations [8,9,13].

We found that a larger spherical domain had to be included in the polarizability calculations than that needed for the structural minimization. However, the computed polarizabilities were relatively insensitive to the size of the grid spacing. This behavior agrees with the fact that polarizabilities mainly depend on the "outer" part of the electron density of a cluster, whereas the "inner" part is responsible for the bonding properties. Therefore, we used $h = 0.8$ a.u., and increased the radius of the boundary sphere up to 16 a.u. In order to determine the stability of our calculations with respect to the magnitude of the applied electric field, we examined the influence of this parameter on the computed polarizabilities for several clusters. We found that the best region of linear response lies between $\delta F = 10^{-4}$–10^{-2} a.u., and that within this range the values of polarizabilities calculated from the total energy and from the dipole moment coincide within 1%. Consequently, for all polarizability calculations we have chosen δF to be 10^{-3} a.u. A test performed on a CO molecule demonstrated that our calculated polarizability of 1.99 Å^3 was in good agreement with the experimental value of 1.95 Å^3 [14]. We also investigated the possible influence of relaxing ionic positions in the finite field calculations. We found that including ionic relaxation does not affect the calculated polarizabilities to within $\sim$(2–3)%.

Our results are summarized in Table I. The static dipole moments were computed by direct summation over all grid points at zero electric field. The listed data for polarizabilities are the average polarizabilities divided by the total number of atoms in the cluster. We compared the data in Table I for single atoms with polarizabilities determined by pseudonatural-orbital calculations [15] and found that our values typically agree with those within (5–10)%. Our calculated polarizabilities for Si_4 and Si_6 are in excellent agreement with other *ab initio* calculations performed with a plane-wave basis, which report $\langle \alpha \rangle = 5.0$, 4.3, and 4.4 Å^3/atom for Si_4, Si_6 (I), and Si_6 (II), respectively [2].

The variation of the computed values for polarizabilities with the number of atoms in the cluster is shown in Fig. 2. As a reference, we included the bulk limit for the polarizability, estimated from the Clausius-Mossotti relation:

$$\alpha = \frac{3}{4\pi}\left(\frac{\varepsilon_b - 1}{\varepsilon_b + 2}\right)v_{\mathrm{at}}\,, \tag{3}$$

where v_{at} is an elementary volume per atom in the crystalline state, and ε_b is the bulk dielectric constant. Equation (3) yields $\alpha = 3.71$ Å^3/atom for silicon, 4.50 Å^3/atom for germanium, and 4.14 Å^3/atom for gallium arsenide. Figure 2 demonstrates that in all cases our values lie higher than the corresponding bulk estimate, and the polarizabilities decrease with increasing the size of the cluster.

In some respects, semiconductor clusters resemble metallic clusters. They tend to have higher coordination numbers than that in the crystalline state. In fact, these structures are thought to be more closely related to the high pressure metallic phases than to the diamond structure [16]. It has been shown that polarizabilities of typical metallic clusters, such as Li_n, Na_n, and K_n, significantly exceed the bulk limit, and tend to decrease with increasing the cluster size [17]. The fact that we found similar tendencies in the polarizabilities of Si_n, Ge_n, and $\mathrm{Ga}_n\mathrm{As}_m$ clusters confirms the "metalliclike" nature of small semiconductor clusters.

The only available experimental data [18,19] report polarizabilities for gallium arsenide and silicon clusters to reside above and below the bulk limit. Unfortunately, those data mostly refer to larger particles ($n = 9$–120 for Si_n and $n + m = 4$–30 for $\mathrm{Ga}_n\mathrm{As}_m$). Therefore, the correlation between computed and measured polarizabilities is not straightforward. The experimental data for gallium arsenide indicate higher polarizabilities for clusters with an odd number of atoms. The suggested explanation [19] connects this phenomenon with the value of the energy gap in a cluster. The simple perturbation theory (using one-electron wave functions) provides the following

TABLE I. Static dipole moments (debyes) and average polarizabilities (Å^3/atom) of semiconductor clusters.

Silicon			Germanium			Gallium arsenide		
Cluster	$\lvert\mu\rvert$	$\langle\alpha\rangle$	Cluster	$\lvert\mu\rvert$	$\langle\alpha\rangle$	Cluster	$\lvert\mu\rvert$	$\langle\alpha\rangle$
Si	0	6.12	Ge	0	6.45	Ga	0	8.63
Si_2	0	6.29	Ge_2	0	6.67	As	0	4.83
Si_3	0.33	5.22	Ge_3	0.43	5.89	GaAs	1.74	6.38
Si_4	0	5.07	Ge_4	0	5.45	$GaAs_2$	0.46	5.16
Si_5	0	4.81	Ge_5	0	5.15	Ga_2As	1.68	6.47
Si_6 (I)	0	4.46	Ge_6 (I)	0	4.87	Ga_2As_2	0	5.66
Si_6 (II)	0.19	4.48	Ge_6 (II)	0.14	4.88	Ga_2As_3	0	4.79
Si_7	0	4.37	Ge_7	0	4.70	Ga_3As_2	0.95	5.17
Si_8	0	4.52	Ge_8	0	4.99	Ga_3As_3	0.41	4.79
Si_9	0.36	4.38	Ge_9	0.28	4.74	Ga_3As_4	0.39	4.81
Si_{10}	0.69	4.31	Ge_{10}	0.68	4.66	Ga_4As_3	0.06	4.87
						Ga_4As_4	0	4.63

expression for polarizability:

$$\alpha_{ii} = 2 \sum_{k,l}{}' \frac{|\langle k|\mu_i|l\rangle|^2}{E_l - E_k}, \qquad (4)$$

where the matrix elements correspond to dipole transitions between occupied and unoccupied states. If one makes the assumption that the contribution from transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) constitute the major part of polarizability, then polarizability can be related to the energy gap, $E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$. In our calculations, the general tendency $\alpha^{n=m+1} > \alpha^{n=m-1}$ for Ga_nAs_m clusters was consistent with $E_g^{n=m+1} < E_g^{n=m-1}$. However, our calculations do not confirm the proposed hypothesis [19] about donorlike and acceptorlike states in small gallium arsenide clusters with odd number of atoms (i.e., $E_g^{n+m=\mathrm{odd}} \ll E_g^{n+m=\mathrm{even}}$). Furthermore we found the average polarizabilities $\alpha^{\mathrm{odd}} = \frac{1}{2}(\alpha^{n=m+1} + \alpha^{n=m-1})$ to be close to α^{even} for adjacent clusters. We also found that in Eq. (4) the higher energy transition matrix elements can be equally important, or even be dominant, depending on the value of the HOMO → LUMO matrix element. For clusters where this matrix element vanishes, polarizability cannot be related to E_g as defined above.

In order to compare our results with experimental data, it is essential to keep in mind that the average polarizability can be directly measured in experiments only if the static dipole moment of the cluster is zero. Otherwise, the experimental value typically includes an additional contribution from the dipole rotating in external electric field. In the high temperature or low field limit, the effective measured polarizability becomes

$$\alpha_{\mathrm{eff}} = \langle\alpha\rangle + \frac{\mu^2}{3kT}, \qquad (5)$$

where $\langle\alpha\rangle$ is the average polarizability and μ is the static dipole moment of the cluster. Evaluating Eq. (5) at room temperature with our data from Table I, we found this correction to be less than 10% for all Si_n and Ge_n clusters with $\mu \neq 0$. However, it can be significant for Ga_nAs_m clusters with high dipole moments, e.g., our calculations yield $\alpha_{\mathrm{eff}} = 18$ Å^3/atom for GaAs, 14 Å^3/atom for Ga_2As, 5.7 Å^3/atom for $GaAs_2$, and 6.6 Å^3/atom for Ga_3As_2. In general (with the exception of the GaAs diatomic molecule), the contribution to the measured polarizabilities from the static dipole moment tends to be greater for Ga_nAs_m clusters with $n \neq m$. This may account, at least in part, for the experimentally observed even/odd oscillations of the polarizabilities with the cluster size.

It is worthwhile to compare our results to related work on semiconductor clusters. For example, the polarizabilities which we calculate are larger than the values obtained for quantum dots [20]. The effects of confinement in quantum dots tend to increase the gap and, as a consequence, lower the polarizability. However, these systems are not comparable to our small clusters. Quantum dots, which are truncated *bulk* fragments passivated at the boundaries, do not possess free surfaces in contrast to the clusters considered here. The contribution to the polarizabilities from the unsaturated bonds at the cluster surface dominate, and result in large polarizabilities. For larger clusters, it is conceivable that the effects of confinement may exceed the contribution from the free surface. This, in addition to the changes in growth patterns from open to more compact geometries as the size is increased [21], may lower the polarizabilities. This would be consistent with the recent experimental work for the larger clusters [18].

In conclusion, we have implemented a real-space *ab initio* computational technique to calculate polarizabilities of small Si_n, Ge_n, and Ga_nAs_m clusters. Our calculations indicate that in all considered cases the polarizabilities lie higher than the value estimated from the "hard sphere" model with the bulk static dielectric constant. This work represents the first systematic theoretical study for the polarizabilities of semiconductor clusters.

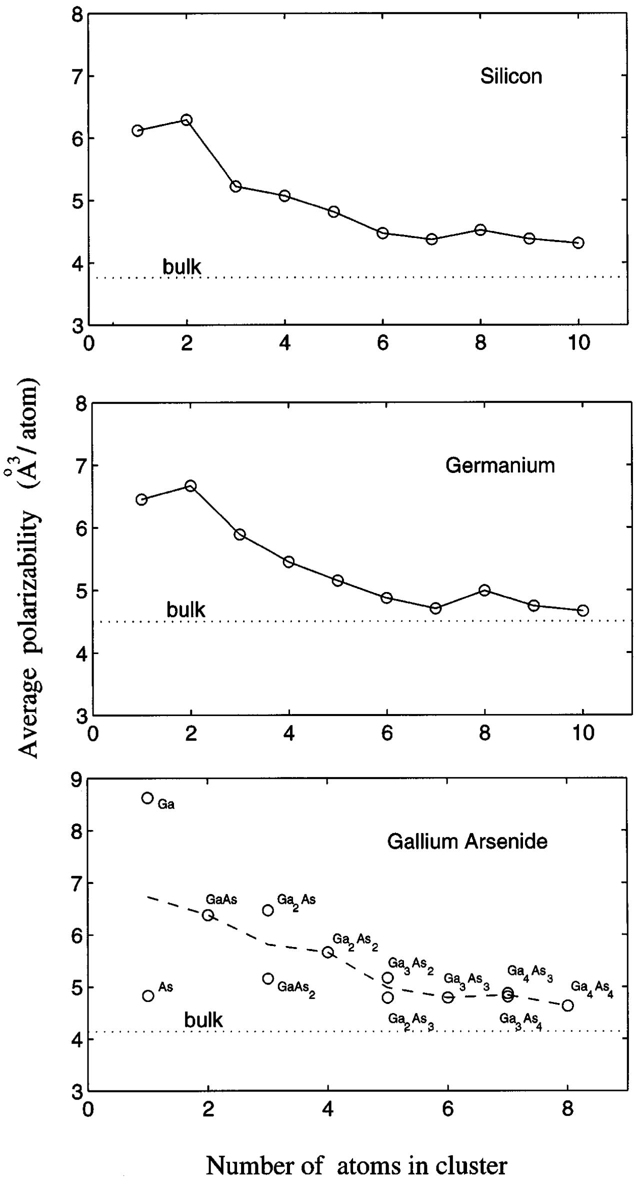

FIG. 2. Average polarizabilities per atom of Si_m, Ge_n, and $\mathrm{Ga}_n\mathrm{As}_m$ clusters vs cluster size. Dotted lines correspond to the bulk polarizabilities calculated according to Eq. (3). For $\mathrm{Ga}_n\mathrm{As}_m$ clusters with an odd number of atoms the dashed line passes through the midpoint between polarizabilities of Ga-rich and As-rich structures.

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