Polarizabilities of Germanium Clusters

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Polarizabilities of Geₙ clusters with 2 to 25 atoms are calculated using coupled-perturbation Hartree-Fock (CPHF) and finite field (FF) method within density functional theory. The polarizabilities of the Geₙ clusters increase rapidly in the size range of 2 to 5 atoms and then fluctuate around the bulk value. The polarizabilities are sensitive dependent on the cluster geometries and electronic structures. The large HOMO-LUMO gap may lead to the small polarizability. As compared with the compact structure and diamond structure, the prolate cluster structure corresponds to a larger polarizability.

In the past two decades, the structural and electronic properties of semiconductor clusters have been extensively studied because of their fundamental interest and potential application in nanoelectronics. The small semiconductor clusters are well understood up to 10 atoms. But our knowledge for larger clusters is still quite limited. The polarizability is one of the most important quantities of the clusters, which can yield the static dielectric constant in the bulk limit through Clausius-Mosotti relation. On the other hand, the polarizability can provide some information on the bonding and geometrical features of the clusters. Thus, comprehensively understanding of the polarizabilities from theoretical calculations is important in cluster science. The jellium model was successfully applied to study the polarizability of large metallic clusters. But for semiconductor clusters, the bonding and geometrical effects are not incorporated in the jellium model. Alternatively, the ab initio calculations based on quantum chemistry methods are needed. There were only few previous ab initio calculations on the polarizabilities of the clusters. Especially, for the germanium clusters, there is only one attempt to calculate the polarizabilities and the cluster size is quite limited.

In our previous studies, the geometries of Geₙ clusters (n = 2 − 25) have been obtained by density functional DMOl calculations incorporated with a genetic algorithm. It was found that the Geₙ clusters follow a prolate growth pattern with n ≥ 13. The stacked layered structure and the compact structure compete with each other in intermediate size range. Based on the previously optimized low-energy structures, in this paper, we will study the polarizabilities of these clusters using the analytically coupled-perturbation Hartree-Fock (CPHF) and numerically finite field (FF) methods within density functional theory. We aim to explore the size dependence of the polarizability, the influence of the atomic and electronic structures on the polarizabilities of the Geₙ cluster.

It is well known that electron correlation plays a primary role in determining molecular polarizabilities. DFT treatment has been proven to make significant improvement to Hartree-Fock results in molecular polarizabilities and hyperpolarizabilities calculations. Within DFT framework, B3LYP functional considers the hybrid between the Hartree-Fock exchange and Kohn-Sham orbitals, while LANL2DZ basis set can give a good description of the bonding and geometrical features of heavy atoms. Thus, B3LYP/LANL2DZ scheme is expected to well describe the cluster polarizabilities at acceptable computational cost. Here, all these calculations are performed at B3LYP/LANL2DZ level by using Gaussian98 package.

The energy in an external electric field can be expanded as

\[ E(F) = E(0) - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \cdots \]  

where \( E(0) \) is the energy without the external field, \( F_i \) are components of the applied field. The dipole moment \( \mu_i \) and the polarizability \( \alpha_{ij} \) are defined as:

\[ \mu_i = -\left( \frac{\partial E}{\partial F_i} \right) \]  

and

\[ \alpha_{ij} = -\left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right) \quad (i, j = x, y, z) \]  

Within Kurtz’s finite field method, the dipole moment and polarizability in a uniform field, can be derived from the follow equations.

\[ \mu_i F_i = -\frac{2}{3} [E(F_i) - E(-F_i)] - \frac{1}{12} [E(2F_i) - E(-2F_i)] \]  

\[ \alpha_{ii} F_i = \frac{5}{2} E(0) - \frac{1}{3} [E(F_i) + E(-F_i)] + \frac{1}{12} [E(2F_i) - E(-2F_i)] \]
To calculate the dipole μ and the polarizability α, at least 13 self-consistent field (SCF) runs are necessary with the field strengths ±Fi and ±2Fi (i = x, y, z). One of the most severe problems in finite-field method is the choice of an appropriate field strength. Sim et al. have assessed the numerical accuracy against different field values and concluded that stable linear and nonlinear polarizabilities can be obtained when F equals 0.001 ~ 0.005 a.u. In this work, the external field is added along x, y, z with the magnitude 0.001 a.u and a tighter SCF convergence criterion of 10\(^{-9}\) is adopted.

The measured data in experiments are usually the average polarizabilities, which can be obtained by

\[
< \alpha > = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

(6)

The optimized structures for Ge\(_{11-25}\) clusters at B3LYP/LANL2DZ level are shown in Fig. 1. Similar equilibrium configurations are found by DMol and Gaussian98. Therefore, the details for the structures will not be discussed here.

![Fig. 1. Lowest energy structures for Ge\(_n\) (n = 11 – 25) clusters.](image)

Table I. The dipole moments µ (Debyes), polarizabilities α(Å\(^3\)/atom) of Si\(_{2-10}\) clusters: \(\alpha^a\): present results, \(\alpha^b\): Ref. 28, \(\alpha^c\): Ref. 32, \(\alpha^d\): Ref. 49, (in bracket): Ref. 28.

| n | µ\(_{\text{CPHF}}\) (PRL) | µ\(_{\text{FF}}\) | α\(^a\) | α\(^b\) | α\(^c\) | α\(^d\) |
|---|-----------------|-------------|--------|--------|--------|--------|
| 2 | 0(0)            | 0           | 4.10   | 1.69   | 0.31   |
| 3 | 0.61(0.43)      | 0.241       | 5.07   | 2.84   | 1.32   |
| 4 | 0(0)            | 0           | 5.14   | 3.23   | 1.14   |
| 5 | 0(0)            | 0           | 5.52   | 3.32   | 1.48   |
| 6 | 0.15(0.14)      | 0           | 5.36   | 3.41   | 1.39   |
| 7 | 0(0)            | 0           | 5.27   | 3.50   | 1.36   |
| 8 | 0.55(0)         | 0.22        | 5.47   | 3.44   | 1.10   |
| 9 | 0.12(0.28)      | 0.05        | 5.39   | 3.48   | 1.22   |
| 10| 0.56(0.68)      | 0.22        | 5.17   | 3.59   | 1.31   |
| 11| 1.35            | 0.53        | 5.24   | 3.53   | 0.99   |
| 12| 1.58            | 0.62        | 5.33   | 3.49   | 1.05   |
| 13| 0.82            | 0.32        | 5.45   | 3.57   | 0.98   |
| 14| 1.30            | 0.51        | 5.41   | 3.61   | 1.20   |
| 15| 0.18            | 0.07        | 5.44   | 3.57   | 0.80   |
| 16| 0.74            | 0.29        | 5.39   | 3.61   | 1.17   |
| 17| 1.11            | 0.24        | 5.52   | 3.59   | 0.94   |
| 18| 0.61            | 2.75        | 5.61   | 3.58   | 0.90   |
| 19| 0.46            | 0.18        | 5.41   | 3.63   | 0.70   |
| 20| 1.06            | 0.46        | 5.51   | 3.61   | 0.89   |
| 21| 1.70            | 0.67        | 5.54   | 3.62   | 0.94   |
| 22| 0.51            | 0.20        | 5.45   | 3.63   | 0.81   |
| 23| 2.89            | 1.14        | 5.62   | 3.62   | 0.82   |
| 24| 2.52            | 0.99        | 5.69   | 3.64   | 0.62   |
| 25| 0.52            | 0.21        | 5.63   | 3.61   | 0.70   |

Table II. The dipole moments µ, polarizabilities α(Å\(^3\)/atom), binding energies \(E_b\) (eV), HOMO-LUMO gaps \(\Delta\) (eV) of Ge\(_n\) clusters: \(\mu_{\text{CPHF}}\) (Debyes): CPHF method; \(\mu_{\text{FF}}\) (a.u.): FF method; in bracket: Ref. 28.

To check the validity of current method, we firstly calculate the dipole polarizability of small silicon clusters. Table I compares our calculations with previous theoretical and experimental results. The current theoretical dipole moments for the clusters Si\(_2-7\) are in agreement with Vasiliev et al. But our results for the dipole moment of Si\(_8-10\) clusters are different due to the substantial difference in geometrical configurations. The present geometric structures for Si clusters are consistent with those obtained by Shvartsburg et al. and Li et al. Our calculated polarizabilities seem to be overestimated as compared with Vasiliev et al., but consistent with Deng et al. Moreover, the present polarizabilities are sensitively dependent on the cluster size and oscillate with the cluster size. While the polarizabilities in Vasiliev’s work tend to decrease with the increase of the size. Experiments show that the polarizabilities fluctuate with the cluster size.
Table II gives the dipole moments, average polarizabilities, binding energies and HOMO-LUMO gap as functions of the cluster size. The dipole moments calculated with CPHF method and FF method are compared and agree well with each other. The dipole moment reflects the symmetry of the geometrical structure: the smaller dipole moment corresponds to the higher symmetry. The dipole moments for the clusters with \( n = 2, 4, 5, 7 \) are nearly zero, corresponding to the high symmetry in these clusters. For Ge\(_8\), the lowest energy structure is D\(_{2h}\) rhombo, while they are trigonal bipyramid with D\(_{3h}\) and pentagonal bipyramid (D\(_{5h}\)) for Ge\(_5\) and Ge\(_7\). In the case of Ge\(_8\), Ge\(_9\) and Ge\(_{10}\), capped pentagonal bipyramid, tricapped trigonal prism and tetracapped trigonal prism have favorable energy, respectively. The dipole moments and the polarizabilities of small Ge clusters are compared with Vasiliev et al.\(^{23}\) and our calculations seem to be a little underestimated.

Fig.2 gives the polarizabilities of Ge\(_n\) clusters as a function of the cluster size for Ge\(_n\). The prolate configuration is preferred for medium-sized Ge clusters, which occupies larger distortion and lower symmetry in comparison with diamond structure. Thus, the polarizability of the clusters is larger than that of the bulk. It is worthy to note that the present results is quite different from Vasilier’s.\(^{24}\) Compared with their method, the present scheme incorporate the electron correlation in the calculation of the polarizability of small clusters.

We further discuss the relationship between the polarizability and the electronic structures of clusters. Fig.3 plots the polarizabilities as a function of the HOMO-LUMO (highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO)) energy gaps. As shown in Fig.3, the large polarizability generally corresponds to the small HOMO-LUMO gap. The clusters with \( n = 8, 11, 13, 15 \) have relatively smaller polarizabilities in comparison with their neighboring size. For example, the HOMO-LUMO gap for Ge\(_8\) is 1.10eV and the polarizability is just 5.17 \( \text{Å}^3/\text{atom} \). The polarizabilities decrease with the increase of the HOMO-LUMO gap except for the clusters Ge\(_2\), Ge\(_5\) and Ge\(_{19} \sim 22\). This can be easily rationalized using the two-level model\(^{22}\),

\[
\alpha \sim \frac{\mu^2}{\Delta_t}
\]

where \( \mu^2 \) is the transition dipole moment from the ground state to the first dipole-allowed excited state and \( \Delta_t \) the corresponding transition energy. Approximately, \( \Delta_t \) can be replaced with HOMO-LUMO energy gap \( \Delta \). From this model, \( \alpha \) increases with decreasing \( \Delta \), consistent with our calculated trend for most Ge clusters. However, \( \alpha \) is not a simply inverse proportion relation to \( \Delta \), since the two quantities are dependent each other. Small \( \Delta \) tends to generate large \( \mu^2 \). In addition, \( \mu^2 \) depends on some other characters, such as selection rule.

However, the polarizability of the cluster is not only dependent on HOMO-LUMO gap but also closely related to geometrical characteristics. For example, the HOMO-LUMO gap of Ge\(_{18}\) is larger than that of Ge\(_{19}\), while the polarizability of the former is larger than that of the latter. This can be attributed to their structural difference. For Ge\(_{18}\), the optimized structure is two interpenetrate pentagonal connected with a bicapped square antiprism Ge\(_{10}\) subunit, while a more compact cage-like geometry is favorable to Ge\(_{19}\). The compact structures have relatively less and shorter bonds, which leads to the valence electrons binding tighter. Thus, a smaller volume is obtained in the compact structure, which causes a smaller polarizability for Ge\(_{19}\). Similarly, the different polariz-
abilities behavior of the clusters with \( n = 19 - 22 \) can be explained in the light of their respectively geometrical characteristics. For \( \text{Ge}_{20} \) and \( \text{Ge}_{21} \), their optimized structures are stacked layer configurations and have the comparable volume, which leads to their almost same polarizabilities. In the case of \( \text{Ge}_{19} \) and \( \text{Ge}_{22} \), since our calculated lowest energy structures are both near-spherical compact structures, they also have the tantamount polarizability.

In conclusion, we have calculated dipole moments and polarizabilities of \( \text{Ge}_n (n = 2 - 25) \) clusters with both CPHF and FF approaches under B3LYP/LANL2DZ scheme. The main results are summarized as following. (1) The Ge clusters with \( n = 2, 4, 5, 7 \) have relatively higher symmetry and the dipole moments are nearly zero. (2) The polarizabilities of small clusters increase rapidly in the range of 2 to 5 and fluctuate around \( 5.4 \, \text{Å}^3/\text{atom} \). Moreover, the polarizabilities of the clusters with \( n = 8, 11, 13, 15 \) are larger than the neighboring ones. (3) The polarizabilities are closely related to the HOMO-LUMO gaps and the geometrical configurations. The larger the HOMO-LUMO gap, the smaller the polarizability of the Ge clusters. The prolate structures corresponds to relatively large polarizabilities in comparison with the compact structures.

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