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Static dielectric response of icosahedral fullerenes from C_{60} to C_{2160} characterized by an all-electron density functional theory

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The static dielectric response of C_{60}, C_{180}, C_{240}, C_{540}, C_{720}, C_{960}, C_{1500}, and C_{2160} fullerenes is characterized by an all-electron density functional method. First, the screened polarizabilities of C_{60}, C_{180}, C_{240}, and C_{540} are determined by the finite-field method using Gaussian basis set containing 35 basis functions per atom. In the second set of calculations, the unscreened polarizabilities are calculated for fullerenes C_{60}–C_{2160} from the self-consistent Kohn-Sham orbitals and eigenvalues using the sum-over-states method. The approximate screened polarizabilities, obtained by applying a correction determined within linear response theory, show excellent agreement with the finite-field polarizabilities. The static dipole polarizability per atom in C_{2160} is (4 Å^3) three times larger than that in C_{60} (1.344 Å^3). Our results reduce the uncertainty in various theoretical models used previously to describe the dielectric response of fullerenes and show that quantum size effects in polarizability are significantly smaller than previously thought.

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I. INTRODUCTION

Reduction in the spatial dimensions in nanoparticles results in a number of interesting properties such as the widening of the band gap, reduction in melting temperature, increased magnetic moments, etc. The fundamental understanding of the size dependence of properties of nanoparticles, i.e., at what size the quantum size effects set in, is important for tailoring these systems for possible nanotechnological applications. Studies along these lines continue to be frontline research in nanoscience.[1–9]

Fullerenes are hollow cages formed by sp^2 bonded carbon atoms. They are finite analogs of graphene with 12 pentagonal defects that introduce curvature and make them closed structures. Unlike the most nanoparticles, however, fullerenes are distinctly different in that they have all the atoms on the surface whereas solid spherical nanoparticles have roughly $N^{1/3}$ atoms on the surface. This feature results in rapid increase in their volume as the number of atoms (i.e., its size) increases. As dipole polarizability is proportional to volume, fullerenes are most suitable for investigating quantum size effects manifested in polarizability. The large dipole polarizability of carbon fullerenes compared to that of metallic or dielectric spheres of same size has been previously interpreted as quantum size effect.[10] A number of studies on the polarizability of fullerenes have been devoted to understanding its size dependence.[10–12] These studies have been mainly based on classical models or have employed drastic approximations to simplify the polarizability calculations. Unfortunately, the predictions of these models are not consistent with each other and show rather large variance. For example, the various predictions of the polarizability of the C_{2160} (see Table I) are 7100 Å^3 (Pariser-Parr-Pople model[11]), 2726 Å^3 (bond-order-bond polarizability[12]), 9548 Å^3 (Penn model-linear response theory[10]), and 17 817 Å^3 (tight binding[10]). The predictions from different models of fullerene polarizabilities and associated quantum size effects differ by almost an order of magnitude. The most reliable methods to determine electronic structure are the first-principles-based quantum-chemical methods. In the present work, we use the first-principles density functional methods to accurately determine the first order electric response of carbon fullerenes of sizes from C_{60} to C_{2160} by computing their static dipole polarizabilities. These calculations provide the most accurate prediction of the dielectric response of fullerenes in the size range C_{60}–C_{2160} and show substantial quenching of quantum size effects by C_{960} in contrast to current understanding. Moreover, the fullerene polarizabilities computed herein also provide an accurate input to the models used in determination of the ultraviolet (UV) spectrum for possible detection of hyperfullerene particles in space.[13]

II. THEORY, RESULTS, AND DISCUSSION

The first essential step in obtaining an accurate estimate of polarizability of fullerene involves accurate determination of the fullerene structure. We optimized the geometry of carbon fullerenes using recent fully analytic and variational formulation of density functional (ADFT) theory.[14–19] Being free of numerical grids, the ADFT implementation is computationally very efficient and allows calculations of matrix elements and energies accurate to machine precision. Its functional form is restricted but its space of atomic parameters is rich. It has been successfully used to study electronic properties of boron nitride, aluminum nitride cages and nanotubes,[20–22] and provides dipole moments, total and atomization energies that are comparable to those obtained using some of the most sophisticated density functional models. In this work, we optimized the geometries of C_{60}, C_{240}, C_{540}, C_{960}, C_{1500}, and C_{2160} fullerenes from the $60N^2$ family of icosahedral fullerenes. Additionally, two fullerenes (C_{180} and C_{720}) from the $180N^2$ family are also optimized. The structures (cf. Fig. 1) are optimized at the all-electron level

TABLE I. The average ionic radius $\bar{r}$ (in Å) and polarizabilities (in Å^3) obtained in various models: bond-order-bond polarizability (BOBP) (Ref. 12), α_{PPP}. Pariser-Parr-Pople approach (Ref. 11), α_{Penn}: classical electrostatic within linear response theory (Penn model) (Ref. 10), TB: tight binding (Ref. 10), α_{SOS}: sum-over-states ADFT (present), α_{RPA}: sum-over-states-ADFT-RPA (present), α_{FF}: finite-field PBE-GGA (DFT) (present), and ϵ: estimates of static dielectric constant for fcc structures.

Fullerene	$\bar{r}$	BOBP	α_{PPP}	α_{Penn}	TB	α_{SOS}	α_{RPA}	α_{FF}	ϵ
C_{60}	3.55	76	80	64	81	292	79	82	4.50
C_{180}	6.13	227	209			1202	300	295	4.76
C_{240}	7.07	303	306	343	581	1754	432	441	4.79
C_{540}	10.27	681	866	1026	1869	4823	1155	1193	4.71
C_{720}	12.17	909	1390			8000	1848		4.96
C_{960}	14.03	1212	2150	2185	4290	12023	2745		5.00
C_{1500}	17.94	1893	4415			29706	5690		5.61
C_{2160}	21.01	2726	7100	9548	17817	38288	8548		5.01

using the triple-zeta-quality (6-311G**) orbital basis[23] and an exchange-correlation basis set that includes f functions, and the exchange-correlation parametrization that gives an exact C_{60} geometry.[24] These approximations give accurate geometries in a very efficient manner, which we verified by reoptimizing the larger C_{240} fullerene using even larger NRLMOL basis (35 basis functions per atom) and using the more complex and popular Perdew-Burke-Ernzerhof (PBE)[25] generalized gradient approximation (GGA). Both models give identical C_{240} geometries within a root-mean-square value of 10^{-3} a.u. for the forces.

For the polarizability calculations the fullerene structures are held rigid, i.e., the ionic (vibronic) contribution to dipole polarizabilities is ignored. This is a tenable assumption as our earlier studies on C_{60} and C_{70} show that in fullerenes electronic part determines the total polarizability with negligible contributions from the ionic vibrations.[26,27]

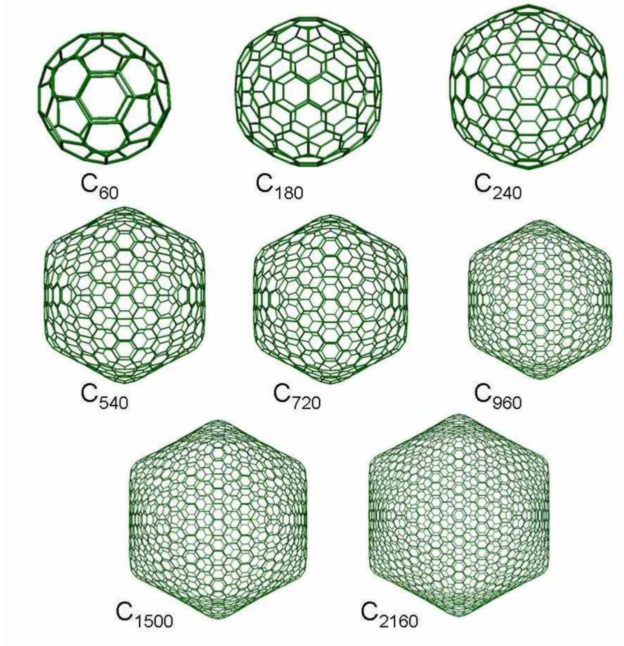

FIG. 1. (Color online) The fullerenes structures optimized at ADFT/6-311G** level of theory for which polarizabilities are calculated.

We have determined polarizabilities within two computational models. In the first set of calculations polarizabilities of C_{60}, C_{180}, C_{240}, and C_{540} are obtained by the *finite-field* method,[28–33] using the NRLMOL code.[34–36] In NRLMOL, optimal numerical grids are used to obtain the energies and the contributions to matrix elements from the exchange-correlation terms. It is well known that an accurate description of electric response requires use of high quality basis sets. Here, we use large Gaussian basis sets consisting of 5 s-, 3 p-, and 1 d-type Gaussians each contracted from 12 primitive functions.[37] This basis set is given in Table II. More details about the basis set can be found in Refs. 26, 37, and 38. Further inclusion of long range d-type basis functions increased polarizability of C_{60} by only 0.6%. Therefore, the polarizabilities α of C_{180}, C_{240}, and C_{540} were computed without any additional diffuse functions to avoid linear dependency of basis sets. The total number of basis functions in the finite-field polarizability calculations with NRLMOL range from 2100 in C_{60} to 18 900 in C_{540}. The latter is com-

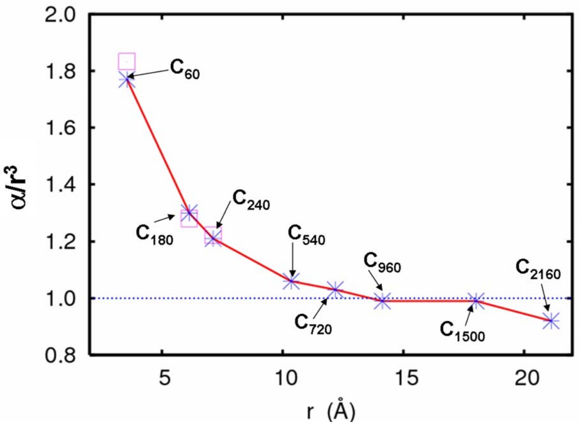

FIG. 2. (Color online) The ratio of polarizability, α_{RPA}, and volume, $\bar{r}^3$, as a function of fullerene radius $\bar{r}$. The squares represent polarizability obtained by the finite-field method.

TABLE II. The details of the Gaussian basis set used in polarizability calculation. The exponent (α), and contraction coefficients $c(1s)$, $c(2s)$, and $c(2p)$ are listed below. The basis set also contains single Gaussians. For the s and p functions we use $\alpha_{10}-\alpha_{12}$. The d functions use $\alpha_9-\alpha_{12}$.

α (bohr^{-2})	$c(1s)$	$c(2s)$	$c(2p)$
22213.361000	0.197922	−0.045005	0.023139
3331.737000	0.369990	−0.084621	0.042649
757.901350	0.636446	−0.144966	0.074659
214.543720	1.012493	−0.235356	0.120241
69.924889	1.448079	−0.342154	0.183512
25.086135	1.717369	−0.445951	0.247068
9.591042	1.493193	−0.452640	0.307142
3.802456	0.689872	−0.322164	0.313727
1.489185	0.086072	−0.012988	0.267263
0.574877	−0.001657	0.201355	0.147566
0.214947	0.000378	0.127699	0.047586
0.077210	−0.000047	0.014135	0.007280

parable to the 38 880 orbital basis functions used in our ADFT calculation on C_{2160}. The mean polarizability is obtained from the diagonal elements of the polarizability matrix whose components can be determined either from the total energies or from the induced dipole moments at various field strengths. The polarizabilities obtained using these two approaches agree within 1%. The finite-field α values are given in the third-to-last column of Table I. Although the finite-field method is perhaps the best approach to calculate polarizabilities, the computational cost becomes prohibitive for larger fullerenes. The cost rises principally due to the very large number of self-consistent cycles required to obtain tightly converged energies (10^{-9} a.u.) in presence of the external electric fields. It is necessary to keep the convergence criteria tight to extract meaningful estimates of polarizability by the finite-field method. Therefore, we resort to an approximate technique that uses the unscreened polarizability obtained by the sum-over-states (SOS) method and the linear response theory and random phase approximation to estimate the screened polarizabilities from the α_{SOS}. In the independent electron model, the working SOS expression for the xy component of polarizability tensor can be written as

$$\alpha_{xy} = 2 \sum_{m}^{unocc} \sum_{n}^{occ} \frac{\langle\psi_m|\hat{x}|\psi_n\rangle\langle\psi_n|\hat{y}|\psi_m\rangle}{|\epsilon_m - \epsilon_n|}. \tag{1}$$

Here, the $\{\psi_i\}$ are single particle orbitals and the ϵ_i is the single particle energy of the ith orbital. The $\alpha_{SOS}=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ is calculated according to Eq. (1) once the self-consistent solution of the Kohn-Sham equations for each fullerene is obtained using the ADFT code. The computational efforts involved in determining the large number of transition dipole moments are reduced by making use of group theoretical techniques. The calculated α_{SOS} for fullerenes $C_{60}-C_{2160}$ are given in the correspondingly labeled column of Table I. The unscreened α_{SOS} for C_{60} is 292 Å^3, which compares well [282 Å^3 (Ref. 39) and 311 (Ref. 40)] with previous predictions with different basis sets and exchange-correlation functionals.

The α_{SOS} determined using Eq. (1) gives unscreened polarizability since the field-induced polarization effects (local field effects) are missed in the calculations. Consequently, the α_{SOS} overestimates the experimentally accessible screened polarizability.[41] For the smallest fullerene (C_{60}), α_{SOS} is roughly 3.6 times larger than the screened polarizability in agreement with previous reports.[39,40] This overestimation slightly increases (to a factor ~4) for C_{180}, C_{240}, and C_{540} as can been seen from comparison of α_{SOS} and α_{FF} from Table I. The screened polarizability can be deduced from α_{SOS} using the linear response theory[42] and the random phase approximation (RPA) by means of the following expression:

$$\alpha_{RPA} = \left[1 + \frac{\alpha_{SOS}}{R^3}\right]^{-1} \alpha_{SOS}. \tag{2}$$

Here, R is the fullerene radius.[42] For fullerenes (larger than C_{60}) that are polyhedral in structure, the average ionic radius can be used. The average ionic radii $\bar{r}$ are also given in Table I. Instead of using the ionic radii of fullerenes in Eq. (2) which tend to overcorrect the screening, it is more appropriate to use an effective radius $\bar{r}+\delta$. The factor δ accounts for the π electron cloud around the bare nuclear skeleton. Its typical values are 1.2–1.3 Å.[42] Similar methods of determining the screened electronic response have been used in the past for carbon fullerenes,[10,43] multishell carbon fullerenes–carbon onions,[44] and (cylindrical) carbon nanotubes.[42] However, as we shall see, an accurate initial self-consistent treatment is necessary to get a meaningful estimate of the screened polarizability from Eq. (2). The α_{RPA} determined using Eq. (2) (with δ=1.23 Å) are listed in Table I. It is apparent that α_{RPA} obtained within the ADFT are quite accurate as can be gleaned from comparison of α_{FF} and α_{RPA} for C_{180}, C_{240}, and C_{540}. The α_{RPA} is within 3% of α_{FF} for these fullerenes. This excellent agreement provides confidence in the α_{RPA} values of the larger fullerenes for which a direct calculation of the self-consistent response by means of the finite-field method is impractical.

The electronic structure of these fullerenes shows that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) belong to the h_u and t_{1u} irreducible representations of the icosahedral point group. The lowest HOMO-LUMO ($h_u \to t_{1u}$) excitation is forbidden by dipole selection rule and does not contribute to the polarizability. The inspection of the response of smaller fullerenes indicates that the low energy excitations are strongly screened by application of Eq. (2). A detailed study of optical spectra will be published elsewhere.

In Table I, the prediction of various models for polarizability is compared. The α_{Penn} is the polarizability determined using a semiclassical model that uses classical electrostatics and linear response theory. The fullerene polarizabilities larger than the α_{Penn} value have been interpreted as quantum size effects.[10] The current understanding, based on the tight-binding study,[10] is that quantum size effects play a very important role in electronic response of fullerenes up to C_{3840}. In contrast, our first-principles calculations (α_{FF} and α_{SOS} in Table I; cf. Fig. 2) show that by C_{2160} the semiclassical α_{Penn} is already larger than the first-principles value. For the smaller fullerenes these effects are also much less pronounced than predicted by tight-binding model. For C_{240}, the tight-binding value of polarizability exceeds finite-field DFT value by 32%. Also evident from Table I is that, while all models well predict known C_{60} polarizability, they are inadequate to provide proper description of response of larger fullerenes. The tight-binding approximation, in particular, greatly exaggerates the response leading to large α values. Similarly as Eq. (2) has been used in tight-binding study,[10] it is clear that proper description of dielectric response requires accurate self-consistent density functional solution. The table also indicates dramatic increase in polarizability per atom with fullerene size. The polarizability per atom systematically increases from 1.34 Å^3 in C_{60} to 4 Å^3 in C_{2160}. There is no obvious reason why the polarizability per atom will not increase indefinitely as the rigid structure of fullerenes will not allow collapse. Furthermore, the fullerenes become energetically more stable with increasing size. The only problem is physically making them.

The α_{RPA} values given in Table I are the most accurate predictions of fullerene polarizabilities. The quantitative agreement with experimental values of polarizabilities requires a careful treatment of all possible contributions to polarizability. The vibrational contributions as noted earlier are insignificant.[26] The excellent agreement between the predicted polarizability and experimental measurements for C_{60} and C_{70} rules out the role of temperature effects.[26,27] Previous studies on carbon nanostructures have indicated negative thermal (volume) expansion at low temperature.[45–47] We estimate the effect of volume expansion by calculating α_{RPA} for all fullerenes within 15% of their equilibrium volume. The α increases practically linearly with increase in fullerene volume within the chosen range of volume expansion (cf. Fig. 3). This, as expected, highlights the importance of accurate geometries for accurate prediction of fullerene polarizability.

Finally, using the Clausius-Mossoti relation, we provide estimates of the dielectric constant of crystalline solids of these fullerenes. Assuming that like C_{60}, all larger fullerenes form an fcc crystal, the number density of fullerene is then $4/V$, where $V=(\sqrt{(8)}r)^3$. The fullerene radius used here is the effective radius as used above (to include the π-electron spill-out effect). Using a value of δ=1.23 Å results in a smaller lattice constant than the experimental value (14.17 Å)[48] but gives a dielectric constant of 4.50, which is in good agreement with experimental values (4.0–4.5).[49] The dielectric constants calculated for the larger fullerenes using the same δ value are in the range 4.7–5.6 (see last column in Table I). These values may vary slightly with the δ but the trend should be the same.

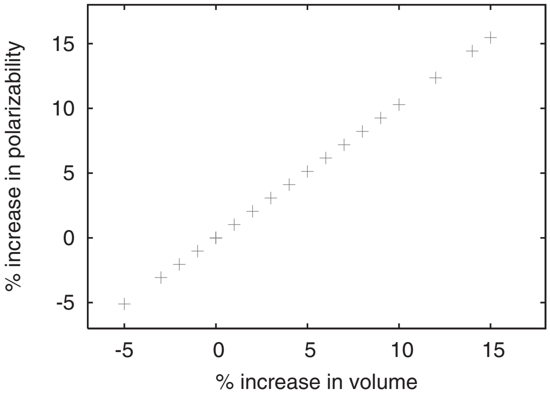

FIG. 3. The percent increase in polarizability, α_{RPA}, as a function of percent increase in volume, $\bar{r}^3$, for C_{960} fullerene.

III. CONCLUSIONS

In summary, static electric response of the icosahedral C_{60}, C_{180}, C_{240}, C_{540}, C_{720}, C_{960}, C_{1500}, and C_{2160} fullerenes is studied in detail by all-electron first-principles density functional methods. Quantitative estimates of the dipole polarizability determined herein provide better understanding of electronic response of fullerenes amongst earlier inconsistent predictions from various models. This work shows that quantum size effects in polarizability are substantially quenched by C_{2160} in sharp contrast to previous tight-binding predictions. These calculations also signal the beginning of an era where tens of thousands of basis functions will be used for accurate electronic structure calculations.

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