

## Quantum Size Effects in the Polarizability of Carbon Fullerenes

G. K. Gueorguiev,<sup>1</sup> J. M. Pacheco,<sup>2</sup> and David Tománek<sup>3</sup>

<sup>1</sup>*Departamento de Física da Universidade, P-3004-516 Coimbra, Portugal*

<sup>2</sup>*Centro de Física Teórica e Computacional, Departamento de Física da Faculdade de Ciências, Complexo Interdisciplinar da Universidade de Lisboa, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa Codex, Portugal*

<sup>3</sup>*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-2320, USA*

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We investigate the size-dependent dielectric response of carbon fullerenes with up to 3840 atoms in the framework of the linear response theory. Our results suggest a significant polarizability enhancement due to quantum size effects with respect to classical or semiclassical calculations. The accuracy of our results, based on a parametrized Hamiltonian, is verified by *ab initio* time dependent density functional calculations for smaller fullerenes. Our findings underline the importance of quantum effects in the electronic response of nano- and mesoscopic systems.

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The physics of mesoscopic systems underwent a major revolution in the mid-1980s with the experimental production of high quality cluster beams. Many fundamental discoveries are associated with the development of such techniques, notably the observation of electronic shell and supershell structure in alkali metal clusters [1], or the discovery of caged structures consisting of carbon [2]. Many of the novel properties associated with such finite systems are, to a great extent, related to the confinement of a large, yet finite, number of electrons in a relatively small volume, thereby inducing what is known as quantum size effects.

Quantum size effects are relevant in distinct areas of physics, playing sometimes analogous roles on energy and length scales that differ by several orders of magnitude. Furthermore, quantum size effects quite often lead to significant fine structure deviations from the physical behavior expected based on semiclassical arguments, which typically account for the observed general trends. This is particularly the case in the size dependence of physical properties of atomic clusters, notably their polarizability.

Carbon fullerenes, as well as nanotubes, constitute an example of atomic clusters, which have received considerable attention during the past decade, both at an experimental as well as theoretical level [3]. In what concerns their polarizability, however, present information is almost exclusively limited to the C<sub>60</sub> cluster. Even for this system, only recently experimental measurements [4] and *ab initio* calculations [5–7] on isolated molecules have been carried out. The lack of microscopic results for other fullerene structures is unfortunate, since the only alternative is to rely on essentially classical estimates [8]. In particular, the size dependence of the polarizability remains, to our knowledge, an open question, which deserves a prompt answer.

The purpose of this Letter is to provide microscopic results for the static polarizability of fullerenes with up to 3840 atoms. We will show that quantum size effects

modify the size dependence of the polarizability to a significant degree. We observe a size-dependent enhancement of this observable with respect to classical and semiclassical results. Indeed, we obtain a steep increase of this enhancement factor as a function of size up to a maximum value of 2 occurring at a size of  $N = 960$ , after which a slow decrease of the enhancement factor is observed towards the semiclassical limit at larger sizes. These conclusions, not accountable for by any classical model of the polarizability, are based on a linear response (LR) model [9] in the framework of a parametrized linear combination of atomic orbitals (LCAO) Hamiltonian with parameters determined by *ab initio* calculations for simpler structures [10]. The accuracy of this model—which has been shown to provide reliable predictions of the static and dynamic polarizabilities of C<sub>60</sub> and C<sub>70</sub> [9,11]—is validated by carrying out additional calculations using *ab initio* density functional theory (DFT) methods [7] for smaller carbon cages.

The classical picture of the polarizability of fullerenes is rather simple and clearcut, in particular, for quasi-spherical systems. Indeed, these can be viewed as spherical shells with an average radius  $R$  and a constant thickness of  $2a$ , confining a relatively constant and size-independent charge density. We adopt the value of  $a \approx 0.9 \text{ \AA}$ , commonly used for carbon fullerenes and nanotubes [12], independent of the system size. If one interprets this spherical shell as that of a conducting material, we obtain for the classical value of the static polarizability the same result as that for a metallic sphere of radius  $(R + a)$ , namely  $\alpha = (R + a)^3$  in atomic units [13]. A similar cubic dependence of the polarizability [ $\alpha = 0.75(R + 1.2)^3 \text{ \AA}^3$ ] has been obtained independently in Ref. [14], employing a semiempirical method. Treating the carbon network as a metallic shell, however, poses a conceptual problem, since the  $sp^2$ -like chemical bonding of carbon atoms is of a covalent nature. It would appear more appropriate [12] to view the carbon shell as a dielectric medium with a finite dielectric constant  $\epsilon$ . In

TABLE I. Size dependence of several properties of  $C_N$  fullerene cages. For each quasi-spherical  $N$ -atom fullerene, we list the average cage radius  $R$ , the HLG  $E_g$ , as well as our results for the static polarizability  $\alpha$ .  $\alpha_{\text{LCAO}}$  stands for the LR-LCAO quantum mechanical value,  $\alpha_{\text{classic}}$  for the classical value, resulting from Eq. (1) with a size-independent value for  $\epsilon$ , and  $\alpha_{\text{Penn}}$  for the semiclassical value obtained via Penn's model. The last column gives the polarizability enhancement factor  $\alpha_{\text{LCAO}}/\alpha_{\text{Penn}}$ , which constitutes the data used to generate Fig. 2.

$N$	$R$ (Å)	$E_g$ (eV)	$\alpha_{\text{LCAO}}$ (Å <sup>3</sup> )	$\alpha_{\text{classic}}$ (Å <sup>3</sup> )	$\alpha_{\text{Penn}}$ (Å <sup>3</sup> )	$\alpha_{\text{LCAO}}/\alpha_{\text{Penn}}$
20	2.08	0.382	20.03	16.19	22.38	0.895
60	3.56	2.080	81.06	55.74	64.33	1.260
240	6.92	1.444	581.19	246.99	343.29	1.693
540	10.32	1.062	1868.82	612.59	1026.82	1.820
960	13.51	0.838	4289.78	1125.88	2185.32	1.963
2160	20.50	0.649	17 816.81	2853.28	9548.13	1.866
3840	26.76	0.513	33 731.11	5119.74	19 862.19	1.698

Ref. [12], a constant value  $\epsilon \approx 8$  has been used in order to reproduce the properties of the  $C_{60}$  molecule. Adopting this value for the effective  $\epsilon$  of any fullerene, independent of its size, and substituting it in the exact result [8] for the polarizability of a spherical dielectric shell, would yield

$$\frac{\alpha}{(R+a)^3} = \frac{(2\epsilon+1)(\epsilon-1)(1-\rho)}{(2\epsilon+1)(\epsilon+2)-2\rho(\epsilon-1)^2}, \quad (1)$$

where  $\rho = [(R-a)/(R+a)]^3$ . This leads to the values listed in Table I under column  $\alpha_{\text{classic}}$  for the fullerenes considered in this study. The assumption of a constant, size-independent  $\epsilon$  is unsatisfactory, however, since it leads to an incorrect asymptotic behavior  $\alpha \rightarrow 0$  for  $R \rightarrow \infty$ . A more appropriate description of the size-dependent dielectric response of the carbon network can be obtained using an approach developed by Penn [15], which expresses the dielectric constant as  $\epsilon \approx 1 + (E_p/E_g)^2$ , where  $E_p$  is the plasmon energy and  $E_g$  the fundamental energy gap. In our case, the latter corresponds to the optical gap of the fullerene shell or, more qualitatively, to the highest occupied molecular orbital–lowest unoccupied molecular orbital gap (HLG) of the fullerene. As is well known [6], the optical response of  $C_{60}$ , similarly to that of graphite, is dominated by two main absorption peaks. These are the  $\pi$  plasmon at  $h\nu \approx 6$  eV and the  $\sigma$  plasmon at  $h\nu \approx 20$  eV, carrying most of the absorption strength and evidencing a moderate size dependence. This behavior suggests that we take for  $E_p$  a constant value of  $\approx 20$  eV, which implies that the size dependence of  $\epsilon$  arises from  $E_g$ . As a result, we expect that  $\epsilon$  will increase with increasing cluster size, reaching an infinite value when  $E_g$  approaches zero, as is expected to happen when  $R \rightarrow \infty$  and one recovers graphite. We shall call this limit semiclassical. Results obtained with the size-dependent  $\epsilon$  in Eq. (1) are also listed in Table I under the column  $\alpha_{\text{Penn}}$ . These results exhibit a size dependence that departs markedly from the classical estimate, in better agreement with the quantum-

mechanical prediction tabulated under column  $\alpha_{\text{LCAO}}$ , discussed below. Moreover, this semiclassical approximation warrants the correct asymptotic behavior as  $R \rightarrow \infty$ .

In the following we shall concentrate on the polarizability calculation in the LR-LCAO framework, which will provide an independent estimate for the size evolution of the static polarizability of the fullerenes, as the number of carbon atoms changes by 3 orders of magnitude.

In the LR model of Ref. [9], the screening effect produced by the valence electrons has been approximated by that due to a classical spherical surface charge distribution. Within the fullerene family, this description is most appropriate for systems with a quasispherical shape, such as  $C_{20}$ ,  $C_{60}$ ,  $C_{240}$ ,  $C_{540}$ ,  $C_{960}$ ,  $C_{2160}$ , and  $C_{3840}$  [16], most of which display icosahedral symmetry. The optimized structures employed were taken from the results of Ref. [17] and make use of the LCAO parametrization developed for carbon in Refs. [10,18]. We maintain the LR-LCAO framework of Ref. [9] for the polarizability calculation of the above fullerenes. For these systems, the polarizability is proportional to the unit tensor [19]. Furthermore, temperature effects are neglected [20]. In Fig. 1 we display four representative cages considered in this work, together with their average radii.

Our electronic structure study is based on a parametrized LCAO Hamiltonian with a four-orbital basis ( $s, p_x, p_y, p_z$ ) per carbon atom,

$$H_{\text{LCAO}} = \sum_{\alpha,i} \epsilon_{\alpha} a_{\alpha,i}^{\dagger} a_{\alpha,i} + \sum_{\alpha,i,\beta,j} V_{\alpha,i,\beta,j} a_{\alpha,i}^{\dagger} a_{\beta,j}. \quad (2)$$

Here, the indices  $i, j$  specify the atoms and the indices  $\alpha, \beta$  the individual orbitals. The off-diagonal matrix elements  $V_{\alpha,i,\beta,j}$  of the Hamiltonian depend on the relative atomic positions. The one-electron eigenstates of this Hamiltonian form the basis for the polarizability calculation. Using the definition for the dipole operator  $D$  and screening term  $W$  introduced in Ref. [9], the

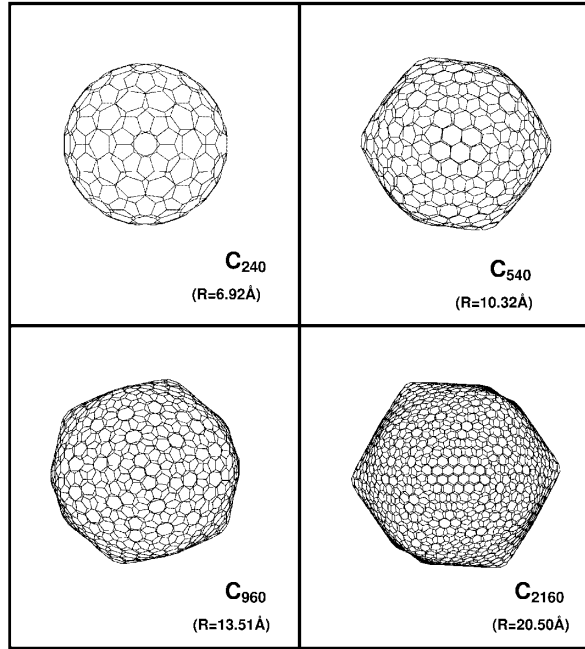


FIG. 1. Atomic structure of four representative fullerene cages considered in this Letter, optimized in Ref. [17] using the LCAO functional of Ref. [18]. Since the scale in the subfigures is not the same, we also provide, in parentheses, the average radii of the cages.

polarizability  $\alpha$  can be obtained by solving the equation

$$\alpha = [1 + \alpha^0 W]^{-1} \alpha^0. \quad (3)$$

The  $2 \times 2$  matrix  $\alpha^0$  is computed by making use of *all* the one-electron states ( $p$  for unoccupied states and  $h$  for occupied states), which diagonalize  $H_{\text{LCAO}}$ , as

$$\alpha_{n,m}^0 = 2 \sum_{p,h} \frac{\langle p | D_z^{(n)} | h \rangle \langle h | D_z^{(m)} | p \rangle}{(\epsilon_p - \epsilon_h)}. \quad (4)$$

In order to compute the static polarizability of the carbon cages, we first determined their electronic ground state using the LCAO Hamiltonian. This provides also explicit values for the HLG energy  $E_g$ , presented in Table I. We then computed the unscreened polarizability matrix  $\alpha^0$  using Eq. (4), and obtained the screened polarizability  $\alpha$  by solving the matrix equation, Eq. (3). Our calculated dielectric response, obtained using the LR-LCAO approach, is shown in Fig. 2 as a function of the average cage radius. For each fullerene, we plot the ratio of the LR-LCAO polarizability and the corresponding semiclassical value, thus eliminating the explicit volume dependence. This polarizability ratio increases steeply as a function of  $R$  up to  $C_{960}$  in an unprecedented manner. This puts in evidence the significant deviation of the quantum from the semiclassical or classical polarizability values as a function of size, also presented in Table I. We find it most interesting that the strong polarizability

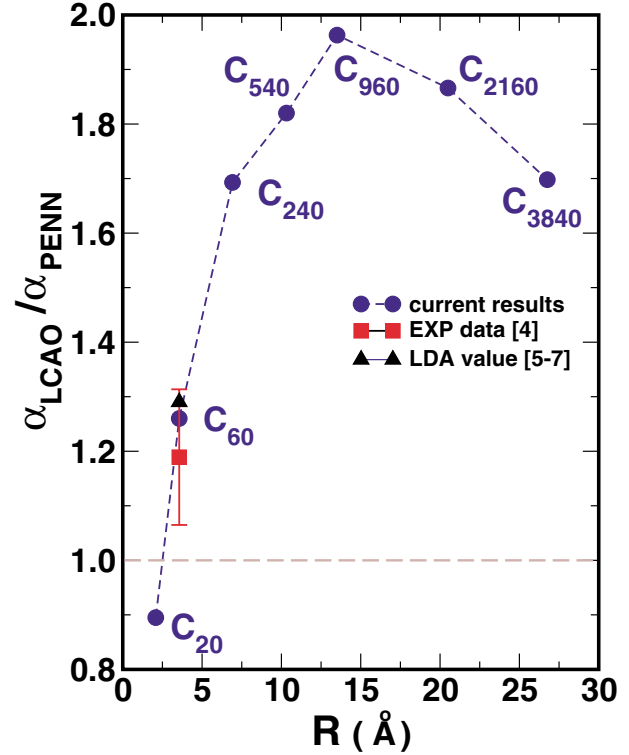


FIG. 2 (color online). The size dependence of the polarizability enhancement factor  $\alpha_{\text{LCAO}}/\alpha_{\text{PENN}}$ , shown by the data points.  $\alpha_{\text{LCAO}}$  is the static polarizability, computed at the LR-LCAO level, and  $\alpha_{\text{PENN}}$  the semiclassical value of the polarizability based on Penn's model. The dotted line is a guide to the eye. For small cages, the static polarizability enhancement first increases with an increasing number of atoms. After reaching the maximum value at  $C_{960}$ , the static polarizability enhancement decreases monotonically. Still, for fullerenes as large as  $C_{3840}$ , the value of the quantum polarizability exceeds the semiclassical value by  $\approx 70\%$ .

enhancement, evidenced in Fig. 2, results primarily from quantum size effects in the carbon cages, which evade any classical description.

To verify the validity of these findings, we first compared our LR-LCAO results to calculations based on an alternate LCAO parametrization [9,10], and found no sizable deviation from our results in Table I and Fig. 2. Second, we performed *ab initio* calculations of the static polarizability for the smaller fullerenes along the lines of Ref. [7], utilizing the same program, ADF [21]. Since response calculations require the use of extended basis sets, we augmented triple-zeta basis sets by additional polarization functions to describe each carbon atom with four valence electrons within the frozen-core approximation. We have used the local density approximation (LDA) to DFT with the parametrization of Vosko, Wilk, and Nusair [22]. The value we obtained for the  $C_{60}$  molecule agrees with independent *ab initio* calculations [5–7]. It should be noted that LDA is well known to underestimate the HLG. However, the polarizability values are also

known to be more reliable: In what concerns  $C_{60}$ , LDA calculations predict  $\alpha \approx 82 \text{ \AA}^3$  [5–7], to be compared to the latest experimental value  $\alpha = 76.5 \pm 8 \text{ \AA}^3$  [4]. Because of memory limitations, we were unable to carry out *ab initio* calculations of fullerenes with more than 80 atoms. Still, in all our calculations, we have found a general agreement between the DFT and the LR-LCAO results. In all cases, the DFT-based polarizabilities were found to exceed those based on LR-LCAO by up to 10%.

Our results predict that the polarizability of fullerenes should be greatly enhanced with respect to previous estimates based on classical arguments, exhibiting a measurable size dependence. Furthermore, as can be seen from Fig. 2, the ratio  $\alpha_{\text{LCAO}}/\alpha_{\text{Penn}}$  grows as a function of size for cluster sizes changing by 3 orders of magnitude. Even for fullerenes as large as  $C_{3840}$ , the polarizability ratio is considerably enhanced with respect to the classical-like limit. This behavior should be contrasted with that of metallic clusters which, similarly to the fullerenes, exhibit a size-independent density. In metal clusters, semiclassical arguments correctly account for the main trend in the size evolution of the polarizability, in stark contrast to fullerenes.

We would like to point out that all fullerene cages consist of very similar networks of  $sp^2$  bonded carbon atoms, which are distributed within a layer that is structurally related to a graphite layer. Consequently, these results should also be relevant for other  $sp^2$  bonded carbon networks, including carbon nanotubes.

As noted before, polarizability provides very important information related to the dispersion interaction between  $sp^2$  bonded carbon nanostructures, such as fullerenes [23]. We expect that the prominent role of quantum size effects in the polarizability of finite carbon networks, predicted in our calculations, should lead to other interesting properties in related materials. Work along these lines is in progress.

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- [1] For an excellent review, see W. de Heer, *Rev. Mod. Phys.* **65**, 611 (1993).
- [2] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, *Nature (London)* **318**, 162 (1985).
- [3] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
- [4] R. Antoine, Ph. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, and C. Guet, *J. Chem. Phys.* **110**, 9771 (1999).
- [5] Mark R. Pederson and Andrew A. Quong, *Phys. Rev. B* **46**, 13 584 (1992).
- [6] F. Alasia, H. E. Roman, R. A. Broglia, Ll. Serra, G. Colò, and J. M. Pacheco, *J. Phys. B* **27**, L643 (1994).
- [7] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *Phys. Rev. Lett.* **78**, 3097 (1997).
- [8] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (John Wiley & Sons, New York, 1983).
- [9] G. F. Bertsch, A. Bulgac, D. Tománek, and Yang Wang, *Phys. Rev. Lett.* **67**, 2690 (1991).
- [10] D. Tománek and M. A. Schluter, *Phys. Rev. Lett.* **67**, 2331 (1991).
- [11] M. S. Hansen, J. M. Pacheco, and G. Onida, *Z. Phys. D* **35**, 141 (1995).
- [12] Ph. Lambin, A. A. Lucas, and J.-P. Vigneron, *Phys. Rev. B* **46**, 1794 (1992).
- [13] We shall use atomic units throughout the manuscript, except where explicitly stated otherwise.
- [14] A. Ruiz, J. Bretón, and J. M. Gomez Llorente, *J. Chem. Phys.* **114**, 1272 (2001).
- [15] D. Penn, *Phys. Rev.* **128**, 2093 (1962).
- [16] The reason for stopping at  $C_{3840}$  has been dictated by computer memory limitations.
- [17] P. Ordejón, J. A. Drabold, R. M. Martin, and S. Itoh, *Phys. Rev. Lett.* **75**, 1324 (1995).
- [18] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, *J. Phys. Condens. Matter* **4**, 6047 (1992).
- [19] F. Willaime and L. M. Falicov, *J. Chem. Phys.* **98**, 6369 (1993), and references therein.
- [20] J. M. Pacheco and W.-D. Schöne, *Phys. Rev. Lett.* **79**, 4986 (1997); S. A. Blundell, C. Guet, and Rajendra R. Zope, *Phys. Rev. Lett.* **84**, 4826 (2000).
- [21] G. te Velde and E. J. Baerends, *J. Comp. Phys.* **99**, 84 (1992).
- [22] S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- [23] J. M. Pacheco and J. P. Prates Ramalho, *Phys. Rev. Lett.* **79**, 3873 (1997).