

Polarizability of Carbon Nanotube Peapods from First-Principles

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Carbon nanotube peapods have been suggested as nanoelectronic devices, such as bucky shuttle memories and three-terminal switching devices. However, relevant physical properties are not fully understood. We calculate the polarizability of carbon nanotube peapods from first-principles. We obtain a substantial reduction in the polarizability of an endohedral C_{60} molecule in various carbon nanotube peapod structures. The reduction depends on the structures and the directions of the external electric fields. The features of polarizability will be important in device applications of carbon nanotube peapods.

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I. INTRODUCTION

Carbon nanotubes (CNTs) have scientific and technological significance because of a wide range of nanoelectronic applications due to their versatile and unique electronic and mechanical properties. CNTs can be metallic or semiconducting, depending on their chiralities [1–3]; they also have exceptionally good mechanical strength [4]. Nanoelectronic applications of CNTs have been proposed in theoretical and experimental works [1–8]. Assembled structures of fullerenes and CNTs are called carbon nanotube peapods [9–12]. The peapod structures have already been studied theoretically [13] and have been suggested as materials for nanoelectronic devices such as bucky shuttle memories and three-terminal switching devices [14,15]. The positions of the fullerene inside the CNT determine the states of the devices. The positions may be controlled by external electric fields, and the dielectric response of the peapod structure should provide relevant information. We present first-principles calculations of the polarizabilities of various CNT peapods decomposed into those of the endohedral fullerene and the encapsulating CNT.

II. CALCULATION

Our calculations are carried out using SIESTA [16] within the generalized-gradient approximation [17] and the norm-conserving pseudopotentials [18] scheme. The basis functions are pseudo-atomic orbitals (PAO) [19] generated by using the split-valence scheme for a double-zeta polarization basis set. The basis set consists of 13

PAO basis functions per one carbon atom : two different sets of basis orbitals for the $2s$ states and the $2p$ states, and the polarization orbitals for the $2p$ states. The radii of confinement are 2.64 Å for the $2s$ states and 3.31 Å for the $2p$ states and the polarization orbitals.

We have calculated one open CNT peapod (OP), two closed CNT peapods (CP1, CP2), and $C_{60}@C_{240}$. The open peapod is composed of nine (10,10) CNT primitive unit cells and a C_{60} molecule, as is shown in Figure 1(a). CP1, which is shown in Figure 1(b), is a closed CNT peapod composed of six (10,10) CNT primitive unit cells capped with half of a C_{240} molecule on each side and a C_{60} molecule. CP2 is a closed CNT peapod similar to CP1, except that a part of CP2 is two (10,10) CNT primitive unit cells. All the structures are relaxed with the conjugate gradient method until the maximum force component acting on an atom is less than 0.07 eV/Å. The supercells are rectangular parallelepipeds, and the size along tube axis is chosen to be large to ensure no interaction between the supercell images. The distance between carbon atoms belonging to different supercell images are larger than the diameter of the (10,10) CNT.

To calculate the longitudinal and the transverse polarizabilities of the systems, we calculate the first derivative

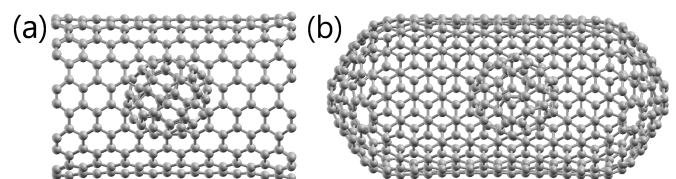


Fig. 1. (a) Open (10,10) CNT peapod (OP). (b) Closed (10,10) CNT peapod (CP1).

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of the dipole moment along an external electric field,

$$\alpha_i = \frac{dp_i}{dE_{\text{ext } i}}, \quad (1)$$

where $\alpha_i = \alpha_{ii}$, and p_i and $E_{\text{ext } i}$ are i -th components of the dipole moment and the external electric field, respectively. We have obtained polarizabilities from a linear regression of the dipole moments in the presence of external electric fields of 0.1, 0.2, 0.3 and 0.4 in units of eV/Å. The dipole moment is obtained from the electronic charge density matrix

$$\rho_{el}(\mathbf{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \varphi_\mu^* \varphi_\nu, \quad (2)$$

where ρ_{el} is the electronic charge density at $\mathbf{r}$ and $\rho_{\mu\nu}$ is the electronic charge density matrix of the PAO basis, φ_μ and φ_ν . Note that μ is defined to be $\{l m n\}$, where l is an atom index and m, n are quantum numbers.

We decompose the electronic charge density of a CNT peapod into two parts. One is for the C_{60} molecule, and the other is for the CNT:

$$\rho_{el}(\mathbf{r}) = \sum_{\mu, \nu \in C_{60}} \rho_{\mu\nu} \varphi_\mu^* \varphi_\nu + \sum_{\mu, \nu \in \text{CNT}} \rho_{\mu\nu} \varphi_\mu^* \varphi_\nu. \quad (3)$$

The dipole moment can be similarly decomposed into two parts with the decomposed charge densities, and the polarizability of either the C_{60} molecule or the CNT can be calculated from the corresponding decomposed dipole moment. The effective electric field for the endohedral C_{60} can be calculated from the decomposed polarizability for the C_{60} molecule. Care has to be taken in choosing the origins for the calculations of decomposed polarizabilities. We have chosen the center of ionic charge of the subsystem, either the C_{60} molecule or the CNT, as the origin for the calculation of its polarizability.

III. RESULTS AND DISCUSSION

Our calculated polarizability of a free C_{60} molecule, $\alpha_{C_{60}}^{\text{free}}$, is 82.14 Å^3 , which is consistent with calculations, within the local density approximation, of about 82 Å^3 [20–22], and experimental values of $\alpha_{C_{60}}^{\text{free}} = 76.5 \pm 8 \text{ Å}^3$ [23] and $\alpha_{C_{60}}^{\text{free}} = 79 \pm 4 \text{ Å}^3$ [24]. We have also calculated the decomposed polarizabilities of $C_{60}@C_{240}$, which is composed of a C_{60} molecule enclosed by a C_{240} molecule. Both C_{60} and C_{240} are icosahedral fullerenes. We have obtained $\alpha_{C_{240}} = 461.47 \text{ Å}^3$ and $\alpha_{C_{60}} = 11.86 \text{ Å}^3$. Therefore, $\frac{\alpha_{C_{60}}}{\alpha_{C_{60}}^{\text{free}}} = 0.1444$. We estimate the effective external electric field, E_{eff} , applied to the endohedral C_{60} of the peapods from the formulas

$$p_{C_{60}} = \alpha_{C_{60}}^{\text{free}} E_{\text{eff}} = \alpha_{C_{60}} E_{\text{ext}} \quad (4)$$

and

$$\frac{E_{\text{eff}}}{E_{\text{ext}}} = \frac{\alpha_{C_{60}}}{\alpha_{C_{60}}^{\text{free}}}, \quad (5)$$

Table 1. Polarizabilities along the longitudinal external electric fields, α^l . L is the length of a CNT peapod. OP, CP1 and CP2 correspond to $C_{60}@C_{360}$, $C_{60}@C_{480}$ and $C_{60}@C_{320}$, respectively. See the text for detailed explanations.

CNT peapod	Capping	L (Å)	α_{CNT}^l (Å ³)	$\alpha_{C_{60}}^l$ (Å ³)	$\frac{\alpha_{C_{60}}^l}{\alpha_{C_{60}}^{\text{free}}}$
OP	Open	21.14	1340.03	19.60	0.2386
CP1	Closed	29.78	1644.22	14.39	0.1752
CP2	Closed	19.82	708.96	17.70	0.2155

Table 2. Polarizabilities along the transverse external electric fields, α^t . See the caption for Table 1.

CNT peapod	Capping	L (Å)	α_{CNT}^t (Å ³)	$\alpha_{C_{60}}^t$ (Å ³)	$\frac{\alpha_{C_{60}}^t}{\alpha_{C_{60}}^{\text{free}}}$
OP	Open	21.14	889.55	26.80	0.3263
CP1	Closed	29.78	976.97	16.91	0.2059
CP2	Closed	19.82	662.90	13.51	0.1644

where $p_{C_{60}}$ is the decomposed dipole moment for the C_{60} molecule. If the ratio $\frac{\alpha_{C_{60}}}{\alpha_{C_{60}}^{\text{free}}}$ is unity, the external effective electric field, E_{eff} , is equal to the external electric field, E_{ext} . If the ratio is smaller than unity, E_{eff} is smaller than E_{ext} , and the relative decrease of E_{ext} is $1 - \frac{\alpha_{C_{60}}}{\alpha_{C_{60}}^{\text{free}}}$. In the case of $C_{60}@C_{240}$, the decrease of E_{ext} is $0.8556 E_{\text{ext}}$.

For the longitudinal external electric fields parallel to the CNT tube axis, the calculated polarizabilities of the CNT peapods are summarized in Table 1. We include the calculated values of $C_{60}@C_{240}$ in the discussion for comparison. The value of $\alpha_{C_{60}}^l$ of OP is the largest among the calculated values because the external electric field can penetrate the short open peapod along the CNT tube axis more easily than it can for the other structures. The value of $\alpha_{C_{60}}^l$ of $C_{60}@C_{240}$ is the smallest among the calculated values. CP1 and CP2 could be considered to be elongated CNT peapods of $C_{60}@C_{240}$, and the results for $C_{60}@C_{240}$ could be considered to be an extreme case of the edge effect. The geometry argument would imply that the longer a closed CNT peapod, the smaller the edge effect, and the larger the value of $\alpha_{C_{60}}^l$, which could explain the smallest value of $\alpha_{C_{60}}^l$ for $C_{60}@C_{240}$. However, the length of CP1 is greater than that of CP2, although $\alpha_{C_{60}}^l$ of CP1 is smaller than that of CP2. The puzzling order can be understood by considering that α_{CNT}^l per C atom of CP1 is larger than that of CP2, indicating a larger depolarizing field for CP1.

For the transverse external electric fields perpendicular to the CNT tube axis, the calculated polarizabilities of the CNT peapods are summarized in Table 2. Again, we include the calculated values of $C_{60}@C_{240}$ in the discussion for comparison. The results are similar to the case of the longitudinal external electric field in that the value

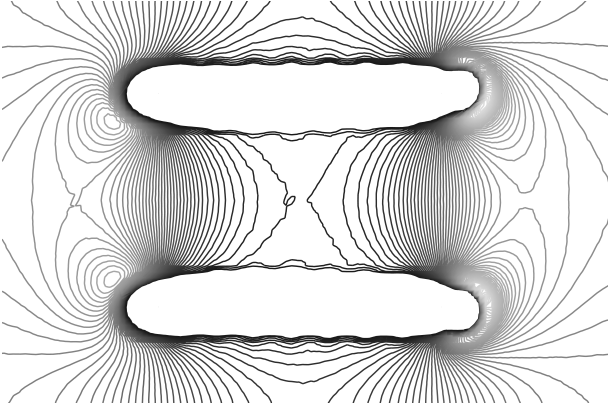


Fig. 2. Equipotential lines of V_H for the open CNT, a part of OP, with no external electric field. Darker lines correspond to lower potentials for an electron. Equipotential lines for $|V_H| < 0.35$ eV are plotted. The spacing of adjacent lines is 0.01 eV.

of $\alpha_{C_{60}}^t$ of OP is the largest among the calculated values. In the case of the transverse external electric fields, the edge effect is smaller than it is for the longitudinal external electric field because charge accumulation at the tube end is smaller. Therefore, the external electric field can penetrate the short open peapod even more easily than it can the other structures, which explains $\alpha_{C_{60}}^t$ being larger than $\alpha_{C_{60}}^l$ in the OP. Again, the value of $\alpha_{C_{60}}$ of $C_{60}@C_{240}$ is the smallest among the calculated values. The geometry argument outlined above can explain the smallest value of $\alpha_{C_{60}}$ for $C_{60}@C_{240}$. Since the values of α_{CNT}^l per C atom of CP1 and CP2 are about the same, the geometry argument can explain $\alpha_{C_{60}}^t$ of CP1 being larger than $\alpha_{C_{60}}^t$ of CP2.

The reduced polarizabilities of the endohedral C_{60} s and, hence, the reduced effective electric fields are influenced by the electric fields from the CNTs. We have calculated the CNT structures with no endohedral C_{60} in the absence of an external electric field. We have plotted the equipotential lines of V_H , the sum of the Hartree potential, and the local pseudopotentials, in Figure 2 and Figure 3.

In Figure 2 for the open CNT, $V_H(\mathbf{r})$ decreases as $\mathbf{r}$ moves toward the CNT. On the tube axis, V_H has the lowest value at the center of the CNT. However, the center is a saddle point of V_H because V_H decreases away from the center in the radial direction. The C_{60} molecule cannot move along any radial direction of the (10,10) CNT because the molecule fits inside the CNT. The C_{60} molecule, if negatively charged with n-type doping, will be attracted toward the center of an open (10,10) CNT. If positively charged with p-type doping, the molecule will be attracted toward the end rings of an open (10,10) CNT. For a larger CNT, if negatively charged with n-type doping, the molecule will be attracted to the center wall of the open CNT. If an external electric field is applied, the saddle point moves away from the applied

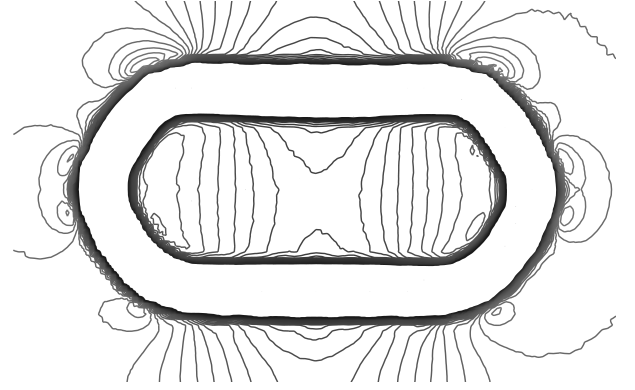


Fig. 3. Equipotential lines of V_H of the closed CNT, a part of CP1, with no external electric field. The range and the spacing of the lines are the same as those of Figure 2.

external electric field, and the C_{60} molecule has new favored positions. The position of the C_{60} molecule may be tuned by using the external longitudinal electric field.

In Figure 3, for the closed CNT, $V_H(\mathbf{r})$ decreases as $\mathbf{r}$ moves toward the CNT as in the case of the open CNT. V_H has a saddle point at the center of the CNT, as is the case in the open CNT. The behavior of the negatively charged endohedral C_{60} molecule should be similar to that of the open peapod. The positively charged endohedral C_{60} molecule will favor end regions. If an external electric field is applied, the saddle point changes in a similar fashion. With a longitudinal external electric field, the energetically favored position of the negatively charged C_{60} molecule inside a closed (10,10) CNT will lie at the end region away from the applied electric field, and vice versa.

IV. CONCLUSIONS

In summary, we have presented first-principles calculations of the polarizabilities of various CNT peapods. We obtain a reduction of the order of $0.7\alpha_{C_{60}}^{\text{free}}$ to $0.8\alpha_{C_{60}}^{\text{free}}$ in the polarizability of an endohedral C_{60} molecule, depending on the CNT peapod structure and the direction of the external electric field. The reduction is larger for the $C_{60}@C_{240}$ structure. The electric fields from the CNTs of the CNT peapod structures are responsible for the reduction. The electric fields inside the CNTs determine energetically favored positions of the endohedral C_{60} molecule. The features of the polarizability will be useful in device applications of carbon nanotube peapods.

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REFERENCES

- [1] J. W. Mintmire, B. I. Dunlap and C. T. White, *Phys. Rev. Lett.* **68**, 631 (1992).
- [2] N. Hamada, S.-I. Sawada and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).
- [3] R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, *Appl. Phys. Lett.* **60**, 2204 (1992).
- [4] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).
- [5] H. Kim, P. C. McIntyre, *J. Korean Phys. Soc.* **48**, 5 (2006).
- [6] J. R. Kim, B. K. Kim, S. R. Kim, *et al.*, *J. Korean Phys. Soc.* **49**, 1694 (2006).
- [7] J. Y. Park, Y. Kim, Y. M. Oh, *J. Korean Phys. Soc.* **51**, 1357 (2007).
- [8] Y.-G. Yoon and O. Efimov, *J. Korean Phys. Soc.* **52**, 75 (2008).
- [9] B. W. Smith, M. Monthieux and D. E. Luzzi, *Nature (London)* **396**, 323 (1998).
- [10] B. Bouteaux, A. Claye, B. W. Smith, M. Monthieux, D. E. Luzzi and J. E. Fischer, *Chem. Phys. Lett.* **310**, 21 (1999).
- [11] J. Sloan, R. E. Dunin-Borkowski, J. L. Hutchison, K. S. Coleman, V. C. Williams, J. B. Claridge, A. P. E. York, C. Xu, S. R. Bailey, G. Brown, S. Friedrichs and M. L. H. Green, *Chem. Phys. Lett.* **316**, 191 (2000).
- [12] K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara and S. Iijima, *Phys. Rev. Lett.* **85**, 5384 (2000).
- [13] S. Okada, S. Saito and A. Oshiyama, *Phys. Rev. Lett.* **86**, 3835 (2001).
- [14] Y.-K. Kwon, D. Tománek and S. Iijima, *Phys. Rev. Lett.* **82**, 1470 (1999).
- [15] J. W. Kang and H. J. Hwang, *Physica E* **23**, 36 (2004).
- [16] D. Sanchez-Portal, P. Ordejon, E. Artacho and J. M. Soler, *Int. J. Quantum Chem.* **65**, 453 (1997).
- [17] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [18] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [19] O. F. Sankey and D. J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989).
- [20] M. R. Pederson and A. A. Quong, *Phys. Rev. B* **46**, 13584 (1992).
- [21] F. Alasia, H. E. Roman, R. A. Broglia, Ll. Serra, G. Colò and J. M. Pacheco, *J. Phys. B* **27**, L643 (1994).
- [22] S. J. A. Van Gisbergen, J. G. Snijders and E. J. Baerends, *Phys. Rev. Lett.* **78**, 3097 (1997).
- [23] R. Antonie, Ph. Dugourd, D. Rayane, E. Benichou and M. Broyer, *J. Chem. Phys.* **110**, 9771 (1999).
- [24] A. Ballard, K. Bonin and J. Louderback, *J. Chem. Phys.* **113**, 5732 (2000).