AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

SAND--94-8641C
CONF-940411--20

FIRST-PRINCIPLES DETERMINATION OF THE POLARIZABILITIES OF CARBON TUBULES AS A FUNCTION OF LENGTH

Andrew A. Quong^a and Mark R. Pederson^b

^aSandia Livermore National Laboratory
Livermore CA 94551-0969

^bComplex System Theory Branch
Naval Research Laboratories,
Washington, DC 20375

RECEIVED
JUN 07 1994
OSTI

ABSTRACT

We use the local-density-approximation to the density-functional theory to determine the axial polarizabilities of fullerene tubules as a function of length and winding topologies. Specifically, we present linear polarizabilities for tubules of composition $C_{12}H_{24}$, $C_{36}H_{24}$, $C_{40}H_{20}$ and $C_{60}H_{24}$. The size-dependent variation in the dipole-coupled gaps between pairs of occupied and unoccupied levels leads to enhancements in the polarizability per valence electron as the length of the tubule increases. The results are compared to recent density-functional based calculations of the linear and nonlinear polarizabilities for fullerene and benzene molecules.

INTRODUCTION

The discovery of carbon tubules during the synthesis of C_{60} has moved carbon research into the area of nano-technology.[1, 2] One of the interesting attributes of these entities is that they exhibit nanocapillarity; that is, they ingest dipolar molecules and even closed shell atoms into the tubule with a low activation energy that depends on the radius of the tubule.[3, 4] There are many potentially useful applications which range from drug delivery, to facile formation of nanoscale wire-like structures, to the atomic-scale manipulation and modification of surfaces. Since one of the primary phenomena that leads to nanocapillarity in these tubules is their large polarizability and since the electronic response of fullerene tubules is interesting by itself we have initiated investigations aimed at understanding how the scale of such systems affects their polarizabilities. In the present paper, we perform very accurate density functional calculations for the polarizabilities of different tubules. In section II, we briefly describe the method used for the calculation of linear and nonlinear polarizabilities of systems and review some recent applications of this method to benzene and fullerene molecules. In section III we discuss the tubule systems that we have used for our studies and present results on the linear polarizability as a function of the number of valence electrons.

THE DENSITY-FUNCTIONAL-BASED DETERMINATION OF POLARIZABILITIES

MASTER

As discussed more completely in Refs. [5, 6], the polarizability of a system of electrons can be determined within the density-functional framework by appending a term which

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Figure 1: The systems studied in this work consist of tubules with composition $C_{12}H_{24}$, $C_{36}H_{24}$ and $C_{60}H_{24}$. The largest of these tubules is illustrated above. The small tubules are hydrogenated equivalently but contain fewer number of carbon layers.

corresponds to the electronic density interacting with the potential due to an electric field.

$$W_t(\mathbf{E}, \rho) = W^{LDA}(\rho) + \int d^3r \rho(\mathbf{r}) \mathbf{E} \cdot \mathbf{r}. \quad (1)$$

By self-consistently varying the Kohn-Sham orbitals from which the electronic density is constructed, and using the Hellmann-Feynman theorem to determine the derivative of the total energy with respect to field strength the relationship between the dipole moment ($\mathbf{p}$), the linear polarizabilities α_x , and the field strength $\mathbf{E}$ is determined to be:

$$p_x = \int d^3r \rho(\mathbf{r}) x = \alpha_x E_x. \quad (2)$$

The polarizability can also be determined by noting that the total energy varies quadratically with field strength with the constant of proportionality equal to half of the polarizability. The two equivalent methods for calculating polarizabilities are important for performing consistency checks especially when the determination of higher order polarizabilities is required. In two recent papers, the local-density-approximation has been utilized to calculate linear and non-linear polarizabilities.[5, 6] In Refs. [5, 6] it is shown that the LDA is capable of yielding very accurate electronic polarizabilities. For example, for the benzene molecule the LDA based linear and nonlinear polarizability was determined to be $10.7 \text{ \AA}^3$ and 1.85×10^{-36} esu in excellent agreement with the experimental values of $10.3 \text{ \AA}^3$ and 2.39×10^{-36} esu respectively. Similarly, the electronic linear and nonlinear polarizabilities of a fullerene molecule were determined to be $82.7 \text{ \AA}^3$ and 313×10^{-36} esu respectively. These

results are also in excellent agreement with the experimental values. See Ref. [6] for details. Very recently, the Kentucky group of Ecklund *et al.* have managed to measure the effects due to the polarization of the C_{60} nuclei.[7] They find that the nuclear contribution to the total fullerene polarizability $\alpha_{mol} = 85 \text{ \AA}^3$ to be $2 \text{ \AA}^3$ and that the dipolar contributions are negligible. This suggests an experimental electronic polarizability of $83 \text{ \AA}^3$ in excellent agreement with our prediction.

LINEAR POLARIZABILITIES OF VARIABLE LENGTH TUBULES

Pictured in Fig. [1] is the largest molecule studied in this work. The $C_{60}H_{24}$ molecule consists of five layers of carbon atoms and two layers of hydrogen atoms. The radius of the tubule is $4.58 \text{ \AA}$ and the height is $4.14 \text{ \AA}$. Each C-C bondlength is $1.423 \text{ \AA}$ and the C-H bondlengths are $1.10 \text{ \AA}$. The tubule has S_{12} point group symmetry and is a member of the A(12,6) tubule classification scheme of Hamada *et al.*[8] The smaller tubules are constructed by removing the outermost layers of carbon atoms and translating the hydrogen layer inward. Since the tubules studied here have aspect ratios of order unity, we expect that the electronic structure at the Fermi level will vary strongly and possibly non-monotonically with the tubule length. Therefore, the polarizability will not necessarily vary smoothly in this regime of aspect ratios. The size-dependent variation of energy gaps between dipole-coupled pairs of occupied and unoccupied states are expected to be the primary source of nonsystematic variation. For example, for the smallest tubule, there are three pairs of states which have nearly equal dipole-coupled gaps of 4.35 eV in contrast to the largest tubule which has two pairs of states that have a dipole-coupled gap of 1.9 eV and two pairs of states with a dipole-coupled gap of 2.44 . We find that the variation of the dipole coupled band gap does cause disproportionate increases in tubule polarizabilities with size. The polarizability per valence electron is found to be 0.28 , 0.33 and $0.40 \text{ \AA}^3$ for the small, medium and large tubule respectively. For comparison we note that for the C_{60} and C_6H_6 molecules the polarizability per valence electron are found to be $0.36 \text{ \AA}^3$ and $0.34 \text{ \AA}^3$ respectively.

We have also performed calculations on an intermediate length tubule of composition $C_{40}H_{20}$ which is of the A(10,0) classification of Hamada *et al.*[8] This tubule consists of four planes of carbon atoms with the outer most planes of carbon atoms tied off by hydrogen atoms. Each plane contains five pairs of dimerized carbon atoms with the dimer bond centers placed on the five equivalent vertices of a pentagon. The resulting tubule exhibits D_{5d} symmetry. The tubule has a radius of $3.91 \text{ \AA}$ and a length of $5.05 \text{ \AA}$. In reasonable accord with the results of the fatter tubules, this tubule has a polarizability of $0.38 \text{ \AA}^3$ per valence electron.

The results presented here begin to address relationships between system size and the electrical response of the system. Qualitatively, one expects that the polarizability per electron will increase with the size of the system but deviations with system size can occur when the HOMO/LUMO gap is significantly decreased for certain geometrical arrangements and when the participating states are strongly coupled by the dipole operator. Learning how to prepare tubules, possibly by selective capping or doping of the tubule ends could aid in the development of materials with interesting dielectric characteristics. Many additional calculations are needed to identify trends and to determine if any of these systems have interesting nonlinear properties.

ACKNOWLEDGEMENTS

We thank Dr. J. K. Johnson for helpful advice and discussions. A.A.Q. was supported by the United States Department of Energy, Office of Basic Science, Materials Science Division. M.R.P. was supported in part by the Office of Naval Research.

REFERENCES

1. S. Wang and P. R. Busek, Chem. Phys. Lett. **182**, 1 (1991).
2. S. Iijima Nature (London) **354**, 56 (1991).
3. M. R. Pederson and J. Q. Broughton, Phys. Rev. Lett **69**, 2689 (1992).
4. P. M. Ajayan and S. Iijima, Nature **361**, 333 (1993).
5. M. R. Pederson and A. A. Quong, Phys. Rev. B **46**, 13584 (1992).
6. A. A. Quong and M. R. Pederson, Phys. Rev. B **46**, 12906 (1992).
7. Ying Wang (private communication) and P. Zhou, A. M. Rao, Y. Wang, J. M. Holden, and P. C. Ecklund, in talk M23.3, Bulletin of the American Physical Society (March 1994).
8. N. Hamda, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DATE

FILMED

6/29/94

END