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First Principle Studies of Electronic Properties of Nitrogen-doped Endohedral Fullerene

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Abstract : The electronic properties of C60 and encapsulated N@C60 has been studied within the Density Functional Theory (DFT) and using SIESTA code. The calculation were performed using pseudopotential and Generalized Gradient Approximation (GGA) for the exchange correlation potential. Our calculation of the band structures and Density of State(DOS), for fcc lattice, show that the presence of a Nitrogen atom in the middle of fullerene cage affects its electronic propertiec, specially the HOMO-LUMO band gap. The energy band gap of N@C60 is much smaller than its value in C60, indicating increase in the conductivity of N@C60.

Key word: DensityFunctional Theory, Endohedral N@C60, Energy gap, Electonic properties.

I. INTRODUCTION

C60 is one of the carbon allotrope which has suitable and strong cage for filling it with atoms, molecules where named endohedral. We can change its physical and chemical properties by inserting impurity in the center of fullerene. It has been shown that their electrical properties depend on the kind of atom, ion, molecule that is inserted as impurity [1-3].

In 1985, La atom trapped in C60 cage and was named La@C60, thereafter Y[4], Sc[5] and some small molecule were encapsulated in fullerenes such as alkaline earth elementslike Be[6], Sr, Gd[7] and alkali metals like K and tetravalent metals and etc. Since the impurities atoms push the electron density around the carbon atoms of fullerene, these compounds are named endohedralmetallofullerenes.

The insertion of Nobel gases atoms and some other non-metal atoms in fullerene cage are much difficult experimentally and such products are named non-metal doped fullerene because these impurities atoms absorb the electron density of the carbon atoms. As a especial case it has been shown that N@C60 has a very interesting electronic and transport properties [8]. For this reasons in the present work we study numerically the electronic properties of C60 and N@C60 to see the effect of the presence of N atom in its electronic properties. We placed the fullerene cages in afcc lattice sites and performed the band structure within the density functional and pseudopotential using the SIESTA code. For the exchange correlation potential the Generalized Gradient Approximation (GGA) was adopted. In the following we describe our method of calculation and the results.

II. METHOD OF CALCULATIONS

We have used a linear scaling, fully self-consistent density functional method for performing first-principles calculations, as implemented in SIESTA code [9-11].In our calculations we have used Density Functional Theory (DFT) based on the work by Hohenberg and Kohn [12]and by Kohn and Sham [13].We have used Generalized Gradient Approximation (GGA) for the exchange-correlation potential. In SIESTA code, core electrons which have not considerable effect in chemical and electronic properties are replaced by efficient Troullier-Martinspseudopotentials[14-15] in their fully separable form. In this code, Pseudo Atomic Orbitals (PAO's) basis set [16] have been used for the expansion of the wave functions of valence electrons. These orbitals are constructed from multiplying of a numerical radius function by an angular function with a definite m and l quantum numbers. In this study, we have calculated DOS and band gap energy of an encapsulated N@C60.From the available basis set in the code, DZP (Double Zeta plus Polarization) was chosen.

We have used supercell approximation. The relaxed supercell wasafcc box with the length of 16.26 A˚. The diameter of C60 was 7.067 A˚.

There is two important parameters in SIESAT code which should be optimized correctly for saving time and also to have an acceptable precision in calculations. These parameters are Kgrid-cutoff and Mesh-cutoff energy.The Mesh-Cutoff energy is used for the calculations in the plane wave expansion of potential integrals. According to the converging of total energy with respect to Mesh-Cutoff energy (Fig.1) it was chosen to be 550 Ryd. The optimized Kgrid-cutoff was chosen from converging total energy to be 7 A˚ .

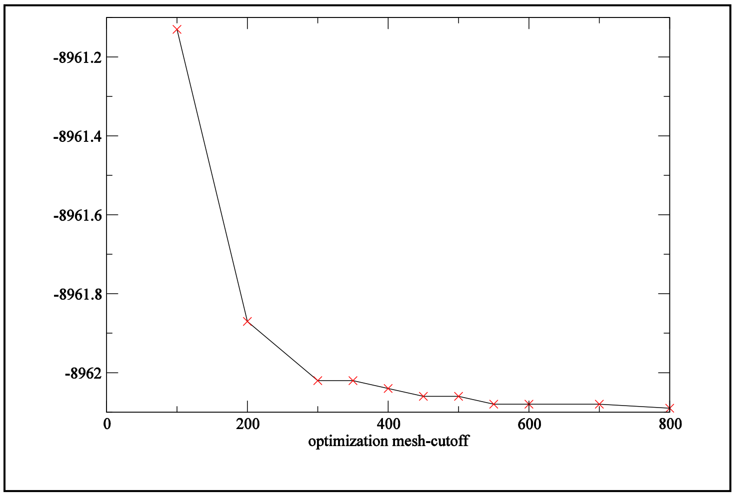

Figure 1. The change of total energy with Mesh-cutoff.

III. RESULTS AND DISCUSSION

The structure N@C60 molecule with the line of high symmetry in the first Brilloen Zone has been shown in Fig. 2. The length of single bond C–C and doble bond C=C,after relaxation, was 1.44 A˚ and 1.39 A˚, respectively. These results are in agreement with the other researcher's results [17].

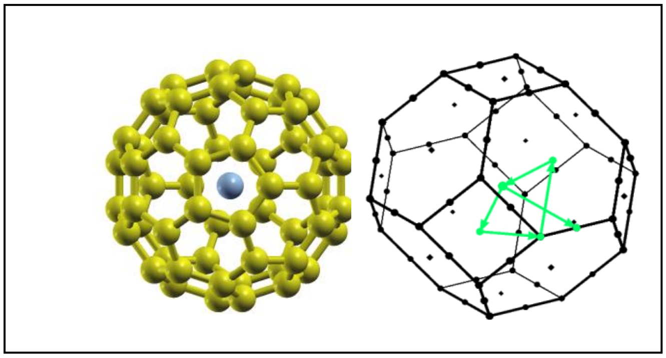

Figure 2. N@C60 molecule (left) and the first Brilloen Zone with the lines of high symmetry(right).

The band structure and Density of State(DOS) of pure C60 has been shown in Fig. 3 and 4. We see that the distance between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO) is about 1.63 eV which show pure C60 molecule have a semiconductor character. This energy gap is comparable with the other researcher’s theoretical works which is 1.64[18] and 1.72[19]eV.

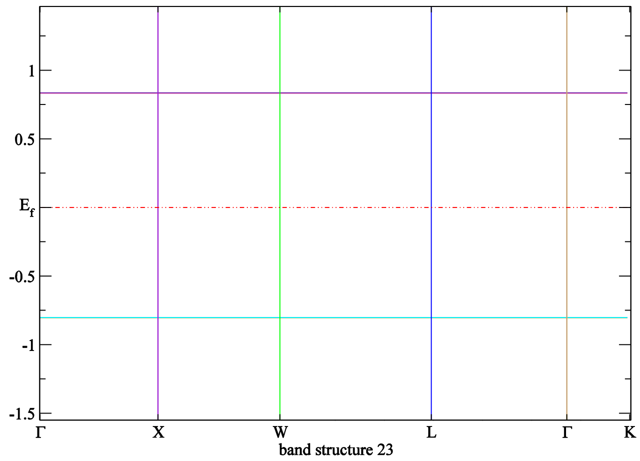

Figure 3. Band structure of pure C60 with lattice constant $23A^0$. Fermi Energy has been set to zero.

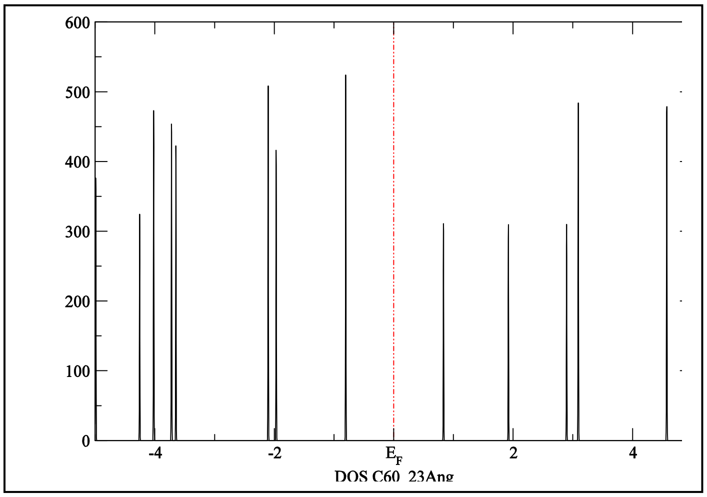

Figure 4. The calculated DOS of pure C60. Fermi Energy has been set to zero.

The results of band structure and DOS calculations for N@C60 are presented in figs .5 and 6, respectively. Here it is clearly seen that the presence of N atom in the center of fullerene has dramatically changes the band structure by creating two narrow bands near the Fermi energy which is an indication of higher conductivity compared with C60.In conclusion the insertion of N atom in the centre of fullerene drastically changes the electronic and properties of C60 considerably and therefore changes its conductivity.

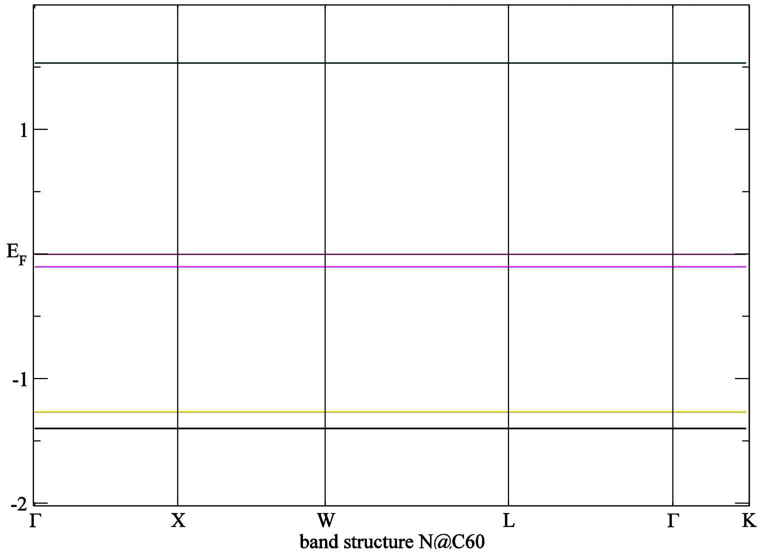

Figure 5. The calvulated band structure of N@C60.Fermi Energy has been set to zero.

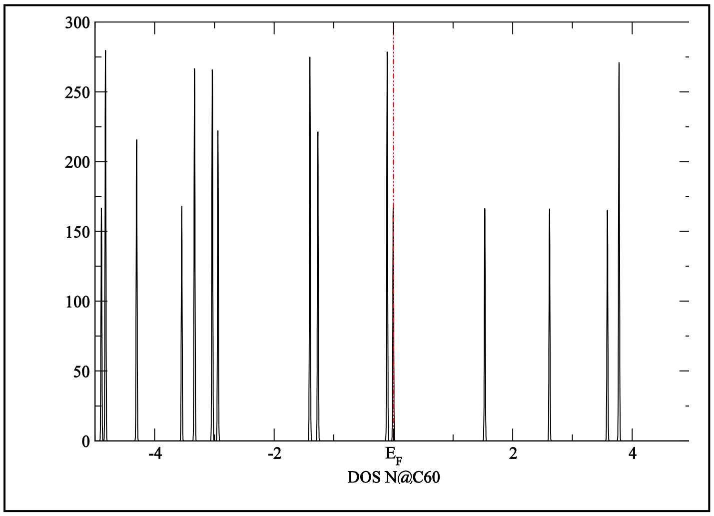

Figure 6. The calculated DOS of N@C60.Fermi Energy has been set to zero.

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References

[1] Smith BW, Monthioux M, Luzzi DE. Encapsulated C60 in carbon nanotubes. Nature (London) 1998;396:323–4.

[2] Kato H, Kanazawa Y, Okumura M, Taninaka A, Yokawa T, Shinohara H. Lanthanoid endohedral metallofullerenols for MRI contrast agents. J Am Chem Soc 2003;125:4391–7.

[3] Saunders M, Cross RJ, Jime´nez-Va´zquez HA, Shimshi R, Khong A. Nobel gas atoms inside fullerenes. Science 1996;271:1693–7.

[4] H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi, Y. Ando, J. Phys. Chem. 96 (1992) 3571.

[5] H. Shinohara, H. Sato, M. Ohkochi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, Nature 357 (1992) 52.

[6] T. Ohtsuki, K. Masumoto, K. Ohno, Y. Maruyma, Y. Kawazoe, K. Sueki, K. Kikuchi, Phys. Rev. Lett. 77 (1996) 3522.

[7] Y. Kubozono, H. Maeda, Y. Takabayashi, K. Hiraoka, T. Nakai, S. Kashino, S. Emura, S. Ukita, T. Sogabe, J. Am. Chem. Soc. 118 (1996) 6998.

[8] J.C. Greer, Chem. Phys. Letters 326 2000. 567–572.

[9] J. Soler et al M, Phys. Condens. Matter14, 2002, 2745.

[10] D. Sanchez-Portal, E. Artacho, P. Ordejon, and J. M. Soler, Quantum Chem. 65, 1997, 453.

[11] P. Ordejon, E. Artacho, and J. M. Soler, Phys. Rev. B53, 1996, R10441.

[12] P. Hohenberg, W. Kohn, Phys. Rev. 136, 1964, B864.

[13] W. Kohn, L.J. Sham, Phys. Rev. 140, 1965, A1133.

[14] N. Troullier and J. L. Martins, Solid State Comm 74, 1990, 613.

[15] N. Troullier and J. L. Martins, Phys. Rev. B43, 1990, 1993.

[16] O. F. Sankey, D. J. Niklewski, Phys. Rev. B40, 1989, 3979.

[17] M. Dienerl, J.M. Alford, Nature 393 (1998) 668.

[18] W.H. Green Jr. et al., J. Phys. Chem. 100 (1996) 14892.

[19] W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T. John, S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, D.R.M. Walton, Nature 353 (1991) 147.