

Density Functional Theory (DFT) modelling of C₆₀ and N@C₆₀

N Kuganathan

Citation

N Kuganathan. *Density Functional Theory (DFT) modelling of C₆₀ and N@C₆₀*. The Internet Journal of Nanotechnology. 2008 Volume 3 Number 1.

Abstract

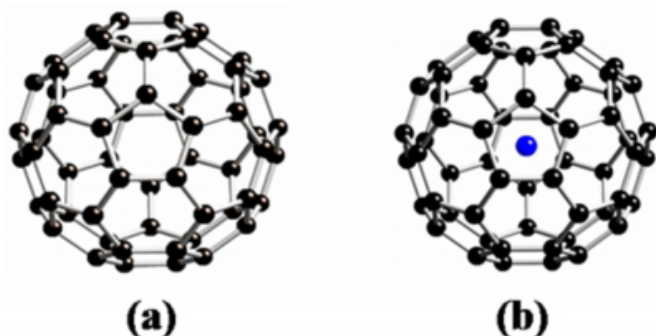
Geometry and electronic structures of C₆₀ and N@C₆₀ are studied using density functional theory within the general gradient approximation (GGA). The calculated bond lengths of C₆₀ are in good agreement with experiment. The results indicate that the endohedral nitrogen-buckminsterfullerene interaction is repulsive and the Nitrogen charge is shown to be contracted. The encapsulated N atom is not covalently bound to the C₆₀ cage. From the Mulliken population analysis, it is found that Nitrogen nearly keeps its atomic electronic configuration. The calculated density of states further confirms the inertness of Nitrogen and both C₆₀ and N@C₆₀ are semiconductors at molecular level.

INTRODUCTION

Prior to 1985 there were two well characterized allotropes of carbon, graphite and diamond. In 1985, fullerenes were discovered and they are new forms of carbon and include a large number of clusters of pure carbon.¹ The most studied molecule among the fullerene is Buckminsterfullerene (C₆₀). It is a soccer-ball shaped molecule formed by 12 pentagons and 20 hexagons with icosahedral symmetry. Encapsulation of atoms inside hollow fullerenes has long attracted great interest since it could lead to new spherical molecules with novel properties unexpected for empty fullerenes. Recently, nitrogen atom has been successfully implanted into C₆₀.² The electron spin resonance spectra of solid N@C₆₀ showed that nitrogen is in its atomic ground state and not covalently bound to the carbon atoms of the fullerene cage.²³

Figure 1

Figure 1: Structures for (a) C and (b) N@C



To investigate the nature of endohedrally encapsulated

nitrogen (N@C₆₀), density functional theory (DFT) calculations were performed using two different DFT codes Amsterdam Density Functional₄ (ADF) and Spanish Initiative for Simulations with Thousands of Atoms₅ (SIESTA).

COMPUTATIONAL DETAILS

The calculations are based on first-principles density functional theory. The ADF and SIESTA codes were used. In the ADF calculations, a triple-zeta basis set with polarization functions was used. For the exchange and correlation term, the generalised gradient approximation (GGA) was used as proposed by Perdew-Becke.⁶ The 1s orbital was considered frozen for both C and N.

In the SIESTA calculations, GGA was used for the exchange-correlation term parameterized by Perdew-Becke-Ernzerhof.⁷ Core electrons are replaced by non-local, standard norm conserving Troullier-Martins pseudopotentials_{8,9,10} for C and N. The reference electronic configuration, cut-off radius and partial core cut-off radius for all pseudopotentials employed here are tabulated (Table 1). For N, a partial core correction is necessary to account for nonlinearity of the exchange and correlation potential between core and valence charge densities.

Figure 2

Table 1: Reference configuration and cut-off radii (a.u.) of the pseudopotentials used in this study.

Atom		C	N
Reference		$2s^2 2p^2 3d^0 4f^0$	$2s^2 2p^3 3d^0 4f^0$
Core radius	<i>s</i>	1.25	1.25
	<i>p</i>	1.25	1.25
	<i>d</i>	1.25	1.25
	<i>f</i>	1.25	1.25
Core cutoff		0.00	1.37

The quality of the pseudopotential was tested comparing the eigenvalues and excitation energies of all-electron calculations on the same series of atomic configurations. The cross-excitation energies for C and N pseudopotentials were not more than 0.04 eV respectively indicating the excellent transferability of these pseudopotentials.

The one-electron Kohn-Sham eigenstates were expanded in a basis of strictly localized NAOs.¹¹ For C and N, a double η basis set for 2s and 2p valence states and a single η basis set for 3d were used.

Structure optimizations were performed using a conjugate gradient algorithm and the forces on the atoms were obtained from the Hellmann-Feynman theorem including Pulay corrections. In all optimised structures forces on the atoms were smaller than 0.04 eV/Å and the stress tensor was less than 0.02 GPa. To represent the charge density a cut-off of 250 Ry for the real space grid integration was used in all calculations. A single k-point (Γ) point was used for all calculations to represent the Brillouin zone due to the large super cell. Cubic super cells with 15 Å were used for all calculations to make sure that the two adjacent structures do not interact with each other.

RESULTS AND DISCUSSION

The experimental and calculated bond lengths are listed in Table 2 and 3.

Figure 3

Table 2: Bond lengths(C-C) calculated for the C and N@C by both ADF and SIESTA methods

Compound	Method	Type	Distance
N@C ₆₀	ADF	C-C	3.553 Å
N@C ₆₀	SIESTA	C-N	3.538 Å

The two bond lengths for C₆₀ are: D_{C-C} = 1.398 Å and D_{C=C} = 1.453 Å in ADF method. In SIESTA method these values are 1.394 Å and 1.447 Å. These values are in good agreement with the experiment.¹² Upon introduction of Nitrogen atom to form N@C₆₀, these bond lengths become D_{C-C} = 1.398 Å and D_{C=C} = 1.456 Å in ADF method and these values are 1.393 Å and 1.447 Å in SIESTA method revealing a slight strain for both bonds.

The closest C-N distances were measured in the optimised structures to understand the nature of bonding. The measured distances are tabulated in Table 3.

Figure 4

Table 3: Closest C-N distances in the optimised composites

Method	Bond	C ₆₀ (Å)	N@C ₆₀ (Å)
ADF	(6,6)	1.398	1.398
ADF	(6,5)	1.453	1.456
SIESTA	(6,6)	1.394	1.393
SIESTA	(6,5)	1.447	1.447
Experiment ¹²	(6,6)	1.401	-----
Experiment ¹²	(6,5)	1.458	-----

In both methods, C-N distances are quite long indicating there are no chemical bonds.

The C₆₀ molecule forms a closed -shell system and the atomic ground state of nitrogen is, a spin quartet. Table 4 summarises the valence charges.

Figure 5

Table 4: Spin density values on N@C

Compou	Meth	Spin	Spin	Net
N@C ₆₀	ADF	3.9600	1.0310	2.8290
N@C ₆₀	SIES	3.9773	1.0291	2.9471

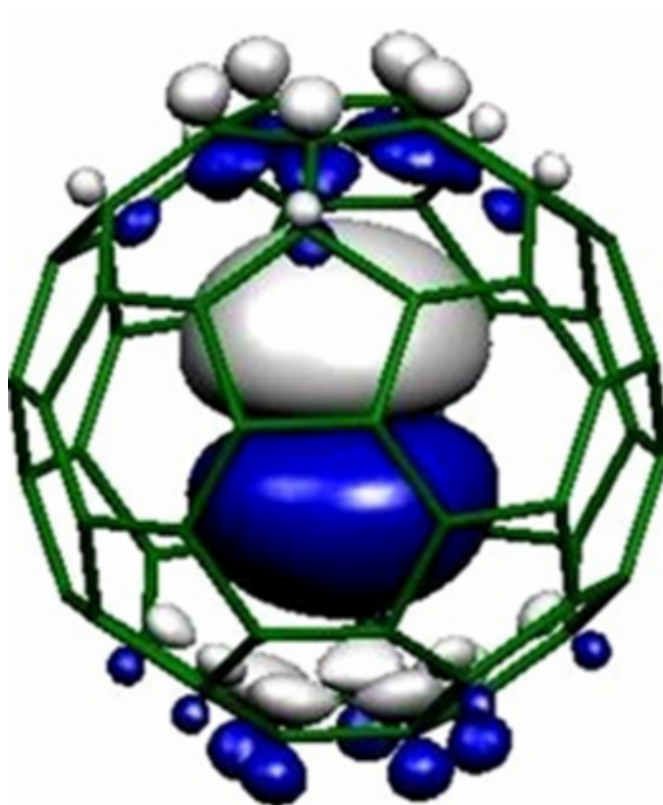
In SIESTA calculations, the Mulliken population for spin up and spin down on N atom are 3.960 and 1.031 respectively and the net spin polarization (defined by the difference between the number of spin up and spin down electrons) is 2.829. There is a very small increase (0.001-0.002e) in electronic population on each carbon atom of C₆₀ cage, clearly showing only a very small charge transfer from the N to the C₆₀ cage.

In ADF calculation spin up and spin down values on N are 3.9773 and 1.0291 respectively and the net spin polarization is 2.9471. A small increase (0.0009e) in electron population on each carbon atom of C₆₀ cage is observed.

The highest occupied molecular orbital (HOMO) of the N@C₆₀ is given in Figure 2.

Figure 6

Figure 2. HOMO of N@C

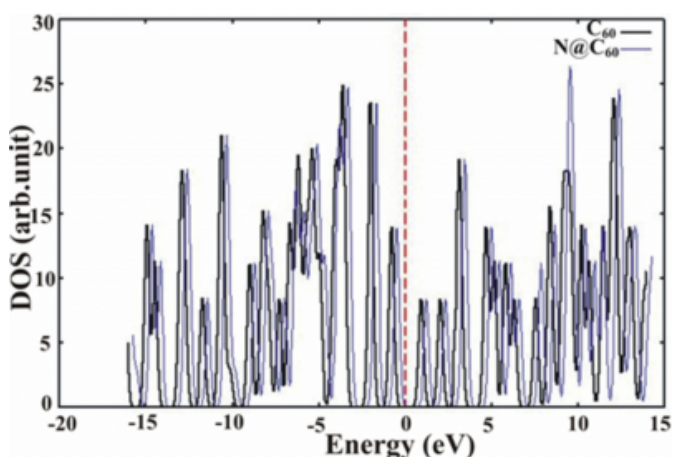


In the HOMO of N@C₆₀, significant contribution from π orbitals of Nitrogen and Carbons in C₆₀ is observed. This further supports the conclusion that charge on N is contracted and charge transfer is from N to C₆₀ cage.

The calculated density of states for both C₆₀ and N@C₆₀ is shown in Figure 3. It is found that there is not much alteration near the Fermi level indicating negligible charge transfer between Nitrogen atom and C₆₀.

Figure 7

Figure 3: Density of states plots for C and N@C.



CONCLUSIONS

In conclusion, the density functional calculations have been performed on C₆₀ and endohedral N@C₆₀. Interaction between the nitrogen atom and the C₆₀ cage is weak to form covalent bonds and alter the atomic electronic configurations of the N atom, as in good agreement with the experiments. Minimal charge transfer is observed between N and the C₆₀ cage. Density of states for both plots further confirms this and shows a band gap of 0.6 eV indicating both the C₆₀ and N@C₆₀ are semiconductors at molecular level

References

1. R. E. Smalley: "Discovering the fullerenes", Rev. Mod. Phys. 1997, 69, 723.
2. T. A. Murphy, T. Pawlik, A. Weidinger, M. Hohne, R. Alcala, J. M. Spaeth: "Observation of Atomlike Nitrogen in Nitrogen-Implanted Solid C₆₀" Phys. Rev. Lett. 1996, 77, 1075.
3. C. Knapp, K. P. Dinse, B. Pietzak, M. Waiblinger, A. Weidinger: "Fourier transform EPR study of N@C₆₀ in solution" Chem. Phys. Lett 1997, 272, 433.
4. G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler: "Chemistry with ADF" J. Comp. Chem 2001, 22, 931.
5. P. Ordejon, D. Sánchez-Portal, A. Garcia, E. Artacho, J. Junquera, J. M. Soler: "Large scale DFT calculations with SIESTA", RIKEN Review 2000, 29, 42.
6. J. P. Perdew: "Density-functional approximation for the correlation energy of the inhomogeneous electron gas" Phys. Rev. B 1986, 33, 8822.
7. J. P. Perdew, K. Burke and M. Ernzerhof: "Generalized Gradient Approximation Made Simple" Phys. Rev. Lett. 1996, 77, 3865.
8. G. B. Bachelet, M. Schlüter: "Relativistic norm-conserving pseudopotentials" Phys. Rev B 1982, 25, 2103.
9. M. Fuchs, M. Scheffler: "Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory" Comput. Phys. Commun. 1999, 119, 67.
10. N. Troullier, J. L. Martins: "Efficient pseudopotentials for plane-wave calculations" Phys. Rev. B 1991, 43, 1993.
11. J. Junquera, O. Paz, D. Sanchez-Portal, E. Artacho: "Numerical atomic orbitals for linear-scaling calculations" Phys. Rev. B 2001, 64, 235111.
12. T. Miyake, S. Saito: "Geometry and electronic structure of rhombohedral C₆₀ polymer" Chem. Phys. Lett. 2003, 380, 589.

Author Information

Navaratnarajah Kuganathan

Department of Chemistry, University of Bath