

DFT COMPUTATIONS OF THE LATTICE CONSTANT, STABLE ATOMIC STRUCTURE AND THE GROUND STATE ENERGY PER ATOM OF FULLERENES (C_{60})

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ABSTRACT

This paper presents the most stable atomic structure and lattice constant of Fullerenes (C_{60}). FHI-aims DFT code was used to predict the stable structure and the computational lattice constant of C_{60} . These were compared with known experimental structures and lattice constants of C_{60} . The results obtained showed that the most stable crystalline structure of C_{60} is the face-centred cubic (fcc) structure, this is in complete agreement with experiment. However, the computed lattice constant of the stable structure is 13.87 Å. This value differs from the experimental value of 14.17 Å by 0.3 Å.

Keywords: Fullerenes, Density Functional Theory (DFT), Atomic Structure, Lattice Constant, Total Energy.

INTRODUCTION

Fullerenes aggregates are a new discovery; their characterization and the determination of their properties is still at an early stage and much work remains to be done. A complete atomic resolution crystal structure of pure C_{60} has not yet been accomplished, but the original soccer-ball model of C_{60} is now generally accepted (Fig. 1). The study of C_{60} and other fullerenes has proved to be exciting from a number of viewpoints. The structure, chemistry, and physical properties of C_{60} have all yielded surprising results and unique behaviour. Yet what has been accomplished so far shows the striking potential of these materials (Fleming *et al.* 1992; Pierson, 1993).

It was originally assumed that the solid aggregate of C_{60} fullerenes had a hexagonal close-packed (hcp) structure. Another common space group that occurs is the body-centered cubic (bcc) structure $Im\bar{3}$. Contrary to these, X-ray diffraction shows that C_{60} crystallizes on an fcc rather than a bcc lattice, a result implying space group $Fm\bar{3}m$ rather than $Im\bar{3}$, providing that all solvent molecules are eliminated (Pierson, 1993; Fleming *et al.* 1992). However, it is also reported that Solid C_{60} undergoes two orientational phase transitions. Above 250K, solid C_{60} has a face-centered cubic (fcc) lattice with the lattice constant of 14.17 Å and the interfullerene distance of about 10 Å, and C_{60} molecules rotate freely. Below 250 K, solid C_{60} has a simple-cubic (sc) lattice (space group $Pa\bar{3}$), (Byun, 2012). In addition, the intermolecular bonding of C_{60} is dominated by van der Waals forces, as confirmed by measurements of the isothermal compressibility (Pierson, 1993). Thus, this research work deals with the prediction of the stable atomic structure and the lattice constant of Fullerenes (C_{60}) using FHI-aims DFT code.

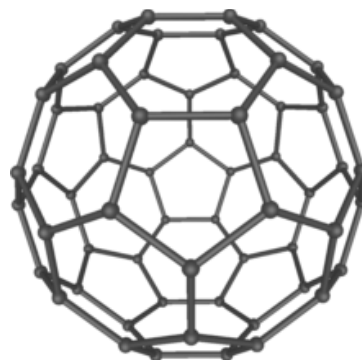


Fig. 1: Bucky-ball shape of Fullerenes (C_{60})

MATERIALS AND METHODS

First principles, or *ab initio* calculations represent the pinnacle of electronic structure calculations. Starting with the fundamental constants and Schrodinger's equation as a postulate, these methods proceed to describe the nature of atomistic systems to a degree that is almost irrefutable. Computational resources and methods have come a long way since the time of Paul Dirac's quote (Carlson, 2006), and some of these complicated equations referred to have in fact become readily solvable. But the complexity of the many electron problem governed by Schrodinger's equation remains burdensome for large atoms. While these methods are rigorous in describing physical effects they are computationally expensive. The methods applied in solving Schrodinger's equation break into two main types: Hartree-Fock (HF) based methods and Density Functional Theory (DFT) methods. While both make approximations to make calculations possible, they represent the best available methods for atomistic modeling.

The original idea of DFT (i.e. using the electron density) is dated back to the individual work of Thomas (1927) and Fermi (1927). In Thomas-Fermi model, they showed that the distribution of electrons in an atom is uniform and can be approximated using statistical considerations. In 1964, Hohenberg and Kohn (HK) proved two simple but important theorems, which later become the basis of DFT. In 1965, in a trade of simplicity for accuracy, Kohn and Sham (KS) invented an ingenious indirect approach to the theory in such a way that the kinetic energy can be computed simply to a good accuracy, leaving a small residual correction that is handled separately. They showed that one can build a theory using simpler formulas, namely;

$$T_S[n] = \langle \psi_i | -\frac{1}{2} \nabla_i^2 | \psi_i \rangle \quad (1)$$

and

$$n(\vec{r}) = \sum_i^N \sum_S |\psi_i(\vec{r}, S)|^2 \quad (2)$$

where ψ_i are the natural spin orbitals. To give a unique value to the KS kinetic energy functional $T_S[n]$ through Eq. (1), KS invoked a corresponding non-interacting reference system, with the Hamiltonian:

$$\hat{H}_S = \sum_i^N (-\frac{1}{2} \nabla_i^2) + \sum_i^N V_S(\vec{r}_i) \quad (3)$$

in which there are no electron-electron repulsion terms, and for which the ground state electron density is exactly $n(\vec{r})$. KS thus established that for any real (interacting) system with ground state density $n(\vec{r})$, there always exist a non-interacting system

with the same ground state density $n(\vec{r})$. For this system there will be an exact determinantal ground state wave function;

$$\Psi_S = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \psi_1 & \psi_2 & \dots & \psi_N \\ \psi_1 & \psi_2 & \dots & \psi_N \\ \dots & \dots & \dots & \dots \\ \psi_1 & \psi_2 & \dots & \psi_N \end{bmatrix} \quad (4)$$

where ψ_i are the N lowest eigenstates of the one electron

Hamiltonian \hat{H}_S

$$\hat{H}_S \psi_i = [(-\frac{1}{2} \nabla_i^2) + V_S(\vec{r}_i)] \psi_i = \epsilon_i \psi_i \quad (5)$$

Now, to produce $T_S[n]$ exactly as the kinetic energy component (Parr and Yang, 1989) of $T[n]$ in HK theorem, KS reformulate the universal functional as;

$$F[n] = T_S[n] + J[n] + E_{xc}[n] \quad (6)$$

where;

$$E_{xc}[n] = T[n] - T_S[n] + V_{ee}[n] - J[n] \quad (7)$$

The defined quantity $E_{xc}[n]$ is called the exchange-correlation energy functional. The corresponding Euler equation for Eq. (7) is;

$$\mu = V_{eff}(\vec{r}) + \frac{\delta T_S[n]}{\delta n(\vec{r})} \quad (8)$$

Where $V_{eff}(\vec{r})$ is the KS effective potential and is defined by;

$$V_{eff}(\vec{r}) = V_{ne}(\vec{r}) + \frac{\delta J[n]}{\delta n(\vec{r})} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \quad (9)$$

$$V_{eff}(\vec{r}) = V_{ne}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad (10)$$

The second term of Eq. (10) is the Hartree potential while the XC potential $V_{xc}(\vec{r})$ is given as

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \quad (11)$$

Therefore, for a given $V_{eff}(\vec{r})$, one gets the $n(\vec{r})$ simply by solving the N one-electron equations;

$$[(-\frac{1}{2} \nabla_i^2) + V_{eff}(\vec{r}_i)] \psi_i = \epsilon_i \psi_i \quad (12)$$

and setting

$$n(\vec{r}) = \sum_i^N \sum_S |\psi_i(\vec{r}, S)|^2 \quad (13)$$

The effective potential from Eq. (9) depends on the electron density; therefore the Kohn-Sham equations have to be solved self-consistently. The electronic total energy E is typically calculated using the sum over the Kohn-Sham eigenvalues;

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \iint \frac{n(\vec{r}_1) n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{xc}[n] - \int V_{xc}(\vec{r}) n(\vec{r}) d\vec{r} \quad (14)$$

The Kohn-Sham scheme is in principle exact. The approximation only enters when we have to decide on an explicit form for the unknown functional for the exchange-correlation energy

$E_{xc}[n]$ and its corresponding potential $V_{xc}(\vec{r})$. The main

goal of modern DFT is therefore to find better approximations to these two functionals. A great variety of different approximations

to $V_{xc}(\vec{r})$ have been developed. For many years the local density

approximation (LDA) has been used (Abdu and Babaji, 2013). In LDA, the exchange correlation energy density at a point in space is taken to be that of the homogeneous electron gas with the local electron density. Thus the total exchange correlation energy functional is approximated as,

$$E_{xc}^{LDA} = \int n(\vec{r}) \epsilon_{xc}(n(\vec{r})) d\vec{r} \quad (15)$$

From which the potential is obtained using Eq. (11). However, LDA can have significant errors in its approximations for some physical and chemical properties computations. Recently, an

effective potential that depend both on the local density and the magnitude of its local gradient are widely used. They are known as generalized gradient approximations (GGA) functionals. The GGA's total exchange correlation energy functional is approximated as,

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int \mathcal{E}_{xc}(n_{\uparrow}, n_{\downarrow}, \vec{\nabla}n_{\uparrow}, \vec{\nabla}n_{\downarrow})n(r)d r \quad (16)$$

There are many GGA versions among which is the Perdew Burke Ernzerhof (pbe) functional (1997) used in this study. On the other hand, there are many DFT computational codes among which is the FHI-aims package. FHI-aims is a computer program package for computational materials science based only on quantum-mechanical first principles mathematical model. It uses solution methods of DFT to compute the total energy and derived quantities of molecular or solid condensed matter in its electronic ground state (Blum *et al*, 2009). In addition, FHI-aims allow describing a wave-function based molecular total energy calculation based on Hartree-Fock and many-body perturbation theory (MP2 and MP4).

The first task is to have a Linux based operating system (OS) (Ubuntu 16.04 version installed for this research work) on a computer. FHI-aims is not supported on windows. Since FHI-aims is distributed in source code form, the next task is to compile a powerful executable program. For this, the following mandatory prerequisites are needed (Blum *et al*, 2009):

- A working FORTRAN compiler. A good example is Intel's ifort compiler.
- A compiled version of the lapack library, and a library providing optimized basic linear algebra subroutines (BLAS). Standard commercial libraries such as Intel's mkl provide both lapack and BLAS support. Having an optimized BLAS library for a specific computer system is critical for the performance of FHI-aims. FHI-aims requires two input files — control.in and geometry.in— located in the same directory from where the FHI-aims binary is invoked. An output file contains the basic information and result of the calculation such as the total energy, atomic forces, etc. The geometry.in file contains all information concerning the atomic structure of the system. This includes the nuclear coordinates, which are specified by the keyword atom, followed by Cartesian coordinates (in units of Å) and the descriptor of the species (Victor *et al*, 2011). The control.in file contains all other physical and technical settings for accurate and efficient convergence of the computations. In particular, it specifies the physical and technical settings for the equations to be solved

The full algorithmic framework embodied in the FHI-aims computer program package is described in (Blum *et al*, 2009). The algorithms are based on numerically tabulated atom-centered orbitals (NAOs) to capture a wide range of molecular and materials properties from quantum-mechanical first principles An all-electron / full-potential treatment that is both computationally efficient and accurate is achieved for periodic and cluster geometries on equal footing, including relaxation and *ab initio* molecular dynamics.

RESULTS AND DISCUSSION

Fullerenes bulk total energies per atom at seven lattice constants at an interval of 0.1 eV were computed for four possible crystalline structures – HCP, BCC, FCC and SC. Results obtained were then analysed and plotted using the plotting software Origin 5.0.

Table 1: Computed Ground State Total energy per atom of

Fullerenes for tier4 light Settings (pbe)

Lattice Constant (Å)	FCC, Total Energy eV/atom.	BCC, Total Energy eV/atom.	SC, Total Energy eV/atom.	HCP, Total Energy eV/atom.
13.87	-1027.18601292	-1027.18584172	-1027.18580194	-1027.18581375
13.97	-1027.18600332	-1027.18583935	-1027.18580125	-1027.18581256
14.07	-1027.18599420	-1027.18583710	-1027.18580059	-1027.18581144
14.17	-1027.18598550	-1027.18583496	-1027.18579997	-1027.18581035
14.27	-1027.18597726	-1027.18583292	-1027.18579937	-1027.18580934
14.37	-1027.18596939	-1027.18583097	-1027.18579880	-1027.18580835
14.47	-1027.18596190	-1027.18582912	-1027.18579826	-1027.18580742

From Table 1 above, it is obvious that, FHI-aims predicts that the most stable structure of Fullerenes is the face-centred cubic (fcc) structure as this structure gives the minimum energy when compared with other structures. This is in complete agreement with experiment (Fleming *et al* 1992; Pierson, 1993). The computed lattice constant of the stable structure is 13.87 Å. This value differs from the experimental value of 14.17 Å by 0.3 eV, and it has a percentage error of 2.12%. Fig. 1 shows that the variation of the total energy per atom with the lattice constant has a linear trend. From the plot, the lattice constant with the minimum energy is 13.87 Å. On the other hand, Abdu and Babaji (2013), also accurately computed the lattice constant and stable atomic structure of Si using FHI-aims code. Hence, this study clearly illustrates that FHI-aims is an efficient and accurate tool for the determination and prediction of materials properties.

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