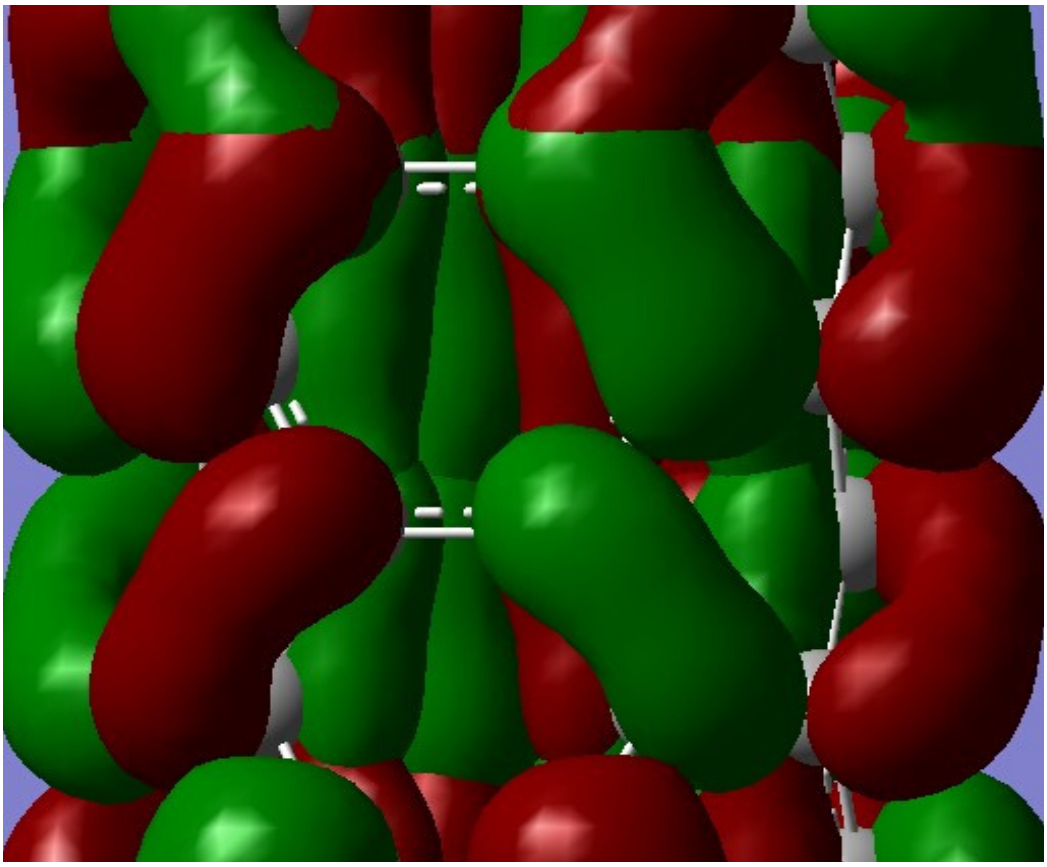
Volume 8, December 2019 ISSN 2542-2545

The HIMALAYAN PHYSICS

A peer-reviewed Journal of Physics



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Him. Phys. **8** 39-46, (2019)

Himalayan Physics

Study of mechanochemistry of carbon nanotube using first principle

Research Article

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Abstract: Mechanochemistry deals with the behavior of molecules under applied stress. Constrained Geometries Simulate External Forces (COGEF) method is used in order to study the mechanics of (3,3) carbon nanotube (CNT) under external stress. This approach is based on the scan of potential energy(PE) due to change in nanotube geometry. Applied force to the system is the negative gradient of change in energy. A hybrid density functional B3LYP along with pseudopotential basis set LanL2DZ as implemented in Gaussian-09 suites of program is used for energy scan of the nanotubes under study. Method comprises constrained geometry optimization of the stretched nanotubes along with their energy scan. The change in successive energies and their corresponding deformation in length helps in determining the externally applied force. We calculated the Young's modulus and force-extension curves. The study elucidates some fundamental electronic processes that undergo in nanosystems with the application of external force. CNT is found to be the elastic and one of the strongest material with rupture force value 38.862 nN . Moreover, we found that it's stability decreases as we deform it. We found that under the effect of external stress semiconducting CNT can behave as good conductor.

Keywords: Carbon Nanotube • DFT • COGEF • HOMO-LUMO

1. Introduction

In last two decades [1–3] new field in chemistry is opened called mechanochemistry, which deals with the study of the molecules exposed to the stresses caused by the external forces resulting change in its geometry. It is less known than thermochemical, electrochemical or photochemical. Whilem Ostwald coined the term mechanochemistry in early 20^{th} centry in his text book on general chemistry [4]. He descibed it as the chemical and physico-chemical changes of substances of all states of aggregation due to the influence of mechanical energy. The history of mechanochemistry reaches the ancient Greek [5].

Computationally we can model mechanochemistry of any material in two ways. First method was developed by Martin Beyer [6] in 2000, known as Constrained Geometries Simulate External Force (COGEF) or isometric approach. In this approach internal coordinate, typically an interatomic distance is fixed to certain value $d_\circ$

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while other DOF are allowed to relax locally. The distance between the distant molecules is increased in stepwise so that we can evaluate COGEF potential by subsequent geometric relaxation at a point. Force required to strain molecule to desired distance is the first derivative of this potential. Here, the maximum force obtained from the negative gradient of the potential is required rupture force and corresponding distance is the breaking point distance. Within this approach, it has been demonstrated [7] that single-reference, correlated wave function theory (WFT) and common exchange-correlation functionals (e.g. PBE or B3LYP) in density functional theory (DFT) are in good agreement with multireference WFT predictions of both the breaking point distance and rupture force. However this approach is not suitable for evaluating bond dissociation energy(BDE) [6].

Marx and coworker [8] introduced the second method called EFEI, commonly known as isotensional approach, which directly incorporates forces as an additional term to the gradient vector of PES. Thus, the potential is tilted without projecting Covalent Mechanochemistry (CMC) reaction to single reactive coordinate as that in COGEF. In this approach we directly apply external force on the molecule and study geometry of the molecule under study.

Carbon nanotube is one of the hottest research topic since more than 18 years due to their excellent physical, chemical and mechanical properties [9]. They are made up of carbon atoms which are rolled and look like a tube. There doesn't exist pure sp^2 hybridization as the bond length between carbon atoms decreases and bond angle changes. σ and π orbitals are no longer perpendicular to each other and there exist mixed hybridization. This is called rehybridization and this effect is well explained by mixture of sp^2 and sp^3-orbitals.. The σ bond plays important role in the mechanical properties of CNT whereas, the weak bond called π bond contributes to the interaction between the layers in MWCNTs, and between SWCNT's in SWCNT bundles. The rolling-up of the graphene-like sheet can be described in terms of the chiral vector C, given by $C = na_1 + ma_2$. An armchair nanotube corresponds to the case of $n = m$, and for a zigzag nanotube, $m = 0$. All other (n,m) chiral vectors correspond to chiral nanotubes.

2. Methodology

In the preset work, hybrid density functional B3LYP along with pseudopotential basis set LanL2DZ as implemented in Gaussian-09 suites of program is used for energy scan of the nanotube under study. According to Beyer [6], B3LYP(Becke, 3-parameter, Lee–Yang–Parr) functional yields reliable results with moderate computational cost even for larger system. This proved to be crucial for this research as our calculation involves geometry optimization of 72 atoms with 372 electrons. It is known that B3LYP fails to account reaction activation barriers, which would suggest that it might not perform very well for regions of the potential energy surface where bonds are significantly lengthened but we here deal with the gradient of energy rather calculation of energy of stretched molecule. Moreover no actual chemical changes takes place in the region of interest. Thus, we assume that the error must lie within the margin of other errors of model. We use LanL2dZ (Los Alamos National Laboratory 2-

double-z) basis set [10–12] as implemented in the GAUSSIAN 09 suite of programs for full geometry optimizations of NT structures. It is a pseudopotential basis set with double z quatlity and overall combination of the valence basis set and ECP is termed as LanL2dZ [11]. ECP replaces the actual many electron system (core+valence) to the virtual system, considering the valence electron which approximately mimics the original system. The use of valence basis set with ECP results basis set that generate the molecular orbitals.

We employed COGEF scheme to calculate the rupture force of the CNT. A series of constrained geometric optimizations is carried out in this approach which is referred as relaxed PE scan. Here, two ends of a molecule are held to increasingly large fixed distances, d:

$$d = |x_i - x_j| \tag{1}$$

and the rest of the molecules are relaxed under this constrained. Then we carry out a constrained minimization to satisfy a given $d_\circ$:

$$V_{COGEF} = V_{BO} - \lambda(d(x) - d_\circ) \tag{2}$$

where V_{BO} is Born-Oppenheimer PES as a fuction of nuclear cartesian coordinates, λ is Lagrange multiplier, and $d_\circ$ is a fixed value of the structural control parameter.

We calculated the Young's modulus of CNT in order to study it's elastic behavior in terms of stress and strain. We obtained Young's modulus as the slope of stress(σ)-strain(ϵ) as:

$$Y = \frac{Stress}{Strain} = \frac{F/A}{\Delta l/l_\circ} \tag{3}$$

$$F = (YA)\epsilon \tag{4}$$

Here, F is the force at the end of CNT and computed through COGEF approach as described above, Δl is the elongation of CNT along its length. From above equation, slope of F vs. ϵ graph is (YA) which we define it as area independent Young's modulus and denote as (Y_s). We first calculate (Y_s) as there always exist uncertainty in defining area(A). So, we consider area as the area of cross-section of end ring of CNT.

We studied the stability of each deformed CNT using B.E/atom values. Here, we calculated the binding energy with respect to the infinitely separated atomic limit. Thus, binding energy per atom for CNT nanotube with ends saturated by hydrogen atoms was calculated as,

$$B.E/atom = \frac{aE(X) - E(X_a)}{a} \tag{5}$$

Here, a and $E(X)$ denotes the total number of carbon atoms and ground state energy of carbon atom. $E(X_a)$ denotes ground state energy of CNT. Thus, positive binding energy represents stable and bound nanotube.

Moreover, we compared the band gap between different states of CNT. For infinite CNT, difference of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gives a measure of band gap. As, CNT under our study is of finite length saturated with hydrogen atom at both ends. So, it give qualitative study of band gap between successive deformed states of CNT. HOMO-LUMO gap is calculated as:

$$E_{HOMO-LUMO} = E_{LUMO} - E_{HOMO} \tag{6}$$

where, E_{HOMO} and E_{LUMO} are energy of highest occupied molecular orbital and least unoccupied molecular orbital respectively.

3. Results and Discussion

We optimized the input file of CNT without any constraints using B3LYP XC functional [6] and pseudopotential LanL2DZ basis set [10–12] in Gaussian 09 program. The values of ground state energy, length and area of cross-section are $-2292.625\ H$, 11.2 Å and 12.90 Å after optimization.

Then, we distorted the CNT structure by successive increase in the length of CNT along a fixed direction. We optimized the material by freezing the end ring atoms of CNT on either side after each deformation. This resulted increase in the value of COGEF potential which is well defined by two graphs given below:

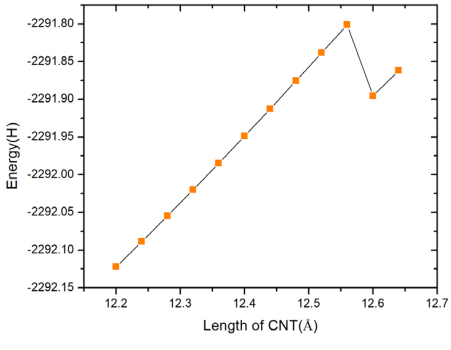

Figure 1. Energy of CNT structure at corresponding length of CNT.

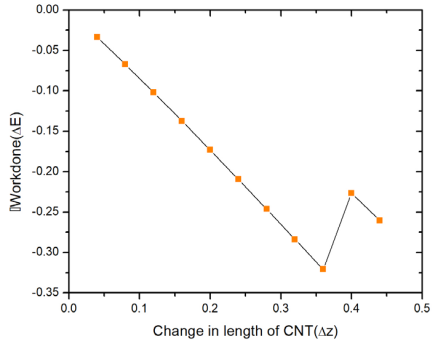

Figure 2. Amount of workdone by the force as a function of constrained length of CNT.

The graph for energy as the function of CNT length and workdone as the function of constrained length is shown in Figs. 1 and 2 respectively. On stretching the CNT along its length, the energy of system goes on increasing. At distance, 12.56 Å we found that the graph has maximum energy value and thus maximum force value. On stretching furthur beyond 12.56 Å with step size 0.02 Å on both end rings we found that the energy significantly falls down indicating the breaking of bond between 12.56 Åand 12.60 Å. Similarly, we found that for $\Delta z < 0.36$ Å , the workdone to stretch the CNT goes on decreasing in successive steps indicating that the

strength of bond to withstand external stress decreases. It attains minimum value at $\Delta z = 0.36$ Å and increases beyond $\Delta z > 0.36\mathring{A}$ indicating that bond must break between distance 0.36 Å and 0.4 Å . This is due to the fact that under effect of external force, system gets deviated from it's ground state and thus energy rises. At particular step the energy of the system decreases significantly as compared to it's last step energy value which is due to the dissociaton of CNT. With step 0.02 Å on either side, we conclude that rupture force and rupture distance are 38.862 nN and 12.56 Å respectively. This value of force is in accordance with the value calculated by Kumar and his team [3]. Experimentally, they showed that SWCNT has cutting and sliding deformation by applying force 30nN and 40 nN.

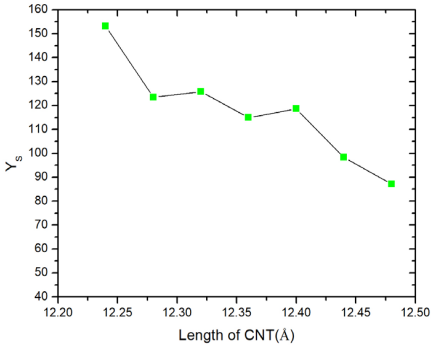

Figure 3. Variation of Y_s as a function of length of CNT.

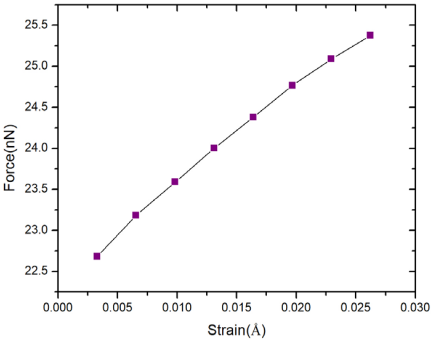

Figure 4. Linear relationship between force and strain for CNT.

We then evaluated the Young's modulus value for our CNT. For that we first calculated the value of Y_s, which is area independent Young's modulus as there is difficulty in assigning the area(A) for the calculation. However, we have considered the area as described in methodology section. We obtained the fluctuating values of Young's modulus(Y) for different stretched states of CNT which is due to quantum nature of CNT. We used classical equation to study the elastic behavior of CNT which excludes many quantum properties of it due to which it's consistency breaks down and might not be constant value. So, we calculated Young's modulus as a average of above datas which values 1.210 Tpa. This value is in accordance with the value obtained by Yu et al. [13] obtanied by direct tensile loading approach. Furthur, Lu [14] mentioned that Young's modulus must be within order of 1 Tpa. We found different values of Young's modulus depending upon choices of method used to calculate them. Moreover, we obtained linear relationship between force and strain which is clearly seen from Fig. 4.

We studied the stability of different deformed states of CNT by plotting B.E Vs CNT length graph. We obtained that B.E decreases with increase in CNT length and reaches to minimum value at breaking distance. On furthur increasing the length of CNT, the value of B.E increases as system shifts towards equlibrium position due to bond breaking of CNT under study.

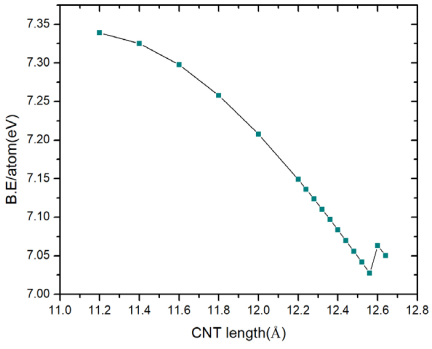

Figure 5. Binding energy as a function of length variation of CNT.

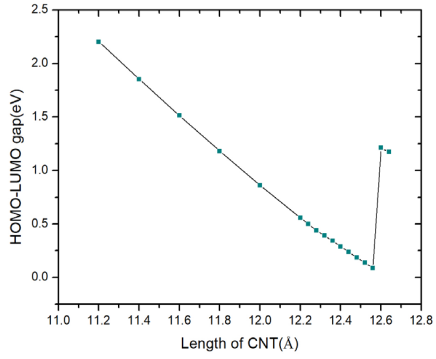

Figure 6. HOMO-LUMO plot as the function of CNT length.

We also calculated HOMO-LUMO gap for each deformed states to study the variation of the energy gap between them. As we elongated the CNT, we obtained that the value of HOMO-LUMO gap decreases upto breaking distance which can be seen from Fig. 6. We also plotted the HOMO-LUMO orbitals for different deformed tube in order to understand the phenomena.

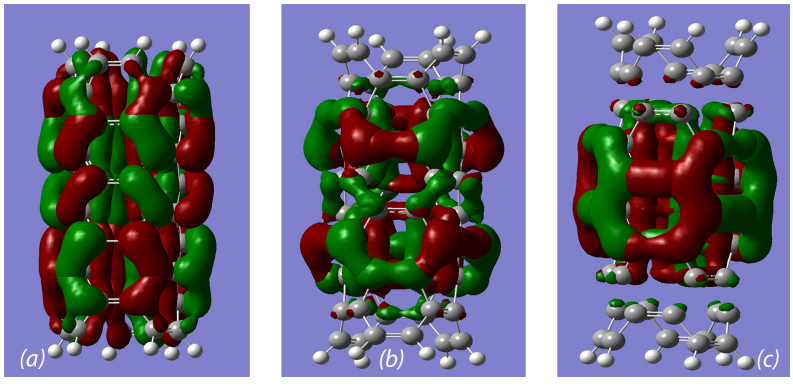

Figure 7. HOMO-LUMO orbital at, (a) 11.2 Å, (b) 12.52 Å length, and (c) 12.56 Å (rupture state)

We found that as the tube is elongated it's HOMO-LUMO orbital tends to concentrate towards the central region of the tube resulting greater overlapping of the orbital(Fig. 7). This clearly signifies that there exist greater hybridization (sp^3 and sp^2) between the orbitals in the central region than in both ends. Moreover, we notice that there exist no orbitals at ends as CNT approaches to it's breaking distance point indicating weakening of bond. At length 12.56 Å it behaves like conductor with band gap about 0.089 eV. This phenomena clearly indicates that CNT becomes more conducting at it's deformed state and verifies that it can behave as both semiconductor and conductor depending upon it's state.

4. Conclusions

We computed COGEF potential using DFT approach along with B3LYP XC functional and pseudopotential basis set LanL2dz for mechanochemical study of carbon nanotube. The force required to dissociate the bond in CNT values 38.862 nN. We obtained breaking distance 12.56 Å for CNT. We calculated Young's modulus value 1.201 Tpa. Moreover, we studied the variation of electronic properties of CNT as a function of external stress. Binding energy per atom of CNT was calculated in order to compare the stability between initial and successive deformed states. We obtained that the binding energy per atom decreases with successive elongation due to the fact that the system is deviated from it's equilibirum ground state. This value increases as the system breaks down and system shifts towards new equilibrium state. We also studied the variation of HOMO-LUMO gap under effect of external stress. For CNT, the value decreases monotonically upto the breaking distance and has minimum value 0.0895 eV at breaking distance point and behaves like conductor. Our calculation on CNT indicates that it can behave both conductor and semi-conductor. As, bond dissociates it's HOMO-LUMO gap increases and behaves as semi-conductor.

5. Acknowledgements

This research was made possible by the help of department of Physics, Prithvi Narayan Campus, Nepal. Moreover, special thanks to all members of Physics Research Initiatives (PRI), Pokhara for their continuous support during our entire research work.

References

[1] Ashkin A. Acceleration and trapping of particles by radiation pressure. Physical review letters. 1970;24(4):156.

[2] Schuetze D, Holz K, Mueller J, Beyer MK, Luening U, Hartke B. Pinpointing mechanochemical bond rupture by embedding the mechanophore into a macrocycle. Angewandte Chemie International Edition. 2015;54(8):2556–2559.

[3] Kumar S, Kaur I, Kumari N, Jain S, Dharamveer K, Jindal V, et al. Atomic force microscope manipulation of multiwalled and single walled carbon nanotubes with reflux and ultrasonic treatments. Applied Nanoscience. 2014;4(1):19–26.

[4] Takacs L. The historical development of mechanochemistry. Chemical Society Reviews. 2013;42(18):7649–7659.

[5] Boldyrev V, Tkáčová K. Mechanochemistry of solids: past, present, and prospects. Journal of materials synthesis and processing. 2000;8(3-4):121–132.

[6] Beyer MK. The mechanical strength of a covalent bond calculated by density functional theory. The Journal

of Chemical Physics. 2000;112(17):7307–7312.

[7] Iozzi MF, Helgaker T, Uggerud E. Assessment of theoretical methods for the determination of the mechanochemical strength of covalent bonds. Molecular Physics. 2009;107(23-24):2537–2546.

[8] Ribas-Arino J, Shiga M, Marx D. Understanding covalent mechanochemistry. Angewandte Chemie International Edition. 2009;48(23):4190–4193.

[9] Iijima S. Helical microtubules of graphitic carbon. nature. 1991;354(6348):56.

[10] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. The Journal of chemical physics. 1985;82(1):270–283.

[11] Wadt WR, Hay PJ. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. The Journal of Chemical Physics. 1985;82(1):284–298.

[12] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. The Journal of Chemical Physics. 1985;82(1):299–310.

[13] Yu MF, Files BS, Arepalli S, Ruoff RS. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. Physical review letters. 2000;84(24):5552.

[14] Lu JP. Elastic properties of carbon nanotubes and nanoropes. Physical Review Letters. 1997;79(7):1297.