INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

RESEARCH ARTICLE

Calculation of Density of States of Pristine and Functionalized Carbon Nanotubes: A DFT Approach

Sarita Tyagi[1,2], **Sunita Negi**[2]*

1 Lecturer, Department of Physics, Government College, Haryana, Faridabad, India
2 School of Engineering & Sciences, G. D Goenka University, Haryana, Gurugram, India

OPEN ACCESS

Received: 30-04-2023
Accepted: 20-09-2023
Published: 31-10-2023

Citation: Tyagi S, Negi S (2023) Calculation of Density of States of Pristine and Functionalized Carbon Nanotubes: A DFT Approach. Indian Journal of Science and Technology 16(40): 3567-3574. https://doi.org/10.17485/IJST/v16i40.1019

* **Corresponding author**.

negisunita.81@gmail.com

Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Abstract

Objectives: Functionalization which is the addition of an external group shows a significant variation in the electron density of a material. To study the impact of chirality and diameter on the Density of States (DOS), different types of carbon nanotubes are sidewall functionalized with electron withdrawing functional groups. The main objective of this work is to investigate how functionalization affects the DOS of nanotubes as a function of chirality and nanotube diameter. **Methods:** This study has been done by Density Functional Theory (DFT) calculations which are a quantum mechanical approach for solving the Schrödinger equation and studying the electronic properties of different materials. DFT calculation is performed on different types of carbon nanotubes with the help of Quantum Espresso software to find its density of states. DFT uses pseudopotential and plane-wave basis sets to represent the electronic wave functions. The DOS of functionalized CNT is compared with that of the pristine CNT. **Findings:** This research aims to examine how chirality affects a sidewall functionalized CNT. A comparison was also made between two distinct functional groups. The metallic CNT is converted into semiconducting CNT and vice-versa when an external group is attached at its vicinity since functionalization modifies its electronic structure. DOS of armchair and chiral carbon nanotubes functionalized with $NH_2$and OH groups on the side wall is compared with its pristine form for the first time. In this study, different groups are adhered to the surface of (4, 4), (4, 2) and (4, 1) CNTs. The diameter and chirality of the CNT have been identified to have a substantial influence on the calculation of the DOS. **Novelty:** An electron withdrawing group is attached to the surface of a carbon nanotube which shows variation in its electronic properties by significantly modifying its density of states. Fermi level shifts and the metallic nanotubes are observed to behave as semi-metallic and vice-versa on functionalization. The curvature effect in the case of small diameter nanotubes hinders the electronic properties of the carbon nanotubes, which can be overcome by functionalization.

Keywords: Single walled carbon nanotube (SWCNT); Double walled carbon nanotube (DWCNT); Density Functional Theory (DFT); Density of States (DOS); Quantum Espresso (QE) software; Sidewall functionalization; Amidogen group (NH_2); Hydroxyl group (OH)

1 Introduction

Carbon Nanotubes are rolled-up graphene sheets that are predicted to be metallic or semiconducting in nature. The electronic properties of the carbon nanotubes depend on their diameter and helicity of the arrangement of graphitic rings within their walls. Its distinctive atomic configuration, mechanical, optical and electrical properties [(1)] make it appealing for a variety of applications in fluids [(2–4)], sensors [(5)], drug delivery [(6)] etc. Defect and covalent sidewall functionalization, as well as noncovalent exohedral and endohedral functionalization, are all potential outcomes of functionalization which is the attachment of an exogenous group [(7,8)] to a material, a carbon nanotube in this case.

When functionalized, the physiochemical characteristics of carbon nanotubes are altered, resulting in a partial charge at the vicinity of carbon nanotubes [(9–11)]. Band structures in crystalline solids are of great interest to both experimental and theoretical researchers for their utility in describing a variety of material properties, including well-known phenomena such as optical absorption and thermal and electronic transport [(12)]. In band structure Density of states (DOS) corresponds to the number of allowed electron energy states per unit energy interval around an energy E. Density of states in the vicinity of Fermi level of SWCNT indicates the nanotube's metallic or semiconducting nature [(13)] i.e. it describes the Fermi level and energy gap. E_g, the Energy gap is the difference between the highest occupied molecular orbital (HOMO) & the lowest unoccupied molecular orbital (LUMO). So the energy gap is a major factor in the determination of electrical conductivity in a material [(14)]. The DOS shows the van Hove singularities caused by one-dimensional structure of CNTs.

The electronic properties of CNTs are due to the sp^2-hybridized carbon atoms and delocalized π network, perpendicular to the nanotube surface. An applied electric field shows changes in carbon nanotube's electronic properties [(15,16)]. In graphene, the carbon atoms have four valence electrons that occupy 2s and 2p orbital ($2s^2\ 2p^2$). As carbon atoms form graphene, three atomic orbital 2s, $2p_x$ and $2p_y$ are hybridized to form three sp^2 hybrid orbital in the same plane, while $2p_z$ orbital remains perpendicular to another orbital. The hybridized orbital is responsible for three σ bonds between adjacent carbon atoms, and the $2p_z$ orbital results in π bonds out of the plane of the graphene sheet. The electronic band structure of CNTs can be derived from the graphene electronic band structure.

According to Saini and others, the amidogen (NH_2) group's electronegative character and nitrogen atom carrying a lone pair of electrons are what generate the charge fluctuation on the carbon atoms [(17)]. The charge variation is observed via DFT calculations (between DOS in states/eV and energy in eV) using Quantum Espresso (QE) software [(18)]. To observe the charge variation, the hydroxyl (OH) group, which is likewise an electronegative group and has a propensity to absorb electrons, is added to the surface of the CNT. Since hydroxyl and amidogen are both highly reactive and electron withdrawing molecules, they could be used as reactive sites for attaching different functional groups. Recently, numerous OH functionalized hydrogenated CNTs had a medication called doxorubicin bonded to their surfaces, demonstrating how functionalization alters a material's electronic configuration, as reported by Karimzadeh and others. [(14)]

For the first time, the density of states of armchair- and chiral-shaped carbon nanotubes functionalized with a single NH_2 or OH group on the side wall are contrasted with those of the materials' unaltered forms in this work to see the effect of single functional group. Different groups are affixed to the surfaces of carbon nanotubes (4, 4), (4, 2), and (4, 1), and the DOS is computed and compared with the pristine forms using DFT. When a functional group is connected to the right kind of CNT, DOS is significantly altered. We notice that the CNT's chirality, length, and diameter all play a very significant impact on how the DOS is determined.

2 Methodology

2.1 Computational details

The density of states of carbon nanotubes can be calculated using a variety of theoretical frameworks and computational techniques, including the tight binding approximation, density functional theory (DFT), and empirical potential methods. In solid-state physics, the density functional theory (DFT) is frequently employed and is ideal for the scenario of weak overlap of atomic wave functions in an insulating crystal.

DFT is extensively used in solid-state physics and performs best when atomic wave functions in an insulating crystal have a weak overlap. The DFT states that the relationship between the coefficient n and m will determine the conducting qualities of various CNT structures. i.e., $\overrightarrow{C}_h = n\overrightarrow{d}_1 + m\overrightarrow{d}_2$, this relates two crystallographic equivalent sites. Here a_1 & a_2 are unit vectors.

$$|\overrightarrow{d}_1| = |\overrightarrow{d}_2| = \sqrt{3}a_{cc}$$

Where a_{cc} is the distance between the nearest neighbor C-atoms. Here $a_{cc} = 1.418\,A$ considered for nanotube formation.

The diameter of CNT is

$$d_t = \frac{\sqrt{3}a_{cc}\sqrt{n^2+nm+m^2}}{\pi} \quad A$$

Whereas the Energy band gap is

$$\frac{0.7}{diameter} \quad eV$$

Where, diameter is in nanometer (nm)

And tangent of the chiral angle θ is

$$tan\theta = \frac{\sqrt{3}m}{[2n+m]}$$

If $(n-m,3|$ = 0, 1, 2, then $|1|$ and $|2|$ shows semiconducting behavior and $|0|$ SWCNTs are metallic in nature at room temperature and exhibit a small chirality dependent energy-gap. The small energy-gap corresponds to quasi-metallic conduction at lower temperature. The minimum value of the energy gap is 0, which corresponds to$p = \frac{2n}{3}$. If n is not an integer multiple of 3 then $p - \frac{2n}{3} = \frac{1}{3}$ [19].

If there is a significant variation in electro-negativity between the constituents, the band shape will change significantly as a result of the redistribution of electron energy. As a result, the screening electrons are largely assigned to low-lying band states, causing the DOS curve to dip to a minimum. If the constituents of the intermetallic compound supply electrons in the same energy range, their wave functions will be extensively mixed, enhancing the bond strength and suggesting a transfer of electrons to a lower energy range, resulting in a pseudo gap. The pseudo gap is a significant depression on the DOS curve close to Fermi level.

2.2 Software Used

2.2.1 Visual Molecular Dynamics (VMD) Software

A computer tool for molecular modeling and visualization called Visual Molecular Dynamic allows users to view and interact with three-dimensional molecular structures [20]. It is primarily designed as a tool for viewing and analyzing the outcomes of molecular dynamics simulations. Additionally, it has capabilities for working with volumetric data, sequence data, and arbitrary graphical objects. The atomic structure in VMD can be in a number of different file types, including PDB and XYZ. During the simulation, VMD displays the dynamic behavior, tracks conformational changes, and examines several carbon nanotube parameters (such as temperature, pressure, and energy). Figure 1 shows a (4, 4) CNT with 80 carbon atoms and a C-C bond length of 1.418 Å.

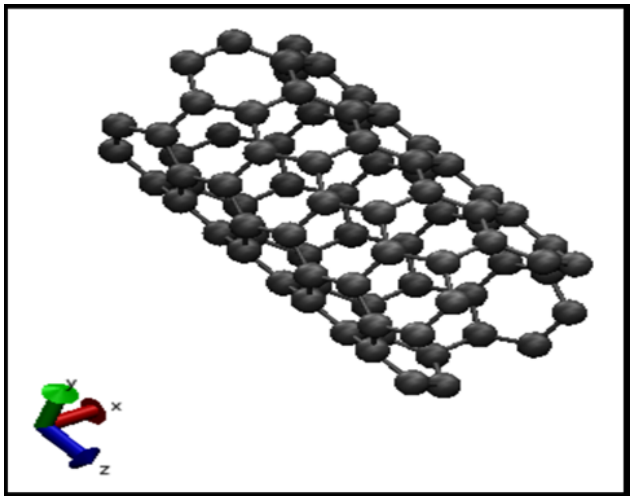

Fig 1. (4,4) CNT created using VMD software

2.2.2 VESTA Software

VESTA (version 3.5.8) is a widely used software package for visualizing, analyzing, and modeling crystal structures. In VESTA, a number of tools are available for analyzing their qualities and creating images suitable for publication [21]. VESTA can automatically determine the space group symmetry of the crystal structure in order to produce symmetry-unique atoms. In VESTA software, crystal data structures can be imported and exported from a variety of file types. It serves as a link between different program by importing the XYZ file format from VMD and exporting it to BURAI in CIF format [Figure 2].

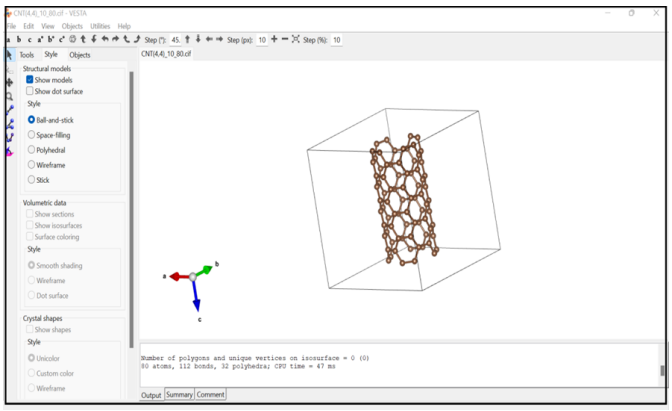

Fig 2. (4, 4) CNT's .CIF file created using VESTA Software

2.2.3 Quantum Espresso (QE) Software

Quantum Espresso (QE) is a comprehensive set of Open-Source computer tools for calculating electronic-structure data and modeling nanoscale materials. Its underpinnings include the density-functional theory (DFT), pseudopotentials, and plane waves [22]. A variety of exchange correlation functionals, including as hybrid functionals, the local density approximation (LDA), and the generalized gradient approximation (GGA), are supported by Quantum Espresso. At limited temperatures, it investigates the dynamical behavior of atoms and molecules. Plane waves, pseudopotentials, density-functional theory (DFT), and other concepts serve as its foundations. The pseudopotentials used are obtained from the Quantum Espresso software library.

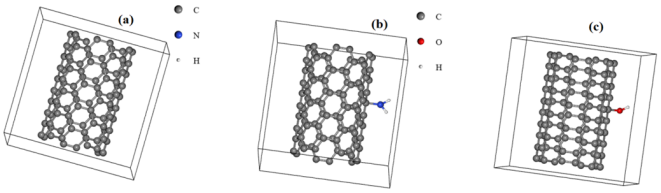

Fig 3. (a) Pristine CNT (b) NH2 functionalized CNT (c) OH functionalized CNT

2.2.4 BURAI

It is the GUI (Graphical User Interface) of Quantum Espresso that finds the density of states (DOS) and band structure other than the optimization, molecular dynamics (MD) and Self-Consistent Field (SCF) calculations of the material used. In order to construct and simulate various cell topologies and evaluate their electrical properties, BURAI software has been employed. CNT is functionalized with different functional groups with the help of BURAI software as shown in (Figure 3) to find out the DOS. Functional groups NH_2 and OH are used to functionalize the CNT on the side wall. The side wall is appropriate for functionalization as compared to the end wall functionalization as it provides a large number of available sites for attachment of the external group. Both the external groups attached are electron withdrawing in nature and are therefore expected to significantly modify the DOS of the pristine CNT. The plane-wave pseudopotential method and the ultrasoft pseudopotential were employed in the calculations of BURAI software.

The flowchart describes the methodology used in this work (Figure 4).

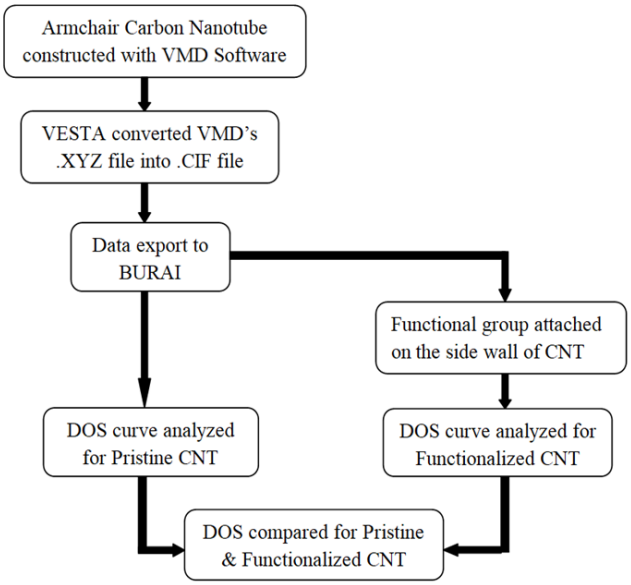

Fig 4. Methodology to find the DOS of CNT

3 Results

Using the VMD software, identical carbon nanotubes of various (n, m) indices are produced. Density functional theory was used to examine the effects of different chiralities on the density of states in carbon nanotubes. The energy density is calculated using the generalized gradient approximation (GGA) with the PBE functional, one of numerous exchange-correlation functionals available in DFT. Approximation and functional are chosen to increase the accuracy. As shown in (Figure 4) of technique section, the density of states (DOS) vs. energy is calculated for several types of pristine and functionalized carbon nanotubes.

In (Table 1), a list of the DOS for various types of CNT is provided. The table also includes other important information, such as the number of atoms, diameter, chiral angle, and energy gap etc. The length of each CNT utilized in the calculation is 10 Å. The band gap energies calculated for CNTs (4, 4), (4, 2), and (4, 1) are, respectively, 1.295 eV, 1.7 eV, and 1.958 eV. Each

of these CNTs has had its side wall functionalized with an NH_2 or OH group. The carbon atoms atomic radius of 0.75 Å and bond width of 1.0 Å was used in all of these computations on SWCNTs. In the DOS graphs, a vertical line drawn at 0 eV serves as a representation of the Fermi level. The Fermi level's left and right sides, respectively, are home to the valence band (VB) and conduction band (CB).

Table 1. Density of Sates (DOS) calculations for different types of Pristine and Functionalized Carbon Nanotubes

CNT	No. of atoms	Diameter of CNT (Å)	Energy Gap (eV)	Chiral angle (ø)	Type of Nanotube	DOS at fermi level (States/eV)		
						P-CNT	NH2-CNT	OH-CNT
(4,4)	80	5.412	1.295	30°	metallic	24.7	9	7.8
(4,2)	56	4.132	1.695	0°<ø<30°	semiconducting	16.7	19.7	17.8
(4,1)	56	3.58	1.958	0°<ø<30°	metallic	29	12.4	11.5

For various types of CNTs in their pristine and functionalized forms, the change in DOS (Table 1) can be observed. It has been found that the functional group dramatically alters the CNT's original electrical structure by significantly modifying its density of states on functionalization.

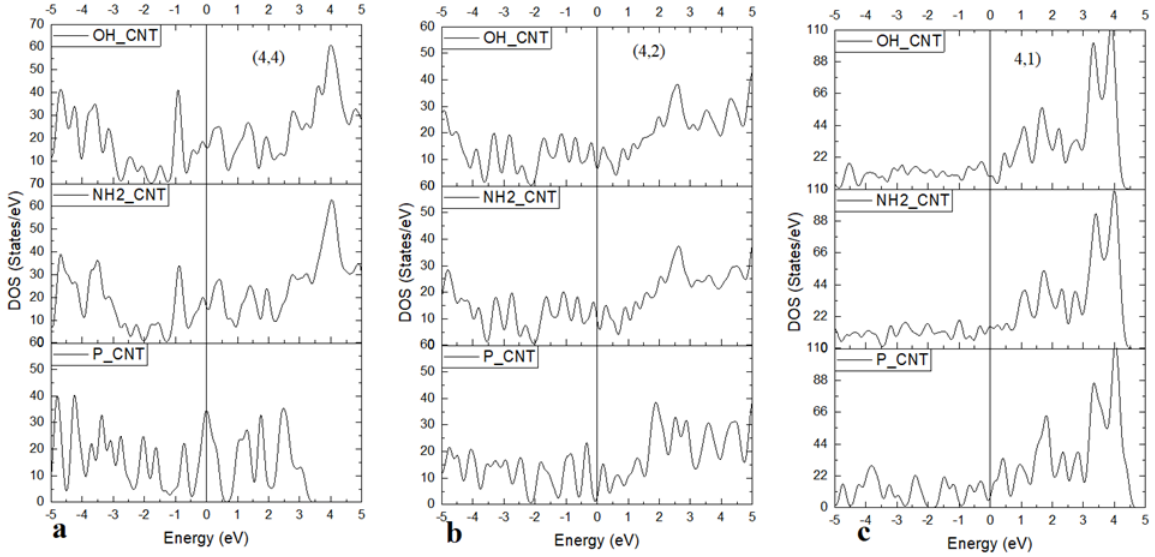

Fig 5. (DOS) of (a) (4, 4) CNT, (b) (4, 2) CNT and (c) (4, 1) CNT in Pristine and Functionalized forms

4 Discussion

We compare the outcomes in the cases of pristine, OH functionalized, and NH_2 functionalized CNT as follows in order to quantify the impact of functional group on the density of states of the carbon nanotubes:

- **Case1:** The metallic features of (4, 4) pristine CNT are shown by the density of states curve in (Figure 5(a)). The Fermi level shifts and the electrical behavior of CNT is seen when amidogen (NH_2) or hydroxyl (OH) groups are introduced on the side wall of it. According to the substance's altered behavior, the peak changes, and functionalized CNT loses some of its metallic characteristics as seen in the DOS. According to the DOS listed in (Table 1), this is the case. In this instance, NH_2 and OH are both seen to exhibit a comparable behavior because of their electronegative nature.
- **Case 2:** The Fermi level in (4, 2) CNT has been moved to a lower level in the DOS plot, as shown by (Figure 5(b)). A gap between the valence band (VB) and conduction band (CB) shows that the material is semiconducting. By functionalizing it with an electronegative group, it becomes metallic. The DOS curves for the NH_2 and OH groups both show remarkably minimal fluctuation outside of the Fermi level. The OH group functionalized CNT exhibits less states at the Fermi level when the two functionalized CNTs are compared.

- **Case 3:** According to the equations in the methodology section, the (4, 1) pristine CNT should behave like a metal, however as seen in (Figure 5(c)), the Fermi level shifts to the left and it displays semiconducting behavior because of the curvature effect. The curvature effect is observed when the diameter of the CNT is less than 4Å. With the exception of at the Fermi level, the outcomes for NH_2 and OH groups when bound to the surface of a CNT are fairly comparable. This is consistent with the pattern of functionalization shown in the (4,4) CNT instance.

Based on the explanation above and the conclusions discussed above, it is clear that the chirality and diameter of the CNT are crucial factors in the DOS calculations. Therefore, picking the appropriate kind of CNT for a certain application will be vital.

5 Conclusion

It has been shown that the density of states considerably alters when groups like NH_2 and OH are functionalized onto carbon nanotubes of different chirality (chiral or armchair). While a chiral CNT can be metallic or semiconducting, armchair CNTs are metallic in nature and exhibit high DOS at the Fermi level. Different groups are attached to the surfaces of CNTs (4, 4), (4, 2), and (4, 1) in this work. The CNT's chirality has been found to have a substantial impact on how the DOS is calculated. The DOS is decreased by the NH_2 group's enhancement of the CNT's electronic structure. In contrast, because the oxygen atom is more electronegative than the nitrogen atom, the OH group reduces the DOS of the CNT more than the NH_2 group.

The curvature effect of the small diameter CNT, however, prevents the same functionalization from having the same effect on the DOS when the CNT diameter is less than 4 Å. This suggests that when a CNT is functionalized with an external group, it changes the electronic properties of the pristine CNT, specifically the HOMO and LUMO of the structure, which changes the energy gap. Although it would be intriguing to know how electron giving groups will affect the CNT's DOS, the current work primarily focuses on electron withdrawing groups. DWCNT can also be used to look into the impact of functionalization on the DOS.

References

1) Dubey R, Dutta D, Sarkar A, Chattopadhyay P. Functionalized carbon nanotubes: synthesis, properties and applications in water purification, drug delivery, and material and biomedical sciences. *Nanoscale Advances*. 2021;3(20):5722–5744. Available from: https://doi.org/10.1039/D1NA00293G.
2) Oveissi S, Toghraie D, Eftekhari SA. Longitudinal vibration and stability analysis of carbon nanotubes conveying viscous fluid. *Physica E: Low-dimensional Systems and Nanostructures*. 2016;83:275–283. Available from: https://doi.org/10.1016/j.physe.2016.05.004.
3) Oveissi S, Eftekhari SA, Toghraie D. Longitudinal vibration and instabilities of carbon nanotubes conveying fluid considering size effects of nanoflow and nanostructure. *Physica E: Low-dimensional Systems and Nanostructures*. 2016;83:164–173. Available from: https://doi.org/10.1016/j.physe.2016.05.010.
4) Talebizadehsardari P, Shahsavar A, Toghraie D, Barnoon P. An experimental investigation for study the rheological behavior of water–carbon nanotube/magnetite nanofluid subjected to a magnetic field. *Physica A: Statistical Mechanics and its Applications*. 2019;534:122129. Available from: https://doi.org/10.1016/j.physa.2019.122129.
5) Maleki R, Afrouzi HH, Hosseini M, Toghraie D, Piranfar A, Rostami S. pH-sensitive loading/releasing of doxorubicin using single-walled carbon nanotube and multi-walled carbon nanotube: A molecular dynamics study. *Computer Methods and Programs in Biomedicine*. 2020;186:105210. Available from: https://doi.org/10.1016/j.cmpb.2019.105210.
6) Maleki R, Afrouzi HH, Hosseini M, Toghraie D, Rostami S. Molecular dynamics simulation of Doxorubicin loading with N-isopropyl acrylamide carbon nanotube in a drug delivery system. *Computer Methods and Programs in Biomedicine*. 2020;184:105303. Available from: https://doi.org/10.1016/j.cmpb.2019.105303.
7) Tyagi S, Negi S. Side wall functionalization of carbon nanotube using MOPAC software. In: EMERGING TECHNOLOGIES; MICRO TO NANO: Proceedings of ETMN-2021;vol. 2752, Issue 1 of AIP Conference Proceedings. AIP Publishing. 2023;p. 30002. Available from: https://doi.org/10.1063/5.0136283.
8) Salah LS, Ouslimani N, Bousba D, Huynen I, Danlée Y, Aksas H. Carbon Nanotubes (CNTs) from Synthesis to Functionalized (CNTs) Using Conventional and New Chemical Approaches. *Journal of Nanomaterials*. 2021;2021:1–31. Available from: https://doi.org/10.1155/2021/4972770.
9) Bibi S, Sarfaraz S, Yar M, Zaman MI, Niaz A, Khan A, et al. Structure and electronic characterization of pristine and functionalized single wall carbon nanotube interacting with sulfide ion: A density functional theory approach. *Journal of Molecular Liquids*. 2022;366:120144. Available from: https://doi.org/10.1016/j.molliq.2022.120144.
10) Nemati-kande E, Pourasadi A, Aghababaei F, Baranipour S, Mehdizadeh A, Sardroodi JJ. Quantum DFT methods to explore the interaction of 1-Adamantylamine with pristine, and P, As, Al, and Ga doped BN nanotubes. *Scientific Reports*. 2022;12(1):1–19. Available from: https://doi.org/10.1038/s41598-022-24200-x.
11) Aasi A, Aghaei SM, Moore MD, Panchapakesan B. Pt-, Rh-, Ru-, and Cu-Single-Wall Carbon Nanotubes Are Exceptional Candidates for Design of Anti-Viral Surfaces: A Theoretical Study. *International Journal of Molecular Sciences*. 2020;21(15):1–23. Available from: https://doi.org/10.3390/ijms21155211.
12) Munro JM, Latimer K, Horton MK, Dwaraknath S, Persson KA. An improved symmetry-based approach to reciprocal space path selection in band structure calculations. *npj Computational Materials*. 2020;6(1):1–6. Available from: https://doi.org/10.1038/s41524-020-00383-7.
13) Su W, Li X, Li L, Yang D, Wang F, Wei X, et al. Chirality-dependent electrical transport properties of carbon nanotubes obtained by experimental measurement. *Nature Communications*. 2023;14(1):1–9. Available from: https://doi.org/10.1038/s41467-023-37443-7.
14) Karimzadeh S, Safaei B, Jen TC. Theorical investigation of adsorption mechanism of doxorubicin anticancer drug on the pristine and functionalized single-walled carbon nanotube surface as a drug delivery vehicle: A DFT study. *Journal of Molecular Liquids*. 2021;322:114890. Available from: https://doi.org/10.1016/j.molliq.2020.114890.

15) Najim A, Bajjou O, Rahmani K, Khenfouch M. First-Principles Study on Electronic and Optical Properties of Single-Walled Carbon Nanotube Under an External Electric Field. *Journal of Molecular Modeling*. 2022;28. Available from: https://doi.org/10.1007/s00894-022-05090-2.
16) Kim G, Bernholc J, Kwon YK. Band gap control of small bundles of carbon nanotubes using applied electric fields: A density functional theory study. *Applied Physics Letters*. 2010;97(6). Available from: https://doi.org/10.1063/1.3478237.
17) Saini R, Negi S. Charge calculation studies done on an end-functionalized double-walled carbon nanotube using MOPAC. *Indian Journal of Physics*. 2020;94(2):189–194. Available from: https://doi.org/10.1007/s12648-019-01473-z.
18) Tyagi S, Negi S. Effect of Diameter on Density of States of Side Wall Functionalized Single Walled Carbon Nanotube. *BioGecko: A Journal for New Zealand Herpetology*. 2023;12(3):3661–3667. Available from: https://biogecko.co.nz/admin/uploads/13540_Biogeckoajournalfornewzealandherpetology_01-06-02.pdf.
19) Sharma AK, Sharma SK. Effect of Diameter and Doping on Electronic Band Structure of Single-Walled Carbon Nanotubes. In: IWPSD 2017: The Physics of Semiconductor Devices ;vol. 215 of Springer Proceedings in Physics. Springer, Cham. 2019;p. 61–68. Available from: https://doi.org/10.1007/978-3-319-97604-4_11.
20) Humphrey W, Dalke A, Schulten K. VMD: Visual molecular dynamics. *Journal of Molecular Graphics*. 1996;14(1):33–38. Available from: https://doi.org/10.1016/0263-7855(96)00018-5.
21) Momma K, Izumi F. VESTA: a three-dimensional visualization system for electronic and structural analysis. *Journal of Applied Crystallography*. 2008;41(3):653–658. Available from: https://doi.org/10.1107/S0021889808012016.
22) Giannozzi P, Baroni S, Bonini N, Calandra M, Car RM, Cavazzoni C, et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*. 2009;21(39):395502. Available from: https://doi.org/10.1088/0953-8984/21/39/395502.