STM JOURNALS

Journal of
Microelectronics and Solid
State Devices

ISSN: 2455-3336
Volume 12, Issue 2, 2025
May–August
DOI (Journal): 10.37591/JoMSD

https://journals.stmjournals.com/jomsd

Review JoMSD

Density Functional Theory (DFT): Understanding and Quantifying Molecular Structure of 2-D Materials

Kaushki Khanna, Darshpreet Singh, Aryendra Singh, Aditi Rai Agnihotri, Usha Shukla*

Abstract

Density Functional Theory (DFT) has emerged as a cornerstone in computational chemistry and materials science, offering a powerful framework for predicting electronic structures and properties of atoms, molecules, and solids. By focusing on electron density rather than wave functions, DFT simplifies the many-body problem through approximations like the local density approximation (LDA) and generalized-gradient approximations (GGAs). The Hohenberg-Kohn theorems establish the theoretical foundation, proving that ground-state properties are uniquely determined by electron density. The Kohn-Sham equations further enable practical applications by mapping interacting systems to non-interacting counterparts. Despite its successes, DFT faces challenges, such as limitations in describing strongly correlated systems and the need for accurate exchange-correlation functionals. This study explores the fundamentals of DFT, including the Thomas-Fermi model and the Kohn-Sham approach, and highlights its applications in chemical reactivity, drug discovery, and catalysis. By bridging theory and computation, DFT continues to drive advancements in understanding and designing materials, though on-going research seeks to address its inherent approximations and expand its capabilities.

Keywords: Density functional theory (DFT), electronic structure, optical properties, first-principles calculations, material science, band gap engineering

INTRODUCTION

One of the most popular computer methods for examining and forecasting the characteristics of individual molecules, bulk solids, and material interfaces, including surfaces, is density functional theory (DFT) [1].

A quick and inexpensive quantum mechanical (QM) method for accurately calculating a variety of materials' physical properties is density functional theory (DFT). Research in this area includes the creation of new analytical methods aimed at creating accurate exchange-correlation functionals as well as the application of this method to forecast the electronic and molecular configuration of atoms, molecules, complexes, and solids in both gas and solution phases [2].

The success of DFT can be traced back to the search for the exchange-correlation functional, which represents complicated many-body events inside one element formalism using density. It might accurately depict the quantum nature of matter if a precise exchange-correlation functional is used.

One amazing success story is density functional theory (DFT). Current efforts are focused on solving electronic structural difficulties in a wide

***Author for Correspondence**
Usha Shukla
E-mail: usha.shukla1@gmail.com

Research Scholar, Amity University Lucknow, Uttar Pradesh, India

Received Date: May 06, 2025
Accepted Date: May 07, 2025
Published Date: May 26, 2025

Citation: Kaushki Khanna, Darshpreet Singh, Aryendra Singh, Aditi Rai Agnihotri, Usha Shukla. Density Functional Theory (DFT): Understanding and Quantifying Molecular Structure of 2-D Materials. Journal of Microelectronics and Solid State Devices. 2025; 12(2): 33–40p.

range of sectors. Nevertheless, DFT's current state has numerous drawbacks: Too sluggish for liquids, too many approximations, failures for systems with strong correlations, etc. [3].

When significant advancements in exchange-correlation energy were considered, it emerged as a compelling substitute for the well-established wave function techniques like Hartree-Fock in the middle of the 1980s. This is because the Hartree-Fock method tackles exchange exactly while ignoring correlation.

Density Functional Theory (DFT) is one of the most widely used methods for "*ab initio*" calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions. The energy functional for electronic systems is then taken into consideration when developing the Kohn-Sham equations. This functional's exchange-correlation component is examined, along with its technically accurate representation in terms of the exchange-correlation hole and its local density approximation [4]. The Thomas-Fermi atomic model is presented first, and then the fundamentals of density functional theory based on Hohenberg, Kohn, and Sham's work are covered [5].

Additionally, DFT serves as the quantitative basis for training novel molecular dynamics, interatomic potentials, enhancing the fidelity of dynamical simulations, and corresponding coarser scale modeling techniques [6]. Numerous body systems are investigated using DFT approaches in a wide range of fields [7].

It has techniques like the generalized-gradient approximations (GGAs), which have proven to be particularly effective for investigating the electronic structures of materials, and the local density approximation (LDA), which is followed by an approximation offering superior structural and magnetic properties. The theoretical underpinnings of this promising method in 1964 by designating density as a "basic variable" and determining all other material characteristics as functionals of its ground state electron density [8]. This study employs Density Functional Theory (DFT) to investigate the electronic and optical properties of 2-D material, providing insights into its potential applications in next-generation optoelectronic devices. By utilizing first-principles calculations, we explore band structure modifications and energy gap tuning, offering a comprehensive understanding of material behavior at the molecular level. The findings contribute to the advancement of material science by enhancing the predictive capabilities of computational methods in designing high-performance functional materials.

ROLE AND GROWING INFLUENCE OF DFT

A one-electron Schrödinger equation took the role of the many-particle issue in density functional theory (DFT), which was a significant advancement. This is accomplished in part by using the exchange-correlation potential, an effective potential that solely depends on the electron density, to describe the Coulomb repulsion between the electrons. This is the origin of the name DFT [9]. Additionally, Figure 1 shows the Electron density of an electronic defect condition at the surface of an anatase crystal (TiO_2) calculated with DFT. Moreover, Figure 2 trends in the number of INSPEC database entries featuring the keywords 'density', 'functional', and 'theory' (DFT-related), compared to those containing 'Hartree' and 'Fock' (Hartree-Fock related), illustrating the growing prominence of DFT in scientific literature relative to overall database growth.

FUNDAMENTALS OF DFT

A simplified version of the Schrodinger equation for a multibody system is the Kohn-Sham equation, a single particle independent Schrodinger equation that may be numerically solved using density functional theory. The physical properties of solids are produced by this computational process; however, this theory is predicated on electron density rather than wave functions, for which scientist Walter Kohn received the 1998 Nobel Prize [2]. The Hohenberg-Kohn theorems were crucial in developing the density-functional theory of many-body systems [8].

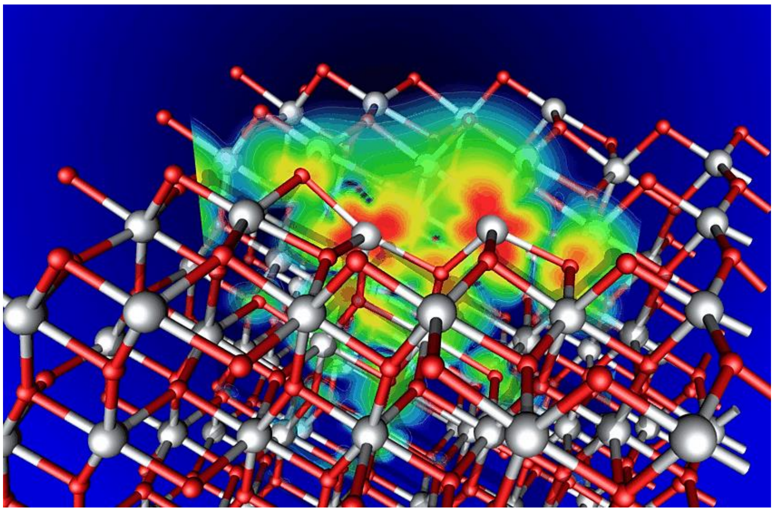

Figure 1. Electron density of an electronic defect condition at the surface of an anatase crystal (TiO_2) calculated with DFT [9].

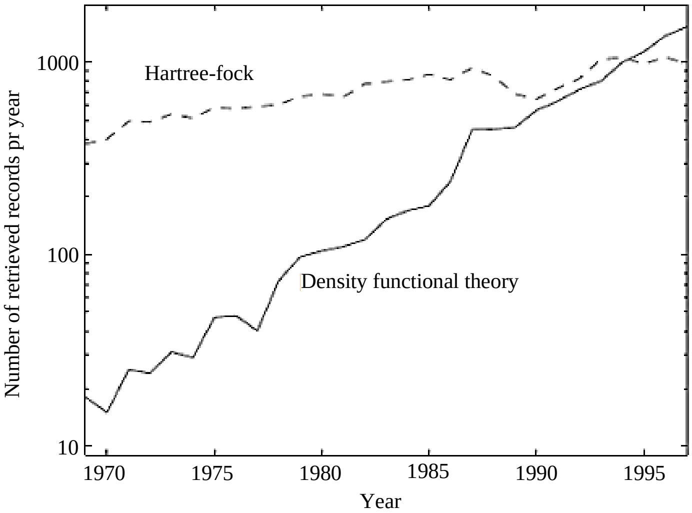

Figure 2. The quantity of entries obtained from the INSPEC databases by searching for the keywords "density", "functional", and "theory" is one sign of the growing usage of DFT. This is contrasted with a comparable search for the terms "Hartree" and "Fock", which tracks the general expansion of the INSPEC databases (about 0.3% of the entries for any given year contain the Hartree-Fock keywords) [4].

Thomas-Fermi-Dirac Approximation

Fermi and Thomas presented an approximation technique that is variational in nature. The goal of the method is to express the total energy as a density functional. Minimization is used to determine the density and energy of the ground state [10]. The minimizing of the energy of any one electron in the statistical atom is the same as the second and third boundary conditions [11]. By concentrating on the electron local density (r) of N electrons, Thomas and Fermi were able to characterize the electronic structure of atoms in 1927 [12].

We examine a stationary state system of N electrons that would follow the stationary Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j} v\left(r_i, r_j\right)\right]\Psi(r_1, \ldots, r_N) = E_i\Psi(r_1, \ldots, r_N)$$

We would try to avoid the complication of searching for the many-electron wave function $\Psi(r_1, \ldots, r_N)$, concentrating on an electron density $\rho(r)$ instead. Being a physical observable, the electron density is easy to measure, compute, and visualize. The density is only probability amplitude to locate a particle close to a specific location in space for a single particle with its associated wave function φ(r); it reads:

$$\rho(r) = \varphi^*(r)\varphi(r)$$

For a system with N particles, the definition of the density is the following:

$$\rho(r) = N \int \Psi^*(r, r_2, \ldots, r_N)\Psi(r, r_2, \ldots, r_N)dr_2 \ldots dr_N$$

That is, the likelihood amplitude of locating any particle in the vicinity of point r in space. In principle, one can attempt to solve the equation repeatedly (subject to certain approximations), i.e., the electron density will be dictated by $\Psi(\{r\})$ and affect, in its turn, the Coulomb potential, and so on till self-consistency. The Thomas-Fermi method, however, focuses on the density ρ(r) as a fundamental quantity to look for, avoiding the consideration of the wave function Ψ entirely (Figure 3) [13].

In this brief note, we contend that the Thomas-Fermi theory, the most basic of all density functional theories, is surprisingly accurate in estimating atom sizes, despite its inability to explain characteristics like molecule binding or the stability of negative ions [14].

The Hohenberg-Kohn Theorems

Our plausibility arguments from the beginning are physically valid, as demonstrated by the first Hohenberg-Kohn theorem. In other words, we are going to demonstrate that the electron density actually dictates the Hamilton operator and, consequently, all of the system's features in a unique way. One may question why it took roughly 40 years after Thomas and Fermi initially employed the density as a fundamental variable before their method was firmly based on physical evidence. The proof first presented by Hohenberg and Kohn in their 1964 work is surprisingly straightforward, and nearly elementary [15].

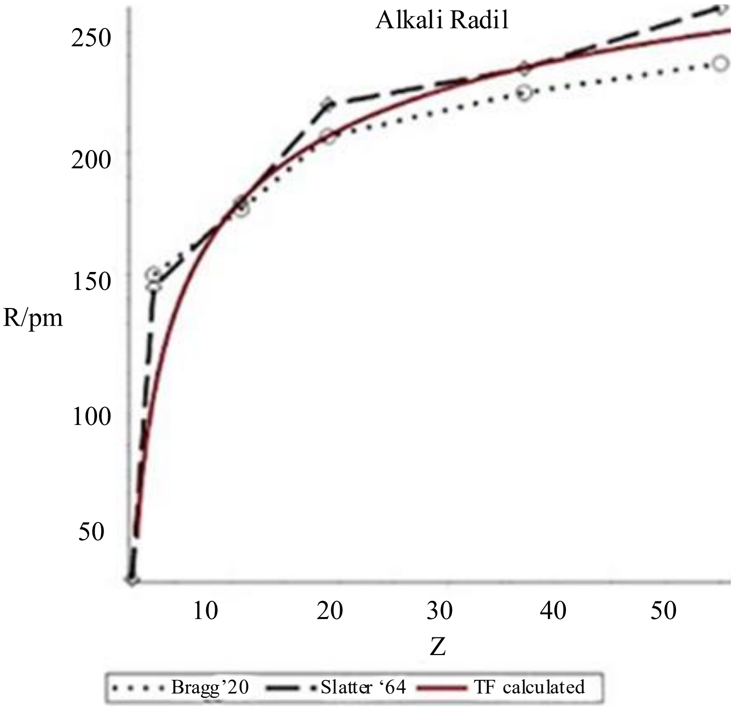

Figure 3. New look at Thomas fermi theory [14].

An isolated chemical system with N electrons will serve as an example of the fundamental concept of DFT [16]. The time-independent Schrödinger equation is solved by the anti-symmetric N-electron wave function Ψ_0 ($r_1, \ldots, r_N$), which describes the electronic ground state of this system and depends on the spatial coordinates of the electrons, {r_i}.

$$\hat{H}\Psi_0 = E_0\Psi_0$$

where E_0 is the associated electronic energy and $\hat{H}$ is the electronic Hamiltonian that is composed of the kinetic energy, electron-electron repulsion, and external potential operators.

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}$$

With

$$\hat{T} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2\,; \quad \hat{U} = \sum_{i<j}\frac{e^2}{4\pi\epsilon_0|r_i - r_j|}\,;\ \hat{V} = \sum_i \hat{v}(i)$$

For an isolated system, the latter reduces to the electron-nuclear attraction operator with a coordinate representation.

$$v(r) = -\sum_K \frac{Z_K e^2}{4\pi\epsilon_0|r - R_K|}$$

where Z_K is the proton number of atom K in the system.

However, the solution of the Schrödinger equation for molecular systems is not simple and necessitates the use of approximations to the N-electron wave function. In contrast, the focus in DFT is set on the one-electron density.

$$n_0(r) = N\int |\Psi_0(r, r_2, \ldots, r_N)|^2 d^3r_2 \ldots d^3r_N$$

This is dependent solely on three variables, specifically the position vector's Cartesian components [16, 17].

Kohn-Sham Equation

Dirac's earlier work, which demonstrated that the exchange energy of a uniform electron gas could be precisely calculated from the charge density along, served as the foundation for Hohenberg, Kohn, and Sham's density functional theory. Although this conventional density functional approach, now referred to as "orbital-free" DFT, establishes a direct relationship with the density alone, in reality, it is a direct approach in which the required equations only include the electron density, making it challenging to derive reasonable approximations for the kinetic energy functional. In order to get around this problem, Kohn and Sham used an indirect method called the Kohn-Sham determinant, which calculates the kinetic energy precisely for a noninteracting reference system. The Kohn-Sham method was the first to turn DFT into a useful computation tool [18].

N electron orbitals ψ_i determine the energy functional.

$$F_{KS}(\{\psi_i\}) = \sum_i \frac{1}{2}\int |\nabla\psi_i|^2$$

$$+\frac{1}{2}\iint \frac{(\rho - m)(x)(\rho - m)(y)}{|x - y|} + E_{xc}\,[\rho].$$

The orbitals are orthonormal, ρ is the electron density given by

$$\rho(x) = \sum_i |\psi_i(x)|^2$$

m is the background charge distribution.

Since it simulates the quantum correlation of electrons, all faults are contained in the final term, the exchange-correlation energy, which involves chemistry. The explicit form, however, is unknown and requires approximation [19].

LOCAL DENSITY APPROXIMATION

The exchange-correlation energy of an electron in a homogeneous electron gas with the same density n(r) is used to approximate the value of $E_{XC}[n(r)]$ in the local density approximation (LDA) [20], i.e.,

$$E_{xc} = \int n(r)\varepsilon_{xc}(n)\ dr$$

The spin polarized variation, also known as the local spin density approximation or LSDA, substitutes the energy density for a polarized homogeneous electron gas for the spin averaged energy density in the equation above.

This approximation, which is the foundation of the majority of contemporary DFT algorithms, is astonishingly accurate despite being so simple. It even performs fairly well in systems with rapidly fluctuating charge densities [21].

Nevertheless, it has a tendency to over predict binding energies and underestimate atomic ground state and ionization energies. Additionally, it is known to favor high spin state structures excessively. Because of these factors, efforts have been made to go beyond the LDA, most notably by incorporating longer range gradient effects through the addition of gradient corrections. But in reality, even if these enhancements appear to produce greater total energies, the resulting structure is frequently inferior and comes at a far higher computational cost. Generally speaking, the LDA gets better with system size and gets worse for tiny molecules.

APPLICATIONS OF DFT

Chemical Reactivity and Molecular Properties

Density Functional Theory (DFT) provides a valuable approach for understanding and quantifying molecular structure and chemical reactivity through electron density functionals. According to the foundational principles of DFT, the electron density alone can determine various ground-state properties, including exchange-correlation energies, molecular stability, and reactivity descriptors. Information-theoretic quantities such as Shannon entropy, Fisher information, and Ghosh-Berkowitz-Parr entropy serve as simple yet effective electron density functionals, offering insights into chemical behavior. These functionals have proven useful in assessing regioselectivity, stereoselectivity, and other key reactivity trends. Additionally, DFT-based methods help evaluate diverse chemical properties, such as electrophilicity, nucleophilicity, acid-base characteristics, and aromaticity, without relying on complex wave function-based calculations. By analyzing electron density distributions, DFT enables the study of both strong covalent interactions and weak noncovalent forces, contributing to a deeper understanding of reaction mechanisms and molecular interactions. This approach simplifies the prediction of isomeric and conformational stability while providing a quantitative framework for chemical concepts [22].

Drug Discovery and Toxicity Prediction

Density Functional Theory (DFT) is widely used in drug discovery and toxicity prediction through Quantitative Structure-Activity Relationship (QSAR) and Quantitative Structure-Toxicity Relationship (QSTR) models. By calculating quantum chemical descriptors such as electronegativity, chemical hardness, and electrophilicity index, DFT provides insights into molecular reactivity and interactions. These descriptors help correlate molecular structure with biological activity, enabling the prediction of pharmacological effects and toxicity without extensive experimental testing. For instance, global descriptors like HOMO-LUMO energies and local descriptors such as Fukui functions identify reactive sites in molecules, which are critical for understanding drug-receptor interactions [23].

DFT-based QSAR models are particularly valuable in virtual screening, where they prioritize potential drug candidates by predicting properties like bioavailability, metabolic stability, and toxicity. This approach reduces costs and accelerates the development of new therapeutics. Additionally, DFT aids in assessing environmental risks by predicting the toxicity of chemical compounds, such as polyaromatic hydrocarbons (PAHs), using electrophilicity and other reactivity indices.

Nitrogen Reduction Catalysis

Density Functional Theory (DFT) is instrumental in evaluating and designing catalysts for the electrochemical nitrogen reduction reaction (ENRR), a promising method for ammonia (NH_3) production. By simulating material properties and reaction pathways, DFT helps identify suitable substrates that can efficiently activate and reduce nitrogen (N_2). For instance, DFT calculations have been used to study defective two-dimensional silicon phosphide (SiP) monolayers as potential catalysts. Introducing a phosphorus defect enhances electron conductivity and N_2 activation while maintaining thermal stability [24].

DFT analysis reveals key catalytic metrics, such as limiting potentials and charge transfer efficiency, which determine the feasibility of the ENRR. It also predicts the suppression of competing reactions like hydrogen evolution or hydrazine (N_2H_4) formation, ensuring selective NH_3 production. These insights guide the rational design of metal-free catalysts, such as group IV–V materials, by optimizing their electronic and structural properties. By reducing reliance on trial-and-error experimentation, DFT accelerates the development of efficient, cost-effective catalysts for sustainable ammonia synthesis.

CONCLUSION

Density Functional Theory has revolutionized quantum mechanical calculations by providing an efficient and scalable method to study complex systems. Its ability to predict electronic, structural, and reactive properties has made it indispensable in chemistry, materials science, and drug design. The Hohenberg-Kohn theorems and Kohn-Sham equations form the bedrock of DFT, while approximations like LDA and GGAs balance accuracy and computational feasibility. However, challenges remain, particularly in treating strongly correlated systems and refining exchange-correlation functionals. Applications in nitrogen reduction catalysis and toxicity prediction underscore DFT's versatility, yet its limitations call for continued innovation. Future advancements may integrate machine learning or hybrid functionals to enhance accuracy. As DFT evolves, it will remain a vital tool for theoretical and applied research, bridging gaps between atomic-scale insights and macroscopic phenomena while pushing the boundaries of computational science.

REFERENCES

1. Sholl DS, Steckel JA. Density functional theory: a practical introduction. John Wiley & Sons; 2022 Dec 15.
2. Aamir M, Ashraf WS, Afzal D, Idrees F, Ahmad R. Fundamentals of Density Functional Theory: Recent Developments, Challenges and Future Horizons. In: Density Functional Theory: Recent Advances, New Perspectives and Applications. InTech Open; London, UK. 2022 May 18: 3.
3. Burke K. Perspective on density functional theory. J Chem Phys. 2012 Apr 21; 136(15): 150901.
4. Argaman N, Makov G. Density functional theory: An introduction. Am J Phys. 2000 Jan 1; 68(1): 69–79.
5. Bretonnet JL. Basics of the density functional theory. AIMS Mater Sci. 2017; 4(6): 1372–405.
6. Orio M, Pantazis DA, Neese F. Density functional theory. Photosynth Res. 2009 Dec; 102: 443–53.
7. Yang J, Nagasaki S, Tsushima S, Yang TT. DFT study of Se (-II) sorption on biotite in reducing conditions. Radiochim Acta. 2025 May 6(0).
8. Pandit M. First Principle Calculation of Electronic Structure. Doctoral dissertation, Master's Thesis. Department of Physics and Astronomy. Rourkela: National Institute of Technology; 2016.
9. Panneerselvam S, Choi S. Nanoinformatics: emerging databases and available tools. Int J Mol Sci. 2014 Apr 25; 15(5): 7158–82.

10. Molinari LG. (10 October 2019). Hartree–Fock and Thomas-Fermi approximations [Online]. Notes for the course of Many Body Theory. Università degli Studi di Milano, Milan. Available from: http://wwwteor.mi.infn.it/~molinari/NOTES/hartree2.pdf.
11. Solovej JP. A new look at Thomas–Fermi theory. Mol Phys. 2016 Apr 17; 114(7–8): 1036–40.
12. Copeland A. Nonlinear Photonics in twisted and nonlocal structures. Dissertation. Texas, USA: Southern Methodist University; 2020.
13. Tomishima Y, Yonei K. Solution of the Thomas-Fermi-Dirac equation with a modified Weizsäcker correction. J Phys Soc Jpn. 1966 Jan; 21(1): 142–53.
14. Englisch H, Englisch R. Hohenberg-Kohn theorem and non-V-representable densities. Phys A: Stat Mech Appl. 1983 Aug 1; 121(1–2): 253–68.
15. Seritan S, Thompson K, Martínez TJ. TeraChem Cloud: A high-performance computing service for scalable distributed GPU-accelerated electronic structure calculations. J Chem Inf Model. 2020 Apr 8; 60(4):2126–37.
16. Agelastos A, Allan B, Brandt J, Cassella P, Enos J, Fullop J, et al. The lightweight distributed metric service: a scalable infrastructure for continuous monitoring of large scale computing systems and applications. SC '14: Proceedings of the International Conference for High Performance Computing, Networking, Storage and Analysis, New Orleans, LA, USA. 2024, Nov 16–21. 2014. p. 154–65. doi:10.1109/SC.2014.18.
17. Annett JF. Efficiency of algorithms for Kohn-Sham density functional theory. Comput Mater Sci. 1995 May 1; 4(1): 23–42.
18. Engel E. Density functional theory. Berlin: Springer-Verlag; 2011.
19. Kohn W. Density functional theory. In: Introductory quantum mechanics with MATLAB: for atoms, molecules, clusters, and nanocrystals. 2019 Jan 4.
20. Lewin M, Lieb EH, Seiringer R. The local density approximation in density functional theory. Pure and Applied Analysis. 2019 Nov 9; 2(1): 35–73.
21. Negele JW. Structure of finite nuclei in the local-density approximation. Phys Rev C. 1970 Apr 1; 1(4): 1260.
22. Rong C, Wang B, Zhao D, Liu S. Information-theoretic approach in density functional theory and its recent applications to chemical problems. Wiley Interdiscip Rev: Comput Mol Sci. 2020 Jul; 10(4): e1461.
23. Sharma P, Ranjan P, Chakraborty T. Applications of conceptual density functional theory in reference to quantitative structure–activity/property relationship. Mol Phys. 2024 Dec 1; 122(23): e2331620.
24. Guo Z, Wang T, Liu H, Qiu S, Zhang X, Xu Y, Langford SJ, Sun C. Defective 2D silicon phosphide monolayers for the nitrogen reduction reaction: a DFT study. Nanoscale. 2022; 14(15): 5782–93.