# An Overview for Beginners on Density Functional Theory in Computational Materials Science and Some of the Related Software Packages

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#### Abstract

This review article explores the basic principles and some practical applications of Density Functional Theory (DFT) in computational materials science, highlighting its significance in predicting and analyzing the electronic, structural, thermodynamic, optical, electrical, and magnetic properties of materials. We begin with discussing the fundamental principles of DFT, including the Hohenberg-Kohn theorems and the Kohn-Sham equations, which provide the framework for solving quantum mechanical equations for many-body systems. The review then explores further approximations used to make these complex calculations feasible, such as the Local Density Approximation (LDA), Generalized Gradient Approximation (GGA), and hybrid functionals. We also mention and classify some popular DFT-based software packages, such as WIEN2k, Quantum ESPRESSO, VASP, ABINIT, and CASTEP, according to their basis set types, computational requirements, and typical use cases. The discussion leads to a focus on WIEN2k, considering the balance of its accuracy and cost, and concluding its choice as a preferred software for our future research in materials science using computational methods.

#### Keywords 📉

Density Functional Theory (DFT), Computational Materials Science, Materials Modeling, and WIEN2k.

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## **1. Introduction**

At their most basic level, materials are made up of atoms. Each atom contains a nucleus, consisting of protons and neutrons. The nuclei in a solid are often treated as point charges, allowing for a simplified representation that neglects the complex interactions between protons and neutrons. Surrounding the nucleus are core electrons, which are tightly bound and situated close to the nucleus, playing a minimal role in chemical interactions. Farther from the nucleus are the valence electrons, which are responsible for bonding between atoms and are important in shaping the material's overall characteristics [1].

At this microscopic level, when dealing with individual atoms and electrons, the behavior of materials must be described using quantum mechanics. This is because, at such small scales, the classical laws of physics, which describe the macroscopic world, no longer apply accurately. Instead, particles like electrons exhibit wave-particle duality, where they can behave both as particles and as waves. Quantum mechanics provides the framework to describe these behaviors, including phenomena such as superposition, entanglement, and tunneling, which have no classical analogs. Moreover, the discrete energy levels, probabilistic nature of electron positions, and the importance of wavefunctions in determining the behavior of electrons are all aspects that can only be captured by quantum mechanical principles [2, 3].

Despite the profound insights that quantum mechanics offers into the behavior of matter at the microscopic level, applying these principles to real-world problems presents significant challenges. These challenges were famously summarized by Paul Dirac in 1929 who stated, "The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are completely known, and the challenge lies in the fact that applying these laws precisely results in equations that are too complex to solve [4]." In other words, we know the laws, we know the equations, but we can't solve them. So, what that tells us is that we have to look at reliable approximations.

This difficulty of solving the Schrödinger equation for manyelectron systems led to the development of several approximations. Two early and important methods are the Hartree approximation and the Hartree-Fock (HF) approximation, both of which attempted to simplify the multi-electron wavefunction. The Hartree approximation assumes that the total wavefunction of a multi-electron system is expressed as a product of single-electron wavefunctions. This approach reduces the many-body problem to a series of single-particle equations. The Hartree potential represents the effective potential an electron experiences, considering Coulomb interactions between electrons while ignoring exchange and correlation effects. This potential represents the classical electrostatic interaction among electrons. However, the Hartree approximation does not consider the Pauli Exclusion Principle, which states that electrons with identical spin cannot share the same quantum state. The Hartree-Fock method improved further the Hartree approximation by incorporating the exchange interaction, which arises because of the Pauli Exclusion Principle. Instead of treating electrons independently, the Hartree-Fock method introduced an antisymmetrized wavefunction known as a Slater determinant, to ensure that electrons with the same spin are kept apart. The Hartree-Fock approximation replaces the Hartree potential with an effective potential that includes an additional exchange term. This exchange term modifies the interaction

between electrons by accounting for the statistical repulsion between likespin electrons [5]. Despite its advantages, the Hartree-Fock method still neglects electron correlation, which refers to the additional interaction effects beyond exchange. This limitation is one of the key reasons why Density Functional Theory (DFT), which includes correlation effects via the exchange-correlation functional, became a widely used method in electronic structure calculations. In other words, this improvement over the two previously mentioned methods lies in how DFT treats the electron-electron interaction. While the Hartree method ignores both exchange and correlation, and the Hartree-Fock method includes only exchange, DFT incorporates both through the exchange-correlation functional. This allows DFT to capture essential many-body effects at a much lower computational cost. And as a result, DFT often produces more accurate predictions of ground-state energies and other material properties, especially in systems where electron correlation plays a critical role.

DFT provides an approach to simplify and solve the quantum mechanical equations governing the behavior of electrons in many-body systems, making it possible to predict and analyze material properties with remarkable accuracy. The development and application of DFT have led to a range of software tools designed to perform these calculations, each with its own strengths and specialized applications [6]. In this review article, we will explore various levels of simplifications which are the theoretical basis of DFT and we will provide a summarized overview of some popular DFT software packages used in computational materials science.

## 2. First simplification: Born-Oppenheimer approximation

Before this approximation, the main challenge was the inability to practically solve the full Schrödinger equation for multi-particle systems, particularly molecules. The coupling between electronic and nuclear motions resulted in an intractable problem due to the high dimensionality and complexity of the wavefunction. This made it extremely difficult to study and understand molecular behavior and to develop models that could accurately predict chemical properties and reactions. The total Hamiltonian, which includes effects from both the nuclei and the electrons, can be expressed as [7]:

 $\hat{H} =$ 

$$-\frac{\hbar^2}{2}\sum_{i}\frac{\nabla_{R_i}^2}{M_i} - \frac{\hbar^2}{2}\sum_{i}\frac{\nabla_{r_i}^2}{M_e} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0}\sum_{i,j}\frac{e^2Z_i}{|R_i - r_j|} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{e^2Z_iZ_j}{|R_i - R_j|}$$
(1)

The first two terms represent the kinetic energy of the nuclei and electrons, respectively. The remaining terms describe the electrostatic interactions among the electrons and each other, between the electrons and nuclei, and among the nuclei.

To address this problem in actual materials, the Born-Oppenheimer approximation is presented as a first level of approximations to simplify the complex task of solving the Schrödinger equation for molecules. This approximation considers the nuclei in a molecule to be significantly heavier and moving much slower than the electrons. Consequently, the motions of electrons and nuclei can be treated separately, assuming that the ions are fixed in their positions and the term containing the kinetic energy of the nuclei will be zero and term containing the electrostatic forces between nuclei will be constant [7]. With this separation, the electronic Hamiltonian is represented as follows:

$$\hat{H} = 0 - \frac{\hbar^2}{2} \sum_{i} \frac{\nabla_{r_i}^2}{M_e} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|R_i - r_j|} + cons$$
(2)

Omitting the zero and constant terms we get:

$$\hat{\mathbf{H}} = \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\mathbf{r}_i}^2}{M_e} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{r}_j|}$$
(3)

Equation (3) can be written as:

$$\hat{\mathbf{H}} = \hat{T} + \hat{V} + \hat{V}_{\text{ext}}$$
(4)

Equation (4) shows that the Hamiltonian ends up with only three terms. The first term,  $\hat{T}$ , represents the kinetic energy of the electrons. The second term,  $\hat{V}$ , accounts for the interaction between the electrons, known as the electron-electron interaction. The final term,  $\hat{V}_{ext}$ , describes the electron-ion attraction, which can be considered now as an external potential to which the electrons are exposed due to the presence of the ions.

As mentioned previously, solving this equation was challenging, so many other approximations had been developed to further simplify the process. Examples of these approximations include the Hartree approximation and the Hartree-Fock approximation which were not very accurate for solids. Therefore, DFT had emerged as a more modern and powerful method that offers reliable solutions to the problem.

## 3. Second simplification: Density Functional Theory

DFT is a quantum mechanical approach for analyzing the electronic structure of multi-particle systems, including atoms, molecules,

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and condensed matter. The theory is founded on several key theorems and principles, including two important theorems of Hohenberg and Kohn and the Kohn-Sham equations [7].

#### **3.1. Hohenberg-Kohn theorems**

In 1964, Pierre Hohenberg and Walter Kohn had investigated a revolutionary idea: what if instead of focusing on the complicated manyelectron wavefunction, they could describe everything just by knowing the electron density function? The electron density function is a much simpler object. It describes the probability of finding electrons at a given point in space while depending on only three spatial coordinates instead of the 3N required for the wavefunction.

#### 3.1.1. The first Hohenberg-Kohn theorem

Hohenberg and Kohn had proved that the ground-state density function of a multi-electron system has one-to-one correspondence with the external potential  $\hat{V}ext$  mentioned above. This means that the ground-state properties of a multi-electron system depend solely on the electron density function [7].

For more clarification, consider two different electron systems with exactly the same ground-state electron density; Hohenberg and Kohn demonstrated that it is impossible for these two systems to have different external potentials (apart from an additive constant). In other words, the electron density alone is enough to uniquely define the external potential and, therefore, the entire Hamiltonian (the operator that describes the total energy of the system).

A mathematically summarized form of this first theorem is:

The total ground-state energy of a quantum mechanical system is uniquely determined by the electron density functional.

 $E = E[n(\mathbf{r})]$ 

; Where  $n(\mathbf{r})$  is the electron density [6]

It can be obviously seen that the resulted simplification is significant, that is, instead of dealing with a function of 3N variables—such as 78 variables for a single iron atom for example —we now have a function of just three variables, the electron density as a function of position.

## 3.1.2. The second Hohenberg-Kohn theorem

Kohn and Hohenberg had shown that the electron density could uniquely determine the system's properties. The next question was: how do you actually find the correct electron density? This question led to the second Hohenberg-Kohn theorem, which applies the variational principle to determine the ground-state density.

The true ground-state electron density is the one that minimizes the total energy functional.

$$E[n(\mathbf{r})] > E_o[n_o(\mathbf{r})]$$

; where  $n_o(\mathbf{r})$  is the ground state density [6]

This is similar to the variational principle in quantum mechanics, where you find the lowest energy by varying the wavefunction. However, here, the focus is on varying the electron density.

Hohenberg and Kohn showed that if you start with any trial electron density and plug it into this energy functional, the resulting energy will always be equal to or greater than the true ground state energy. When you find the density that minimizes this energy functional, it can be assumed that you've found the true ground state density, and the corresponding energy is the true ground state energy.

While the Hohenberg-Kohn theorems establish a strong theoretical basis for using the electron density as the central quantity in quantum mechanical calculations, they do not provide a practical method for determining the energy functional or solving for the ground-state density. The main difficulty arises from the complexity of the many-body problem, where electron-electron interactions make direct computation of the total energy extremely challenging. To make DFT usable in practice, an approach was needed to approximate these interactions in a computationally feasible way. This need led to the development of the Kohn-Sham formulation.

## 3.2. The Kohn-Sham equations: Making the theory practical

In 1965, Walter Kohn, along with his collaborator Lu Jeu Sham, provided the solution. They introduced what are now known as the Kohn-Sham equations, which reformulated the problem in a way that made it computationally tractable.

Kohn-Sham simplified Hohenberg-Kohn theory by substituting the real interacting electron system with an auxiliary system of noninteracting electrons, incorporating interaction effects through an exchange-correlation potential. In more explaining words, imagine that the electrons are not interacting with each other at all. They only interact with an "effective potential" that we will construct. This effective potential is carefully designed to mimic the effects of the real interactions in the original problem [7, 8]. Then, the Kohn-Sham equations for a system of non-interacting electrons moving in an effective potential  $V_{eff}(r)$  are:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(r)\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

; where

 $\psi_i(r)$ : are the Kohn-Sham orbitals (the wavefunctions of the non-interacting electrons).

 $\epsilon_i$ : are the eigenvalues corresponding to these orbitals.

 $V_{eff}(r)$ : is the effective potential experienced by the Kohn-Sham electrons. The effective potential  $V_{eff}(r)$  is made up of three parts:

- 1. External potential  $V_{ext}(r)$ : This is the potential due to the nuclei in the system.
- 2. Hartree potential  $V_H(r)$ : This accounts for the classical electrostatic interaction between electrons.
- 3. Exchange-correlation potential  $V_{XC}(r)$ : This includes all the quantum mechanical effects of exchange and correlation.

So, The Kohn-Sham equations can be written:

$$\left(-\frac{1}{2}\nabla^2 + V_H(r) + V_{XC}(r) + V_{ext}(r)\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

## 3.3. The Exchange-Correlation (XC) Function

The exchange-correlation function  $E_{XC}(n)$  is perhaps the most complex part of the Kohn-Sham equations. It encompasses all the intricate quantum mechanical effects that aren't captured by the Hartree potential alone [7]. These include:

- Exchange interactions: Arising from the Pauli Exclusion Principle, which states that two electrons with the same spin cannot share the same quantum state.
- Correlation effects: Arising from the fact that electrons avoid each other more than what is accounted for by the Hartree potential due to their mutual repulsion and correlated motion.

Mathematically, the exchange-correlation function is a functional of the electron density n(r) *i.e.*  $E_{XC}[n(r)]$  The exact form of  $E_{XC}[n(r)]$  is not known, but there are various approximations used in practice [7], such as:

- Local Density Approximation (LDA): It assumes that the exchange-correlation energy at each point in space depends only on the local density. LDA assumes a uniform electron gas model, making it particularly effective for systems with nearly constant electron density, such as simple metals and some bulk solids. Despite its simplicity, LDA often overestimates binding energies and struggles with systems where the electron density varies rapidly, such as molecules and surfaces [9].
- Generalized Gradient Approximation (GGA): It considers not just the local density, but also its gradient (how the density changes in space), allowing for a more accurate description of systems with varying electron densities. However, GGA still faces challenges when the interactions between electrons are particularly complex or when electrons influence each other over long distances [9].
- Meta-GGA functionals: Include extra terms like the second derivative of the electron density. These functionals offer improved accuracy in capturing intermediate-range interactions and more

detailed electron correlations. However, this increased accuracy comes at the cost of greater computational demand, limiting their use in large or complex systems [9].

• Hybrid functionals: represent another significant advancement by incorporating a portion of exact exchange energy from Hartree-Fock theory into the DFT framework. By mixing exact exchange with GGA or LDA exchange-correlation energies, hybrid functionals can achieve higher accuracy, particularly in systems where exact exchange interactions are critical. This makes hybrid functionals particularly effective for studying organic molecules, transition metal complexes, and systems involving significant charge transfer. However, the inclusion of exact exchange makes hybrid functionals more computationally expensive, limiting their practicality for very large systems or complex unit cells [9].

In summary, selecting a DFT functional depends on the particular material or system under investigation and the desired balance between computational cost and accuracy. LDA is often a good starting point for bulk solids, while GGA is more versatile and widely used. Meta-GGA and hybrid functionals offer higher accuracy but at a greater computational expense, making them suitable for more complex or delicate systems [9].

The exchange-correlation potential  $V_{XC}(r)$  is a functional derivative of the exchange-correlation energy:

$$V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)} \quad [9].$$

## 4. Applications of DFT in computational materials science

Density Functional Theory has become a key tool in materials science due to its ability to provide accurate predictions of structural, electronic, and magnetic properties while significantly reducing computational costs compared to traditional wavefunction-based methods. Its predictive power enables researchers to screen, design, and optimize materials before experimental validation, accelerating discovery and reducing trial-and-error in the lab. One key application is in electronic structure calculations, where DFT allows researchers to determine a material's band structure and density of states (DOS). The band structure reveals the energy levels electrons can occupy, crucial for predicting electrical conductivity and semiconducting behavior, while the DOS provides insights into the distribution of electrons among these energy levels [10]. Reshak and Azam [11] employed DFT to investigate the electronic structure, electronic charge density, Fermi surface, and optical properties of the Sm<sub>2</sub>NiMnO<sub>6</sub> compound. The specific implementation involves using the full potential linear augmented plane wave (FP-LAPW) method within the WIEN2K code. To handle the exchange-correlation potential, the study used LDA, GGA, and Engel-Vosko GGA (EVGGA) to solve the Kohn-Sham equations. The article mentioned that the calculated bond lengths and bond angles from the DFT calculations are in good agreement with existing experimental data. However, it also stated that there is no tentative data on the band structure of this compound in the literature to be compared with the results.

In terms of structural properties, DFT is employed to predict equilibrium lattice parameters, which define the crystal structure, and to calculate elastic constants such as bulk modulus and Young's modulus, which describe how a material deforms under stress. These calculations are fundamental for understanding a material's geometric structure and

mechanical strength [12-14]. Ghaleb and Ahmed [15] calculated structural properties of Zinc blende ZnS using DFT as implemented in the CASTEP code. GGA and LDA were used to measure exchange-correlation energy. The equilibrium lattice constant was calculated by fitting the outcome data of the equilibrium energy and volume to the 2<sup>nd</sup> order Murnaghan's equation of state (EOS). The bulk modulus was calculated using Murnaghan's equation of state. The elastic constants C11, C12, and C44, which define the mechanical stability of the material, were calculated by measuring the total energy. The estimated lattice constant, bulk modulus, and elastic constant outcomes agreed very well with existing experiments.

DFT also plays a significant role in thermodynamics, helping construct phase diagrams that illustrate the stability of different phases under varying conditions. Additionally, it calculates the free energy of a system, aiding in predicting phase stability and reaction spontaneity [16, 17]. In [18], DFT was employed to compute the thermodynamic properties of Na<sub>2</sub>MgSiO<sub>4</sub>, including heat capacity, entropy, Helmholtz free energy, thermal expansion coefficient, and bulk modulus. The calculated heat capacity was validated against experimental data obtained via differential scanning calorimetry (DSC), demonstrating good agreement.

For optical properties, DFT can predict the dielectric function and absorption spectra of materials. The dielectric function defines a material's response to an electric field, crucial for insulating properties and electronic devices, while the absorption spectra indicate how materials absorb light at different wavelengths, important for applications like solar cells [19, 20]. Gerbi [21] employed DFT and time-dependent density functional perturbation theory (TDDFPT) to explore the electronic and optical properties of monolayer MoS<sub>2</sub>, assessing its potential for optoelectronic and quantum applications. By examining the band structure, absorption spectrum, dielectric function, and joint density of states (JDOS), the study identified MoS<sub>2</sub>'s direct bandgap, the role of Mo-d and S-p orbitals, and its potential in photonic applications, UV detection, and high-energy light emitters.

Magnetic properties is another area where DFT shows unique distinction, as it helps calculate magnetic moments and magnetic ordering in materials, essential for the development of magnetic materials and spintronic devices, which exploit electron spin [19, 20].

DFT is also crucial for studying nanomaterials, whose electronic and mechanical properties can differ significantly from bulk materials due to quantum confinement effects. This makes DFT a fundamental tool for advancing nanotechnology and materials engineering [22].

While DFT is a powerful tool, it has notable limitations because the practical implementations require approximations for the exchangecorrelation functional. These approximations may introduce systematic errors. As discussed by Cohen, Mori-Sánchez, and Yang [23], two major sources of error in standard functionals are the delocalization error and the static correlation error. The delocalization error arises because current functionals artificially spread the electron density and fail to cancel selfinteractions, even for single-electron systems. This artificial spread of the electron density happens because, in DFT, the electron density is treated as a continuous, non-local quantity. When only one electron is present, its own density still interacts with itself, leading to an artificial selfrepulsion. This unphysical interaction should not exist, but most standard

functionals do not eliminate it, resulting in errors in energy calculations and electron distributions. On the other hand, the static correlation error arises because DFT's usual way of handling electrons is using just one arrangement of these electrons. Therefore, it struggles when electrons are in more than one arrangement at the same time, like when a chemical bond is broken. This leads to big errors when predicting what happens as bonds break or when describing materials with lots of electron interactions.

## 5. Widely used DFT software packages

Over the years, various software packages have been developed to implement DFT calculations, enabling researchers to study and predict the electronic structure and properties of materials at the atomic level. Each DFT software package has its own unique set of features, algorithms, and capabilities, designed to address specific types of materials, computational methods, and research needs [24].

The classification of popular DFT tools, as presented in Table 1, can be organized based on various criteria, such as basis set type, typical use cases, computational demand, and licensing.

## 5.1. Basis Set Types

In computational materials science, basis sets are used to approximate wavefunctions and electron densities. A basis set is a collection of mathematical functions used to represent the spatial distribution of electrons in a system. DFT tools are often categorized into those using plane-wave basis sets, such as Quantum ESPRESSO, VASP, ABINIT, and CASTEP, which are ideal for periodic systems like

crystalline solids. On the other hand, tools like Gaussian, ORCA, and SIESTA utilize localized basis sets, which are atomic-like functions, making them well-suited for molecular and non-periodic systems [24]. CP2K employs a hybrid approach, combining atomic-like functions with plane waves, making it highly efficient for large systems and mixedphase simulations [25]. WIEN2k, utilizing the Full-Potential (Linearized) Augmented Plane Wave (FP-LAPW) method, stands out for its precision 0 in solid-state calculations [26].

#### **5.2.** Typical Use Cases

In terms of typical use cases, Quantum ESPRESSO, VASP, WIEN2k, ABINIT, and CASTEP are highly regarded in the field of materials science, particularly for investigating the electronic properties of bulk materials and surfaces. For quantum chemistry and molecular modeling, Gaussian, ORCA, and NWChem are preferred due to their versatility in handling molecular systems. CP2K and SIESTA shine in scenarios involving large-scale simulations, such as those involving complex biological molecules or solid-liquid interfaces. Tools like WIEN2k, VASP, and ABINIT also support advanced electronic structure methods, making them indispensable for researchers needing high precision in electronic and magnetic property calculations [27].

#### **5.3.** Computational Demand

Considering computational demand, WIEN2k and VASP are known for their high computational requirements due to the precision of their methods [26, 28]. Quantum ESPRESSO, ABINIT, and CASTEP offer a balance between accuracy and computational efficiency, making them applicable to various solid-state systems [27]. For large systems where computational efficiency is critical, SIESTA, ORCA, and CP2K south south

provide more resource-efficient solutions, while Gaussian offers flexibility depending on the choice of basis sets and functionals [24, 29, 30].

## 5.4. Licensing

Regarding licensing, VASP, Gaussian, and WIEN2k require commercial licenses, which may limit accessibility but provide robust support and advanced features [30-32]. In contrast, open-source tools like CASTEP, Quantum ESPRESSO, ABINIT, SIESTA, CP2K, ORCA, and NWChem are freely available to the academic community, encouraging widespread use and active development [27, 33, 34].

Category		Software Tools
Basis Set Type	Plane-Wave	Quantum ESPRESSO, VASP, ABINIT,
		CASTEP
	Localized	Gaussian, ORCA, SIESTA, NWChem
	Hybrid	СР2К
	Full-Potential	WIEN2k
	LAPW	
Typical Use Cases	Materials Science	WIEN2k, Quantum ESPRESSO, VASP,
		ABINIT, CASTEP
	Quantum	
	Chemistry	Gaussian, ORCA, NWChem
	Large Systems	CP2K, SIESTA
	High	WIEN2k, VASP
Computational	Moderate	Quantum ESPRESSO, ABINIT, CASTEP
Demand	Lower	SIESTA, ORCA, CP2K
Š.	Flexible	Gaussian
Licensing	Commercial	WIEN2k, VASP, Gaussian
	Open-Source	CASTEP, Quantum ESPRESSO, ABINIT,
		SIESTA, CP2K, ORCA, NWChem

**Table 1:** Summary of Classification of Popular DFT Tools Based on basis set type,

 methodology focus, computational demand, and licensing

Given our research focus in materials science, the programs of interest include WIEN2k, Quantum ESPRESSO, VASP, ABINIT, and CASTEP. However, when considering both accuracy and capabilities, we narrowed down this list to WIEN2k and VASP. WIEN2k, priced at 400

euros for academic use, is much more affordable compared to VASP, which costs 2000 euros. Therefore, we will primarily concentrate on WIEN2k in the following section.

## 6. WIEN2k: Key Features and Applications

#### **6.1. Key Features**

WIEN2k is a computational tool designed for accurate electronic structure calculations in solids. The name "WIEN2k" [35] originates from its development location, Vienna, and the year 2000 when a major update to the WIEN code [36] was released, leading to the modern version widely used today. It uses the Full-Potential Augmented Plane Wave plus Local Orbitals (APW+lo) method. This method divides space into two distinct regions: the muffin-tin spheres centered around each atom, where wavefunctions are expanded in spherical harmonics, and the interstitial region between the atoms, where wavefunctions are expressed as plane waves. This approach provides a highly accurate representation of the electronic wavefunctions in all regions of the crystal [26].

WIEN2k is composed of a series of programs, mainly written in Fortran 90, which are interconnected through tcsh-shell scripts. This structure makes WIEN2k very adaptable, allowing users to select and run a particular program for a specific task. However, it requires users to understand which individual program to use for each task based on input file instructions. The software can be operated through the command line or via a web-based graphical user interface called "w2web," which can be accessed through any standard web browser [26].

The key features of WIEN2k can be summarized in the following points:

- Full-Potential Treatment: Unlike methods that use pseudopotentials to approximate the core electrons, the APW+lo method does not rely on any such approximation. It treats all electrons explicitly and self-consistently, ensuring a detailed and precise description of the electronic structure [26].
- Augmented Plane Waves (APW): In the interstitial regions of the crystal, wavefunctions are expanded in plane waves. Near atomic cores, where electron density changes rapidly, the wavefunctions are augmented using atomic-like functions (spherical harmonics). This combination allows for the accurate description of both core and valence electrons [26].
- Local Orbitals (lo): To further enhance accuracy, WIEN2k uses local orbitals for core or semi-core states. These orbitals are added to describe localized electrons that cannot be captured well by the APW basis set alone. This inclusion ensures flexibility and precision, especially in systems with heavy elements where relativistic effects become significant [26].

This combination of plane waves in the interstitial regions, atomiclike functions near the cores, and local orbitals for localized electrons provides an exceptionally accurate representation of both the bonding environment and the electron distribution in solids.

WIEN2k's use of this combination method allows it to handle a wide range of materials, including those with complex electronic structures, such as semiconductors, metals, and insulators.

As a result of these distinctive features, WIEN2k has been widely used in computational materials science to predict and analyze the electronic, structural, optical, electrical and magnetic properties of different materials, as will be shown briefly in a few examples in the following section.

#### **6.2.** Applications

In ref. [37] the authors utilized the WIEN2k software package to explore the effects of Fe doping on the electrical, electronic, and optical characteristics of ZnO compounds. The WIEN2k package was used to model the electronic band structure and DOS for both pure and Fe-doped ZnO. Their study found that Fe doping has reduced the band gap, from 2.7 eV in pure ZnO to 2.2 eV in the doped version. The article also reported the dielectric function, infrared-light and visible-light absorption, and other optical properties of ZnO, which has changed significantly upon Fe doping. WIEN2k calculations along with semiclassical Boltzmann transport theory were used by the authors to determine the electrical properties of ZnO. The study found that Fe doping has enhanced the electrical conductivity but reduced the carrier mobility.

In ref. [38], a comprehensive study of  $Y_x Ga_{1-x} As$  –ternary alloys, examining how varying the yttrium concentration (x = 0, 0.25, 0.5, 0.75, and 1) influences the alloy's structural, electronic, optical, and elastic properties with the aid of WIEN2k software. The researchers applied several exchange-correlation functionals for different aspects of the calculations: Wu-Cohen generalized gradient approximation (WC-GGA) for structural properties, Engel-Vosko GGA (EV-GGA) for accurate electronic properties, and the Trans-Blaha modified Becke-Johnson (TBmBJ) exchange potential to improve band gap predictions. These calculations were conducted at the level of FP-L(APW)+lo structured within DFT. Their computed results were found to be in good agreement with the available experimental measurements and theoretical predictions.

In ref. [39], the WIEN2K software was employed to examine the thermodynamic, electronic, and structural properties of antimony-doped indium phosphorus alloys  $(InP_{1-x}Sb_x)$  through FP-LAPW method. The authors utilized WIEN2K to simulate unit cells for the binary compounds InP and InSb, subsequently extending the computations to their ternary alloy compositions. The study successfully determined critical properties, including the bandgap energies, elastic constants, and thermodynamic behavior, thereby providing valuable insights into the optoelectronic applications of these alloys.

In the DFT analysis of Ba<sub>2</sub>NbRhO<sub>6</sub> in ref. [40], WIEN2k was also used to determine the electronic band structure, including the bandgap, as well as the structural properties like lattice parameters and atomic positions. Additionally, it was employed to compute the phonon dispersion relation, confirming the material's thermodynamic stability. Furthermore, the optical and thermoelectric properties, such as the dielectric function, refractive index, absorption coefficient, electrical conductivity, Seebeck coefficient, and power factor, were calculated.

For the study of  $Mn_2NTx$  MXenes in ref. [41], WIEN2k was the chosen tool in investigating the studied materials. It was used to calculate the electronic band structure, particularly to understand the influence of surface functionalization on the electronic behavior. Moreover, it was employed to determine the optical properties, including absorption, refraction, and reflection.

In ref. [42], WIEN2k was used too, to optimize the crystal structure and calculate the lattice parameters and bond lengths of  $A_2PdCl_6$  lead-free perovskite. Additionally, it was used to determine the electronic band

structure, including the bandgap, as well as the optical properties, such as the optical conductivity, dielectric constant, and absorption coefficient.

There are thousands of research papers that have used WIEN2k and we would like to recommend the following recent articles for beginners for further exploration of the capabilities of this software [43-52]. However, in spite of these capabilities, WIEN2k has some limitations. First, setting up calculations requires a good understanding of DFT and careful selection of parameters to ensure accurate results. For larger problems, the size of the calculations may exceed the memory available on regular computers, meaning you'll need access to highperformance computing clusters. Additionally, WIEN2k relies on specific software libraries (like ScaLAPACK and LAPACK), and its performance can vary depending on the hardware and how well these libraries are optimized.

## 7. Conclusions

DFT is widely used as the theoretical basis in computational materials science for developing successful software packages used to explore a wide range of material properties at the atomic level. When considering accuracy, cost and many case studies all together, WIEN2k proves versatility and accuracy in modeling complex materials, making it a valuable tool for exploring promising materials in future research work.

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## **Declaration of Conflicting Interests**

The author(s) declared no potential conflicts of interest concerning the research, authorship, and/or publication of this article.

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