

An Introduction to Density Functional Theory

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Density Functional Theory (DFT) is one of the most widely used computational methods in quantum mechanics, providing a powerful framework for studying the electronic structure of matter. By modeling the behavior of electrons within atoms, molecules, and solids, DFT has become an essential tool in fields such as chemistry, physics, and materials science. Unlike traditional wave-function-based methods, DFT simplifies the complex many-body problem by focusing on electron density as the fundamental quantity, rather than dealing directly with the more complicated wave functions. This shift

allows DFT to efficiently describe systems with many particles while maintaining a high level of accuracy. The development of DFT was spearheaded by Walter Kohn, who was awarded the Nobel Prize in Chemistry in 1998 for his pioneering work. Kohn's contributions revolutionized the way scientists solve the Schrödinger equation for multi-electron systems. Today, DFT strikes a balance between computational cost and precision, making it suitable for large-scale simulations in both research and industrial applications. It is indispensable for investigating a wide range of properties, from chemical reactivity and molecular dynamics to the electronic, mechanical, and optical behavior of materials, helping to unlock new insights into the fundamental nature of matter.

This chapter provides an overview of fundamental quantum mechanics, the challenges it presents, and how Density Functional Theory (DFT) addresses these challenges to enable efficient analysis of complex systems.

1 Basic Quantum Mechanics

To understand the foundation of Density Functional Theory (DFT), it is essential to first revisit the fundamental principles of quantum mechanics. Quantum mechanics provides the framework for describing the behavior of particles at the atomic and subatomic levels. Central to this framework is the Schrödinger equation, which governs the dynamics of quantum systems and allows us to derive important properties such as energy levels and wave functions. The Schrödinger equation can be expressed in both time-dependent and time-independent forms. We will focus on the time-independent Schrödinger equation, which is particularly relevant for stationary states of quantum systems. The solutions to this equation give wave functions, which describe the likelihood of where particles are and how they move, as well as the energy eigenvalues, which represent the possible energy levels of the system. Together, these help us understand how electrons behave in atoms and molecules.

1.1 Schrödinger Equation

The Schrödinger equation is a fundamental equation in quantum mechanics that describes the quantum state of a physical system. It is crucial for understanding the behavior of particles at the atomic and subatomic levels, such as electrons, photons, and other quantum objects. First formulated by Erwin Schrödinger in 1925, this equation provides a mathematical framework for predicting the properties and behavior of quantum systems.

The mathematical form of the Schrödinger equation is

$$\hat{H}\Psi = E\Psi, \quad (1)$$

where, \hat{H} is the Hamiltonian operator, Ψ is the wave function of the system, and E is the energy eigenvalue corresponding to the quantum state described by Ψ . This equation is crucial in finding the stationary states of quantum systems. The Hamiltonian, \hat{H} , represents the total energy operator of the system and is typically composed of two parts: the kinetic energy operator, $\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$ and the potential energy operator, $\hat{V} = V(\mathbf{r})$. The kinetic energy operator describes the motion of particles, while the potential energy operator accounts for the forces acting on them due to their positions within the system. Together, these components determine the total energy of the quantum system. Hence, the Schrödinger equation in three dimensions becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \quad (2)$$

1.2 Wave Functions and Probability Density

The wave function, $\Psi(\mathbf{r})$, is a fundamental concept in quantum mechanics. It encapsulates all the information about the quantum state of a system, including the likelihood of finding particles in particular positions \mathbf{r} and with specific properties. In essence, Ψ encodes the physical behavior of the system and allows us to calculate observable quantities, such as energy, by solving the Schrödinger equation. The wave function is generally a complex function that depends on the position of particles in the system. While Ψ itself does not have direct physical meaning, it is crucial for calculating observable properties of particles. The square of the wave function, $|\Psi|^2$, represents the probability distribution for the positions of particles, offering critical insights into their behavior within the quantum system.

2 The Many-Body Problem

The many-body problem in quantum mechanics addresses the challenge of describing systems comprising multiple interacting atoms. Unlike single-atom systems, which can often be analyzed using analytical solutions, many-body systems involve intricate interactions that lead to emergent phenomena, such as correlations and collective behaviors. The Hamiltonian of a many-body system consisting of nuclei and electrons can be written as,

$$\hat{H} = \hat{T}_{\text{nuclei}} + \hat{T}_{\text{electrons}} + \hat{V}_{\text{nn}} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ne}} \quad (3)$$

with the terms representing:

- \hat{T}_{nuclei} : the kinetic energy of the nuclei,
- $\hat{T}_{\text{electrons}}$: the kinetic energy of the electrons,
- \hat{V}_{nn} : the nucleus-nucleus Coulomb repulsion,
- \hat{V}_{ee} : the electron-electron Coulomb repulsion,
- \hat{V}_{ne} : the attractive interaction between nuclei and electrons.

These interaction terms make solving the Schrödinger equation for large systems of atoms exceedingly complex. The Coulomb interactions \hat{V}_{nn} , \hat{V}_{ee} and \hat{V}_{ne} describe the forces between particles, which must be accounted for when determining the total energy of the system. As the number of atoms increases, the number of interactions grows rapidly, making direct analytical or numerical solutions impractical. With the explicit forms of the kinetic energies and interaction terms, the many-body Hamiltonian for a system consisting of nuclei and electrons becomes:

$$\hat{H} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}. \quad (4)$$

Here, the indices I and J run over the nuclei, while i and j run over the electrons. \mathbf{R}_I and M_I are the position and mass of the nuclei, respectively, and \mathbf{r}_i and m_e are the position and mass of the electrons. The terms $|\mathbf{R}_I - \mathbf{R}_J|$, $|\mathbf{R}_I - \mathbf{r}_i|$, and $|\mathbf{r}_i - \mathbf{r}_j|$ represent the distances between nuclei-nuclei, nuclei-electrons, and electrons-electrons, respectively. Z_I is the atomic number of the I -th nucleus.

Solving the many-body Hamiltonian presents several significant challenges in quantum mechanics, particularly in systems involving both electrons and nuclei. The high dimensionality of the problem is a major hurdle; for a system with N electron and M nuclei, the wave function depends on $3(N + M)$ variables, making analytical solutions increasingly intractable as N and M increase. Additionally, the Coulomb interactions between electrons introduce complex correlations, complicating the treatment of each electron as an independent particle. Furthermore, since electrons are fermions, they must adhere to the Pauli exclusion principle, requiring that the many-body wave function is antisymmetric under the exchange of particles, which adds another layer of complexity. The potential energy terms in the Hamiltonian, which encompass nucleus-nucleus and nucleus-electron

interactions, further contribute to the difficulty. While analytical solutions are only feasible for very simple systems, such as the hydrogen atom, most many-body systems with multiple electrons and nuclei do not permit exact solutions.

2.1 Born-Oppenheimer Approximation

Given the complexities associated with the many-body Hamiltonian, particularly in systems containing both electrons and nuclei, it becomes essential to simplify the problem for practical analysis. One of the most widely used approaches is the Born-Oppenheimer approximation, which exploits the significant difference in mass and, consequently, the motion between electrons and nuclei. Since nuclei are much more massive than electrons, their motion can be considered relatively slow compared to the fast-moving electrons. This allows us to treat the nuclei as fixed in space while solving for the electronic wave functions. By separating the total wave function into electronic and nuclear components, the Born-Oppenheimer approximation reduces the complexity of the many-body Schrödinger equation.

Under this approximation, the total Hamiltonian can be expressed as a sum of two parts: the electronic Hamiltonian \hat{H}_{el} , which describes the motion of electrons in the field of fixed nuclei, and the nuclear Hamiltonian \hat{H}_{nuc} , which accounts for the motion of the nuclei interacting with each other. The total Hamiltonian \hat{H} is then given by:

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{nuc}} \quad (5)$$

where

$$\hat{H}_{\text{el}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (6)$$

and

$$\hat{H}_{\text{nuc}} = \sum_I \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 + \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (7)$$

This simplification allows for easier calculations since the focus is primarily on the electronic structure. In many cases, especially in density functional theory, the nuclei are often treated as fixed due to their relatively large mass compared to electrons. This approximation streamlines the calculations by reducing the complexity of the system to that of the electrons interacting in a static potential created by the fixed nuclei. However, if nuclear motion needs to be included, the Schrödinger equation for the nuclei can be solved, treating them as quantum mechanical entities. The total energy E_{total} of the system is then obtained as the sum of the electronic energy and the nuclear energy.

This dual approach captures the intricate interplay between electronic and nuclear dynamics, providing a comprehensive view of the system's energy by accounting for both contributions.

Once the electronic Hamiltonian \hat{H}_{el} is defined, the electronic Schrödinger equation can be expressed as:

$$\hat{H}_{\text{el}}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (8)$$

In this equation, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the many-body wave function, which depends on the positions of all N electrons, and E represents the total energy of the system. Solving this many-body electronic Schrödinger equation poses several challenges. The wave function Ψ is a complex function of all electron coordinates, making it difficult to handle analytically, especially as N increases. Additionally, capturing the correlation between electrons, particularly in systems with strong electron-electron interactions, adds to the complexity. Using all approximations introduced up to now, it is possible to calculate a problem similar to H_2^+ , a single ionized hydrogen molecule. To get results for larger systems, further approximations have to be made.

2.2 Hartree-Fock Approximation and Its Limitations

The Hartree-Fock approximation is a fundamental method in quantum chemistry that provides a way to approximate the many-body wave function of a system of electrons. In this framework, the many-body wave function is expressed as a Slater determinant, which captures the antisymmetry of the wave function required by the Pauli exclusion principle. The Slater determinant is a mathematical construct that combines single-particle wave functions (orbitals) for each electron into a single function, ensuring that the overall wave function changes sign when two electrons are exchanged.

Despite its advantages, the Hartree-Fock approximation has significant limitations. One of the primary drawbacks is that it assumes a mean-field approximation where each electron moves in an average field created by all other electrons. This simplification neglects the electron correlation effects, which are crucial in accurately describing the behavior of many-electron systems, particularly in cases where strong correlations are present. As a result, the Hartree-Fock method often leads to inaccuracies in calculated properties such as bond lengths, reaction energies, and excitation energies.

Furthermore, while the Slater determinant effectively accounts for the antisymmetry of the wave function, it does not capture the dynamic correlation between electrons, which arises from their instantaneous interactions. Additionally, the computational cost of

the Hartree-Fock method scales as $O(N^4)$, where N is the number of electrons in the system. This scaling arises because the method involves calculating integrals over all pairs of electron orbitals. As the number of electrons increases, the number of required calculations grows rapidly, making it computationally expensive for larger systems.

3 Density Functional Theory

Density Functional Theory (DFT) is a powerful quantum mechanical modeling method widely used to investigate the electronic structure of many-body systems. Unlike traditional methods that rely on wave functions, DFT is based on the electron density, which is considered a fundamental variable. The key idea behind DFT is that all properties of a system can be determined from its electron density rather than the many-body wave function. This approach simplifies the problem of solving the Schrödinger equation, as it reduces the complexity associated with many-body interactions. DFT is particularly advantageous because it balances accuracy and computational efficiency, allowing researchers to study larger and more complex systems than would be feasible with wave-function-based methods. By leveraging the Hohenberg-Kohn theorems and the Kohn-Sham equations, DFT provides a practical framework for exploring a wide range of physical, chemical, and material properties.

3.1 The Electron Density

In Density Functional Theory (DFT), the electron density $n(\mathbf{r})$ serves as the central variable for describing a quantum system. The electron density represents the probability of finding an electron at a particular point in space and can be derived from the many-body wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ by integrating over all electron coordinates. This relationship is expressed mathematically as:

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (9)$$

Additionally, we must remember that all electrons are identical; thus, we cannot label them as electron 1 or electron N . Instead, we can determine the probability of any order or set of N electrons being located at the coordinates \mathbf{r}_1 to \mathbf{r}_N .

While the wave function contains comprehensive information about the quantum state of a system, it is the electron density that ultimately determines all measurable properties. The total number of electrons N in the system can also be calculated from the electron

density using the equation:

$$N = \int n(\mathbf{r}) d\mathbf{r}. \quad (10)$$

This integration highlights that the electron density encodes vital information about the total number of electrons, making it a fundamental aspect of DFT. By focusing on $n(\mathbf{r})$ instead of the complex multi-dimensional wave function, DFT simplifies calculations, making it a practical and efficient approach for studying the electronic structure of various materials.

3.2 Hohenberg-Kohn Theorems

Density functional theory as we know it today was born in 1964 when a landmark paper by Hohenberg and Kohn appeared in the *Physical Review*. The theorems they introduced represent the major theoretical pillars on which all modern-day density functional theories are built. These theorems laid the groundwork for the fundamental relationship between electron density and the properties of quantum systems, making DFT a powerful alternative to wave-function-based methods.

The Hohenberg-Kohn theorems are central to the formulation of DFT, and they can be summarized as follows:

First theorem: The ground-state electron density $n(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$ acting on the electrons. This means that if the electron density of a system is known, the external potential can be uniquely inferred, allowing for the derivation of all ground-state properties, including the total energy, from the electron density.

According to the first theorem, the ground-state density and the external potential correspond in a one-to-one manner. Since the external potential is fixed, the Hamiltonian, and hence the wave function Ψ , is determined by the ground-state density $n_0(\mathbf{r})$. The proof of this theorem is straightforward: Consider the ground states of two N -electron systems, characterized by two different external potentials $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$, which differ by more than an additive constant. The corresponding Hamiltonians, \hat{H} and \hat{H}' , would both have the same ground-state density $n(\mathbf{r})$, but different ground-state wave functions, Ψ and Ψ' , with $\hat{H}\Psi = E_0\Psi$ and $\hat{H}'\Psi' = E'_0\Psi'$. Since Ψ' is not the ground state of \hat{H} , it

follows that

$$\begin{aligned}
E_0 &< \langle \Psi' | \hat{H} | \Psi' \rangle \\
&< \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\
&< E'_0 + \int n_0(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] d\mathbf{r}
\end{aligned} \tag{11}$$

Similarly,

$$\begin{aligned}
E'_0 &< \langle \Psi | \hat{H}' | \Psi \rangle \\
&< \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\
&< E_0 + \int n_0(\mathbf{r}) [V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})] d\mathbf{r}.
\end{aligned} \tag{12}$$

Adding equation (11) and equation (12) leads to the contradiction,

$$E_0 + E'_0 < E_0 + E'_0 \tag{13}$$

Hence, no two different external potentials $V_{\text{ext}}(\mathbf{r})$ can give rise to the same ground state density $n_0(\mathbf{r})$ which determines the external potential $V_{\text{ext}}(\mathbf{r})$, except for a constant. That is to say, there is a one-to-one mapping between the ground state density $n_0(\mathbf{r})$ and the external potential $V_{\text{ext}}(\mathbf{r})$, although the exact formula is unknown.

Second theorem: For any trial electron density $n(\mathbf{r})$, the energy functional $E[n]$ will yield a value that is greater than or equal to the ground-state energy E_0 . The equality holds when the trial density corresponds to the true ground-state density. This variational principle implies that one can minimize the energy functional $E[n]$ with respect to the electron density to find the ground state of a system.

There exists a universal functional $F[n(\mathbf{r})]$ of the density, independent of the external potential $V_{\text{ext}}(\mathbf{r})$, such that the minimum value of the energy functional

$$E[n(\mathbf{r})] \equiv \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[n(\mathbf{r})] \tag{14}$$

yields the exact ground-state energy of the system. The exact ground-state density $n_0(\mathbf{r})$ minimizes this functional. Thus, the exact ground-state energy and density are fully determined by the functional $E[n(\mathbf{r})]$. The universal functional $F[n(\mathbf{r})]$ can be written as:

$$F[n(\mathbf{r})] \equiv T[n(\mathbf{r})] + E_{\text{int}}[n(\mathbf{r})] \tag{15}$$

where $T[n(\mathbf{r})]$ is the kinetic energy and $E_{\text{int}}[n(\mathbf{r})]$ is the interaction energy of the particles. According to the variational principle, for any wave function Ψ' , the energy functional

$$E[\Psi'] \equiv \langle \Psi' | \hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi' \rangle \tag{16}$$

reaches its global minimum only when Ψ' is the ground-state wave function Ψ_0 , with the constraint that the total number of particles is conserved. According to the first

Hohenberg-Kohn theorem, Ψ' must correspond to a ground state with particle density $n'(\mathbf{r})$ and external potential $V'_{\text{ext}}(\mathbf{r})$, making $E[\Psi']$ a functional of $n'(\mathbf{r})$. Applying the variational principle:

$$E[\Psi'] = \int n'(\mathbf{r})V'_{\text{ext}}(\mathbf{r})d\mathbf{r} + F[n'(\mathbf{r})] > E[\Psi_0] = \int n_0(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + F[n_0(\mathbf{r})] = E[n_0(\mathbf{r})] \quad (17)$$

Thus, the energy functional $E[\Psi] \equiv \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ evaluated for the correct ground-state density $n_0(\mathbf{r})$ is lower than the value of this functional for any other density $n(\mathbf{r})$. Therefore, by minimizing the total energy functional of the system with respect to variations in the density $n(\mathbf{r})$, one can find the exact ground-state density and energy. This functional, however, only determines ground-state properties and does not provide any insight into excited states.

3.3 Advantage and Disadvantage of Hohenberg-Kohn Theorems

The Hohenberg-Kohn theorems are fundamental to density functional theory and offer significant advantages in computational chemistry and materials science. One of the primary benefits is their ability to relate the ground-state properties of many-electron systems directly to electron density, simplifying calculations compared to wave-function-based methods. The first theorem establishes a unique mapping between the ground-state electron density and the external potential, ensuring that all ground-state properties can be derived from the electron density alone. Additionally, the second theorem introduces a variational principle that allows for the efficient optimization of electron density to find the ground state. By shifting the focus from finding a function of $3N$ variables (the wave function) to a function of three variables (the electron density), the Hohenberg-Kohn theorems significantly simplify the process of resolving the Schrödinger equation. These theorems make DFT a versatile tool applicable to a wide range of systems, from small molecules to large biological complexes.

However, the Hohenberg-Kohn theorems also come with notable disadvantages. They are limited to ground-state properties, providing no direct insight into excited states, which poses challenges in studying electronic excitations and charge transfer processes. The effectiveness of DFT is highly dependent on the choice of exchange-correlation functional, which may not accurately capture all correlation effects, especially in systems with strong electron-electron interactions. Furthermore, while DFT is generally computationally less intensive than wave-function methods, the calculations of exchange-correlation energies can still be demanding. The reliance on external potentials and the interpretation challenges associated with electron density further highlight the limitations of the

Hohenberg-Kohn theorems, necessitating careful consideration when applying DFT to complex systems.

3.4 Kohn-Sham Equation: Reformulating Many-Body Problems

The Kohn-Sham equation is a central component of density functional theory that allows for the practical calculation of electronic structures in many-body systems. It stems from the foundational Hohenberg-Kohn theorems, which established the uniqueness of the ground-state electron density and its relationship with the external potential. The Kohn-Sham framework reformulates the complex many-body problem into a set of simpler, non-interacting single-particle equations, making it more tractable for computational purposes.

In the Kohn-Sham approach, the true interacting electron system is mapped onto an auxiliary system of non-interacting electrons that yield the same electron density as the original system. This is achieved through the Kohn-Sham equations, which can be expressed as:

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (18)$$

where $V_{\text{eff}}(\mathbf{r})$ is the effective potential that includes the external potential and the exchange-correlation potential. The Kohn-Sham orbitals $\psi_i(\mathbf{r})$ are used to construct the electron density $n(\mathbf{r})$ as:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2. \quad (19)$$

This approach significantly reduces the complexity of solving the many-body Schrödinger equation by allowing for the treatment of a system of independent particles, while still capturing the essential effects of electron correlation through the exchange-correlation functional.

The effective potential in the Kohn-Sham framework can be expressed as:

$$V_{\text{eff}} = V_{\text{ext}} + V_{\text{Hartree}}[n(\mathbf{r})] + V_{\text{xc}}[n(\mathbf{r})]. \quad (20)$$

Here, V_{ext} represents the external potential acting on the electrons in the system. This potential typically arises from the interaction between the electrons and fixed nuclei or any other external fields applied to the system. In many cases, V_{ext} is described by the Coulomb potential due to the nuclei, reflecting how electrons experience attraction towards positively charged atomic cores. This term plays a crucial role in determining

the overall potential landscape in which the electrons move, significantly influencing the electronic structure of the system.

The term $V_{\text{Hartree}}[n(\mathbf{r})]$ is the Hartree potential, which describes the classical electrostatic interaction between electrons in a many-body system. It accounts for the repulsion between charged particles, reflecting that the potential energy experienced by an electron is due to the distribution of other electrons around it. The Hartree potential is calculated as:

$$V_{\text{Hartree}}[n(\mathbf{r})] = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (21)$$

This formulation integrates the electron density $n(\mathbf{r}')$ over all space, considering the effect of all other electrons on a given electron located at \mathbf{r} . This approach provides a mean-field treatment of electron-electron repulsion, avoiding the complexity of considering every pair of interactions explicitly.

The exchange-correlation potential $V_{\text{xc}}[n(\mathbf{r})]$ represents the quantum mechanical effects of exchange and correlation among electrons. It is defined as:

$$V_{\text{xc}}[n(\mathbf{r})] = \frac{\delta E_{\text{xc}}[n]}{\delta n}. \quad (22)$$

The exchange term arises from the antisymmetry requirement of the total wave function for fermions, accounting for the reduction in energy when two electrons are spatially separated. The correlation term reflects the correlated motion of electrons that cannot be captured by a mean-field approach, accounting for the ways in which the presence of one electron affects the probability distribution of another electron's position and momentum.

From these considerations, the Kohn-Sham Hamiltonian can be formulated as:

$$\hat{H}_{\text{KS}} = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{ext}} + V_{\text{Hartree}}[n(\mathbf{r})] + V_{\text{xc}}[n(\mathbf{r})]. \quad (23)$$

The major distinction between the Kohn-Sham formulation and the Hartree formulation lies in the inclusion of both exchange and correlation effects in the effective potential, providing a more accurate description of many-body systems.

Solving the Kohn-Sham equation is a crucial step in density functional theory for obtaining the ground-state electron density of a many-body system. In a condensed matter system, the Kohn-Sham equation provides a method to derive the exact density and energy of the ground state. The process begins with an initial electron density $n(\mathbf{r})$, typically a superposition of atomic electron densities. The effective Kohn-Sham potential V_{eff} is then calculated, and the Kohn-Sham equation is solved to obtain single-particle

eigenvalues and wave functions. A new electron density is subsequently calculated from these wave functions.

This iterative process is commonly performed numerically through self-consistent iterations, as illustrated in the flowchart figure 1. The self-consistency can be determined by monitoring the change in total energy, electron density from the previous iteration, or the total force acting on the atoms being less than a specified small quantity, or by using a combination of these criteria. If self-consistency is not achieved, the calculated electron density is mixed with the density from previous iterations to derive a new electron density, and the process repeats. This continues until self-consistency is reached. Once convergence is achieved, various quantities can be calculated, including total energy, forces, stress, eigenvalues, electron density of states, and band structure, among others.

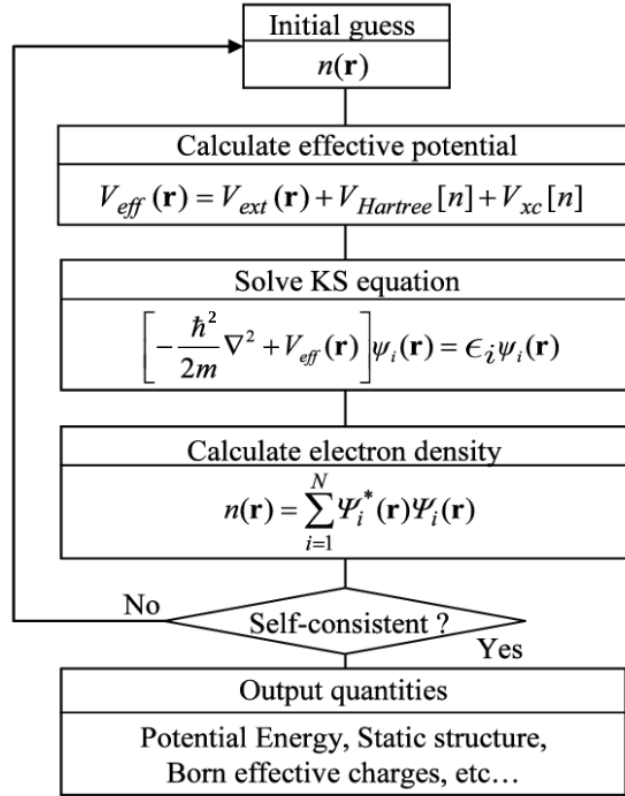


Figure 1: Flowchart illustrating the iterative process for solving the Kohn-Sham equation in density functional theory to obtain the ground-state electron density and associated properties of a many-body system.

3.5 The Role and Calculation of Exchange-Correlation

In density functional theory, the exchange-correlation potential, $V_{xc}[n(\mathbf{r})]$, is a critical component that captures the complex quantum mechanical effects of electron exchange and correlation. However, V_{xc} is not derived exactly but is instead approximated due to the computational challenges of dealing with many-electron systems. One of the most common approximations is the Local Density Approximation (LDA), where V_{xc} is considered to depend solely on the local electron density. This approximation is based on the idea that in regions where the electron density is nearly uniform, the behavior of electrons can be likened to that of a homogeneous electron gas. While simple, LDA can perform reasonably well for certain materials, especially solids with nearly uniform electron densities.

To improve upon the LDA, the Generalized Gradient Approximation (GGA) introduces a dependence on the spatial gradients of the electron density. By including information about how the density changes in space, GGA provides more accurate results for systems where the density varies significantly, such as in molecules or surfaces. These improvements make GGA one of the most widely used approximations in modern DFT calculations. More advanced methods, such as hybrid functionals, combine the exchange from exact Hartree-Fock theory with the approximate exchange-correlation from LDA or GGA. Hybrid functionals, like B3LYP, tend to improve accuracy further, particularly for molecular systems, by including a portion of exact exchange, which LDA and GGA inherently miss.

In practice, the calculation of V_{xc} is an iterative process within the self-consistent field (SCF) method. The DFT algorithm begins with an initial guess for the electron density, usually based on atomic configurations. Using this initial density, the Kohn-Sham equations are solved to update the potential and electron density. The exchange-correlation potential, V_{xc} , is recalculated at each step based on the updated density. This process continues until the electron density converges to a self-consistent solution, meaning that the input and output densities agree within a set tolerance. Recent developments also include meta-GGA functionals, which incorporate even higher-order density-related terms, such as the kinetic energy density, to account for more complex interactions. While computationally more expensive, these functionals can offer improved accuracy for systems with intricate electronic structures. Thus, although V_{xc} is not known exactly, various approximations—from LDA and GGA to hybrid and meta-GGA functionals—allow DFT to achieve a good balance between accuracy and computational efficiency for a wide range of materials and molecular systems.

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