

Fundamentals of Density Functional Theory

the 6th Electronic Structure Calculations Summer School

KAIST, 14 July 2025

INSTRUCTOR: Jaejun Yu

jyu@snu.ac.kr

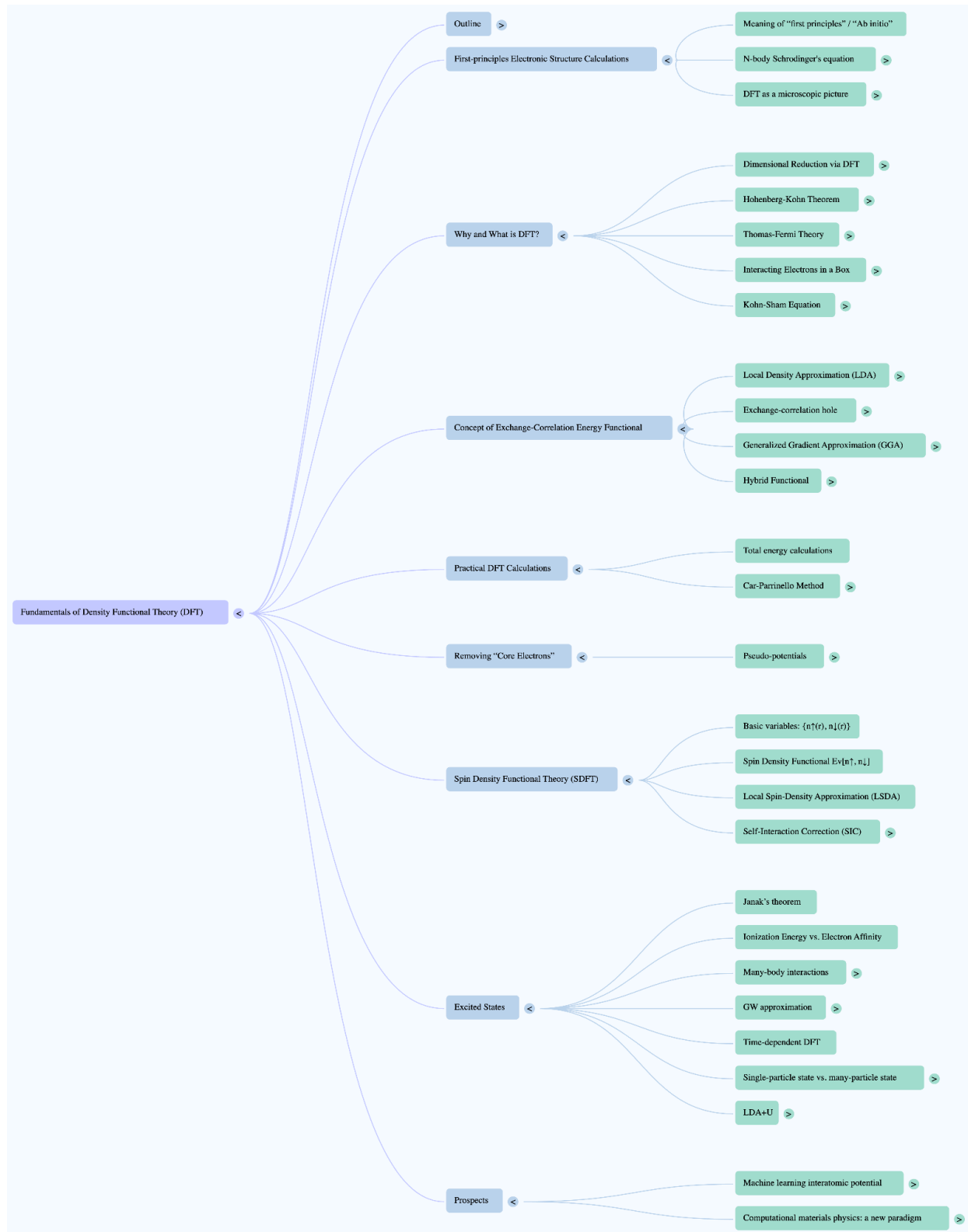
Abstract

We will discuss basic concepts, theories, and methods behind density functional theory (DFT). DFT is a computational quantum mechanical modeling method used in physics, chemistry, and materials science to investigate the electronic structure of many-body systems, particularly atoms, molecules, and condensed phases. We hope to provide a broad perspective on current electronic structure theory and background for practical computations, starting points of advanced topics such as exchange-correlational functional, pseudo-potential theory, time-dependent DFT, many-body perturbation theory, and DFT-DMFT (dynamical mean-field theory). This course aims at graduate and post-graduate students in theoretical and computational condensed matter physics.

References

- Richard M. Martin, Electronic Structure: basic theory and practical methods (Cambridge University Press, 2004) (ISBN 0 521 78285 6)
- J. Toulouse, Introduction to Density Functional Theory, https://www.lct.jussieu.fr/presentation_istpc_24 (2024).
- C. Fiolhais F. Nogueira M. Marques (Eds.), A Primer in Density Functional Theory, https://wiki.physics.udel.edu/wiki_qttg/images/0/0b/BOOK%3Dprimer_dft.pdf, (2002).

Density Functional Theory: Study Guide



Part 1: Fundamentals of Density Functional Theory

A. First-Principles Electronic Structure Calculations

- **What does "first principles" mean in this context?** Basic proposition/assumption not deducible from others.
 - "Ab initio": starting from the beginning.
 - In practice: "starting from the self-consistent electronic structure based on density functional theory."
- **N-body Schrödinger Equation:**

"The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble."
— P.A.M. Dirac (1929).
- **Challenges:** solving N-body Schrödinger equations is practically limited to a few cases, even with approximations, due to the complexity of N-dimensional space.
 - **Dimensional Reduction via DFT:** DFT aims to reduce the N-dimensional problem to a 3-dimensional functional space, making it computationally tractable.
 - It shifts from solving complex N-particle Schrödinger equations to utilizing solutions of one-particle Schrödinger equations.

B. What is "Density Functional Theory (DFT)"?

- **Hohenberg-Kohn Theorem:**
 - **Theorem 1:** The exact many-body wavefunction (and all ground state properties) of the interacting many-body system is uniquely determined by the charge density $n(r)$.
 - **Theorem 2:** There exists a unique universal functional of the density, $F[n(r)]$, independent of the external potential $v(r)$, such that $E_v = \int v(r)n(r)dr + F[n(r)]$ has its minimum value at the correct ground-state energy associated with $v(r)$.
- **Thomas-Fermi Theory:** An early attempt to describe kinetic energy for inhomogeneous systems as a function of local density $n(r)$.
- **Interacting Electrons in a Box (Jellium):** For large density systems, the total energy can be expressed as a perturbation expansion including kinetic energy (T_0), exchange energy (E_x), and correlation energy (E_c).
 - The precise form of the exchange-correlation energy (E_{xc}) is known only for the homogeneous interacting electron gas.

- **Kohn-Sham Equations:**

- Goal: Find $n(r)$ for the ground state by applying the variational method to minimize $E_V[n]$ under the constraint $\int n(r)dr = N$.
- Kohn-Sham particles: Fictitious (non-interacting fermion) N -particles moving under an effective potential (v_{eff}).
- Mapping: Maps the density of "interacting N -electrons" onto that of fictitious non-interacting electrons under an effective potential, ensuring $n(r) = n_0(r)$.
- Self-consistent solutions: The Kohn-Sham equations are solved iteratively until the calculated density converges (self-consistency).
- Total Energy Functional (KS formalism): $E_V[n] = T_s[n] + E_H[n] + E_{\text{xc}}[n] + \int v(r)n(r)dr + E_{\text{ion}}$.
- $T_s[n]$: Kinetic energy of fictitious Kohn-Sham particles.
- $E_H[n]$: Classical Coulomb (Hartree) interaction energy.
- $E_{\text{xc}}[n]$: Exchange-correlation energy, encompassing the difference between interacting and non-interacting kinetic and electron-electron interaction energies.
- E_{ion} : Ion-ion interaction energy.

C. Concept of Exchange-Correlation Energy Functional

- **Local Density Approximation (LDA):** Assumes the exchange-correlation potential (v_{xc}) is a function of local density, not a functional.
 - Approximates the functional $F[n(r)]$ as an integral of the homogeneous electron gas (HEG) energy density over the local density.
 - **Strengths:** Errors in approximation of exchange (E_x) and correlation (E_c) tend to cancel each other. Satisfies the sum rule for the exchange-correlation hole.
 - **Weaknesses:** Fails for excited state properties, band-gap problems, self-interaction problems, mirror image charges, and two-body correlations.
- **Exchange-Correlation Hole:** Describes the depletion of electron density around a reference electron due to exchange and correlation effects.
 - **Sum rule:** $\int n_{\text{hole_xc}}(r_2|r_1)dr_2 = -1$ (meaning one electron is "missing" from the vicinity of another due to these effects).
- **Generalized Gradient Approximation (GGA):** Goes beyond LDA by including the gradient of the density, preserving the sum rule.
 - Provides a more realistic account of energy barriers and adsorption energies.
 - Improved description of the exchange hole compared to LDA.
 - Still limited in curing strong interaction problems.

-
- **Hybrid Functional:** Combines a portion of exact Hartree-Fock exchange (EHF) with DFT exchange-correlation (Exc) functionals (e.g., B3PW91, Becke's hybrid functional).
 - Aims to improve accuracy, especially for thermochemistry and band gaps, by incorporating non-local exchange.

Part 2: Practical DFT Calculations and Advanced Topics

A. Practical DFT Calculations

- **Total Energy Calculations:** The total energy of the system is calculated using the converged density from the self-consistent Kohn-Sham equations.
- **Choice of Basis Functions:** Atomic orbital basis: Linear combination of atomic orbitals.
- **Plane wave basis:** Superposition of plane waves, often used for periodic systems.
- **Real-space grid:** Represents functions on a discrete grid.
- **Car-Parrinello Method:** A molecular dynamics method that performs first-principles simulations.
 - Uses a Lagrangian formulation to simultaneously evolve both the atomic positions and the electronic orbitals. This allows for efficient calculation of ionic forces.

B. Removing “Core Electrons”: Why and How?

- **Pseudo-potentials:** Why: Core electrons are tightly bound and do not significantly participate in chemical bonding. Explicitly treating them increases computational cost unnecessarily.
- **How:** Pseudo-potentials replace the strong core electron potential and the core electrons themselves with an effective potential that acts on the valence electrons. This potential is constructed to match the true atomic wavefunction outside a core radius, but is smoother inside, allowing for more efficient plane-wave expansions.

C. Spin Density Functional Theory

- **Variables:** In the presence of a magnetic field $B(r)$, the basic variables become spin-up ($n_{\uparrow}(r)$) and spin-down ($n_{\downarrow}(r)$) densities.
- **Total Density:** $n(r) = n_{\uparrow}(r) + n_{\downarrow}(r)$.
- **Magnetization Density:** $m_z(r) = n_{\uparrow}(r) - n_{\downarrow}(r)$.
- **Spin Density Functional:** $E_v[n_{\uparrow}, n_{\downarrow}]$ includes terms for external potential, magnetic field interaction, kinetic energy, Hartree energy, and exchange-correlation energy.

- **Local Spin-Density Approximation (LSDA):** Extends LDA to spin-polarized systems by making the exchange-correlation energy a function of both spin densities.
- **Self-Interaction Correction (SIC):** Addresses the problem where approximate exchange-correlation functionals do not perfectly cancel the self-interaction energy of an electron with itself (which should be zero).
 - This is particularly important for localized electrons, where $E_H[n\alpha] + E_x[n\alpha, 0]$ should ideally be zero for a single electron system. SIC aims to subtract these unphysical self-interaction terms.

D. Excited States

- **Janak's Theorem:** States that the derivative of the total energy with respect to the occupation number of a Kohn-Sham orbital is equal to the Kohn-Sham eigenvalue ($\partial E / \partial n_i = \epsilon_i$). This is analogous to Koopman's theorem in Hartree-Fock.
- **Excitation Properties:** Related to ionization energy (I) and electron affinity (A).
 - $I = E(N) - E(N-1)$
 - $A = E(N+1) - E(N)$
 - Excitation energy $\Delta E = E(N+1) + E(N-1) - 2E(N)$
- **Challenges with DFT for Excited States:** KS equation deals with fictitious non-interacting particles, while excited quasi-particles experience real interactions.
- **Band gap problem:** LDA/GGA often underestimate band gaps.
 - Need to consider many-body interactions.
- **GW Approximation:** A method for calculating electronic excited state properties (e.g., quasiparticle energies, band gaps) that goes beyond standard DFT.
 - Approximates the self-energy (Σ) using Green's function (G) and screened Coulomb interaction (W).
- **Single-particle state vs. Many-particle state:** DFT, in its standard form, provides Kohn-Sham orbitals and energies for fictitious non-interacting particles.
 - Real physical quantities like ionization energies and electron affinities correspond to many-particle states (quasi-particles).
- **LDA+U:** A method designed to improve DFT's description of strongly correlated electron systems (e.g., transition metal oxides) where strong on-site Coulomb interactions are present.
 - Adds a Hubbard U term to the standard LDA/GGA functional to account for these strong correlations.

E. Prospects

- **Computational Materials Physics: A New Paradigm:** DFT is a powerful technique for theoretical condensed matter physics.
 - Major contributions to materials science and biological science.
 - **Computational materials design:** Predictive power for new materials' structures, physical properties, phase transitions, surface chemistry, catalysis, and more.
 - **Machine Learning Interatomic Potential:** Motivation: Standard DFT calculations are computationally expensive (scaling as $O(N^3)$ or $O(N^2)$ with the number of electrons, N_e). Self-consistency issues and difficulty in describing time-evolution over energy barriers.
- **Approach:** High-dimensional Neural Network Potentials (NNPs) use machine learning to map the atomic energy (E_{atomic}) from DFT calculations.
 - Assumes total energy (E_{total}) is a sum of individual atomic contributions based on their local chemical environment.
 - Local environments are encoded using "structural descriptors" (e.g., atom-centered symmetry functions like radial and angular distribution functions), ensuring rotational and translational invariance.
- NNPs can achieve $O(N)$ scaling, making large-scale simulations computationally feasible.
 - Accuracy depends on the quality and diversity of the training set (DFT data for total energies and forces).

Part 2: Quiz (Short Answer)

1. What is the fundamental difference between solving the N-body Schrödinger equation and performing a DFT calculation?
2. Explain the significance of the two Hohenberg-Kohn theorems in the context of Density Functional Theory.
3. What is the "Kohn-Sham particle" and how does its concept simplify the problem of interacting electrons?
4. Briefly describe the Local Density Approximation (LDA) and one of its main strengths and one of its main weaknesses.
5. How does the Generalized Gradient Approximation (GGA) improve upon LDA, and what limitation does it still share with LDA?
6. What is a "hybrid functional" in DFT, and why is it used?
7. Explain the purpose of "pseudo-potentials" in practical DFT calculations.
8. How does Spin Density Functional Theory (SDFT) extend basic DFT, and what additional variables are considered?
9. Why is standard DFT often insufficient for accurately describing excited states, and what are two methods mentioned to address this limitation?
10. What is the primary motivation for developing Machine Learning Interatomic Potentials (MLIPs) in computational materials physics, and how do they achieve their efficiency?

Part 3: Answer Key

1. The N-body Schrödinger equation directly solves for the many-body wavefunction in a high-dimensional space, which is computationally intractable for most systems. DFT, based on the Hohenberg-Kohn theorems, instead focuses on the much simpler 3-dimensional electron density, reducing the dimensionality of the problem to make it soluble.
2. The first Hohenberg-Kohn theorem states that the ground state electron density uniquely determines all ground state properties, including the many-body wavefunction. The second theorem establishes that a universal energy functional of the density exists and has its minimum value at the true ground state density, providing the variational principle for DFT.
3. A "Kohn-Sham particle" is a fictitious, non-interacting fermion that moves under an effective potential. This concept allows the complex interacting many-electron system to be mapped onto a simpler, solvable system of non-interacting particles that have the same ground state electron density as the real system.
4. LDA approximates the exchange-correlation energy based solely on the local electron density, assuming it behaves like a homogeneous electron gas. Its strength is that errors in exchange and correlation often cancel out, leading to surprisingly good results for some properties. A main weakness is its failure to accurately predict band gaps and its inability to deal with self-interaction errors.
5. GGA improves upon LDA by incorporating the gradient of the electron density in its functional form, leading to a more realistic description of inhomogeneous systems. While it provides better energy barriers and adsorption energies, it still struggles with strong interaction problems and often underestimates band gaps, similar to LDA.
6. A "hybrid functional" combines a portion of exact exchange calculated from Hartree-Fock theory with a DFT exchange-correlation functional. It is used to improve the accuracy of DFT calculations, particularly for properties like band gaps and thermochemistry, by incorporating non-local exchange effects that are missing in pure local or semi-local functionals.
7. Pseudo-potentials are used to simplify DFT calculations by effectively removing core electrons from the explicit calculation. They replace the strong nuclear potential and tightly bound core electrons with a smoother, effective potential that acts only on the valence electrons, significantly reducing the computational cost and allowing for more efficient basis sets like plane waves.
8. Spin Density Functional Theory extends basic DFT by treating spin-up and spin-down electron densities as independent variables, in addition to the total electron density. This

-
- allows for the description of magnetic systems and phenomena where electron spins are polarized, considering both the total density $n(r)$ and the magnetization density $m_z(r)$.
9. Standard DFT is insufficient for excited states because the Kohn-Sham equations describe fictitious non-interacting particles, whereas excited quasi-particles experience real many-body interactions. Two methods mentioned to address this are the GW approximation, which calculates quasiparticle energies, and LDA+U, which accounts for strong on-site Coulomb interactions in correlated systems.
 10. The primary motivation for MLIPs is to overcome the high computational cost of traditional DFT calculations ($O(N^3)$ or $O(N^2)$). MLIPs achieve efficiency by summing atomic energy contributions based on local chemical environments described by structural descriptors, effectively reducing the scaling to $O(N)$ and enabling large-scale simulations that are inaccessible to full DFT.

Part 4: Essay Format Questions

Discuss the historical challenges in applying quantum mechanics to many-body systems, and explain in detail how Density Functional Theory (DFT), particularly through the Kohn-Sham framework, addresses these challenges. Focus on the concept of dimensional reduction and the role of fictitious particles.

Compare and contrast the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. Include their theoretical underpinnings, their respective strengths and weaknesses, and provide examples of physical properties where one might be preferred over the other.

Elaborate on the concept of the exchange-correlation hole within DFT. How does its sum rule relate to the fundamental properties of electron systems, and what implications does its accurate description have for the performance of different exchange-correlation functionals?

DFT, in its standard formulation, is primarily a ground-state theory. Discuss the limitations of applying standard DFT to excited state properties, such as band gaps and ionization energies. Explain how advanced methods like the GW approximation and LDA+U attempt to overcome these limitations.

Explore the emerging paradigm of integrating machine learning into computational materials physics, specifically focusing on Machine Learning Interatomic Potentials (MLIPs). Discuss the computational challenges that MLIPs aim to solve, their underlying principles (e.g., atom-centered local environments, structural descriptors), and the potential impact of this approach on large-scale materials simulations.

Part 5: Glossary of Key Terms

- **First Principles (Ab Initio):** Calculations that start from fundamental physical laws (like the N-body Schrödinger equation) without empirical parameters. In practice for DFT, it means starting from the self-consistent electronic structure based on DFT.
- **N-body Schrödinger Equation:** The fundamental quantum mechanical equation describing the behavior of a system with N interacting particles. It is analytically insoluble for most systems of interest due to its high dimensionality.
- **Density Functional Theory (DFT):** A quantum mechanical method used in physics and chemistry to investigate the electronic structure (primarily the ground state) of many-body systems, particularly atoms, molecules, and condensed phases. It focuses on the electron density rather than the complex many-body wavefunction.
- **Hohenberg-Kohn Theorems:** Two fundamental theorems of DFT. The first states that the ground state electron density uniquely determines the external potential and, therefore, all properties of the system. The second establishes that a universal functional for the energy exists and is minimized by the true ground state density.
- **Kohn-Sham Equations:** A set of effective single-particle equations introduced within DFT that formally map the interacting many-electron system onto an auxiliary system of non-interacting electrons that yield the same ground-state electron density.
- **Kohn-Sham Particles:** Fictitious, non-interacting fermions described by the Kohn-Sham equations, which move in an effective potential and have the same ground-state density as the real interacting electrons.
- **Effective Potential (V_{eff}):** The potential experienced by the fictitious Kohn-Sham particles. It includes the external potential, the classical Hartree potential, and the exchange-correlation potential.
- **Self-Consistent Solutions:** The iterative process in DFT where the electron density is calculated, then used to update the effective potential, and new densities are calculated until the density (and thus energy) converges.
- **Exchange-Correlation Energy Functional ($E_{\text{xc}}[\mathbf{n}]$):** The crucial, unknown component of the DFT total energy functional. It accounts for all non-classical many-body effects, including the quantum mechanical exchange energy and the correlation energy.
- **Local Density Approximation (LDA):** The simplest approximation for the exchange-correlation functional, where E_{xc} at a given point is approximated based solely on the local electron density, as if it were part of a homogeneous electron gas.
- **Exchange-Correlation Hole ($n_{\text{hole_xc}}$):** A conceptual tool in DFT that describes the reduced probability of finding another electron near a given electron due to exchange and correlation effects. It obeys a sum rule of -1.

-
- **Generalized Gradient Approximation (GGA):** An improvement over LDA that incorporates not only the local electron density but also its gradient (rate of change) in the exchange-correlation functional, leading to more accurate results for many systems.
 - **Hybrid Functional:** A type of exchange-correlation functional that combines a portion of exact Hartree-Fock exchange with the DFT exchange and correlation components. Used to improve accuracy for properties like band gaps and thermochemistry.
 - **Car-Parrinello Method:** A molecular dynamics simulation method that combines density functional theory with classical molecular dynamics, allowing for simultaneous evolution of electronic and ionic degrees of freedom.
 - **Pseudo-potentials:** A computational technique used to simplify DFT calculations by replacing the explicit treatment of core electrons and the strong nuclear potential with an effective, smoother potential that acts only on the valence electrons.
 - **Spin Density Functional Theory (SDFT):** An extension of DFT that treats spin-up and spin-down electron densities as independent variables, enabling the study of spin-polarized and magnetic systems.
 - **Self-Interaction Correction (SIC):** Methods applied to approximate exchange-correlation functionals to remove unphysical self-interaction errors, where an electron spuriously interacts with its own charge density.
 - **Janak's Theorem:** A theorem in DFT stating that the Kohn-Sham eigenvalues are equal to the derivative of the total energy with respect to the occupation number of the corresponding orbital.
 - **GW Approximation:** A many-body perturbation theory method used to calculate electronic excited state properties (e.g., quasiparticle energies and band gaps) by approximating the electron's self-energy.
 - **LDA+U:** A DFT-based method that adds a Hubbard U term to the standard LDA/GGA functional to better describe strongly correlated electron systems, particularly those with localized d or f electrons.
 - **Machine Learning Interatomic Potential (MLIP):** A computational approach that uses machine learning algorithms to learn the relationship between atomic configurations and their energies/forces from a database of ab initio (DFT) calculations, enabling much faster simulations than direct DFT.
 - **Atom-centered Symmetry Functions (ACSFs):** Mathematical descriptors used in MLIPs to characterize the local chemical environment of each atom in a rotationally and translationally invariant manner.