Project Report

on

Density Functional Theory
Challenges and Future Advancements

MM 719

Introduction to Ab-initio Methods in Materials Modelling

Submission

by

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1 Introduction

The high accuracy computation of numerous physical properties of solids is accomplished using density functional theory (DFT), a low-cost and time-saving quantum mechanical (QM) theory. The research in this area covers a broad spectrum, from the creation of original analytical methods centred on the creation of precise **exchange-correlation functional** to the application of this method to forecast the molecular and electronic configuration of atoms, molecules, complexes, and solids in both gas and solution phases. The search for the exchange-correlation functional, which makes use of density to depict complex **many-body systems** inside a one element formalism, is what led to the development of DFT. A precise exchange-correlation functional may accurately capture the quantum character of matter if used.

The most effective way for computing the **electronic structure of matter** at the moment is density functional theory, a **variational approach**. It can be used to atoms, molecules, solids, nuclei, as well as quantum and classical fluids. DFT precisely simplifies calculations of the ground state characteristics of systems of interacting particles to the solution of **single-particle Hartree-type equations**. This is why it has proven most helpful for systems with a large number of electrons.

Hohenberg-Kohn established the basis for DFT, which is today used to investigate the uniqueness of materials, by demonstrating that every characteristic of a system in its ground state is a distinct ground state density functional.

[1].

2 Theories

The Kohn-Sham equation, which is a single particle independent **Schrodinger equation** that can be numerically solved with density functional theory, can be used to solve the Schrodinger Equation for a many body system. This computation results in the solids' physical properties. In 1964, **Hohenberg, Kohn, and Sham** established the foundation for DFT by demonstrating

that the functional of a many-body problem's (non-degenerated) ground state electron charge density could completely define all attributes in the absence of a magnetic field.

2.1 The Hohenberg - Kohn (HK) Theorems

In 1964, Hohenberg and Kohn made two ostensibly straightforward theorems that made it possible to use DFT.

2.1.1 First Theorem

A many-body system's external potential, $V_{ext}(\vec{r})$, is a special function of electron density $\rho((\vec{r})$, having a special association between potential and electron density; $V_{ext}(\vec{r})$ and $\rho((\vec{r})$ respectively, whereas this electron density can be used to characterize all of the system's information.

The associated Hamiltonian of energy can be represented as; According to theory, electrons move in a field created by the external potential V_{ext} and interact with one another in addition to their external potential.

$$H = T + V_{ext} + U \tag{1}$$

Where T, U, andV_{ext} stand for the coulomb interaction, the KE of electrons, and the external potential respectively.

2.1.2 Second Theorem

The electron density that reduces the functional's total energy corresponds to an electron's actual ground state density.

Consider the case where ρ(r) is the density of the many-body system's ground state and ρ'(r) is any other state. In this situation, the functional for total energy is expressed as E[ρ]>E[ρ]. Additionally, suppose that F[ρ(r)] is a universal functional that holds true for fixed electrons

at all external potentials. In mathematics, this is represented as:

$$\mathbf{F}[\rho(\mathbf{r})]=\mathbf{T}[\rho(\mathbf{r})]+\mathbf{U}[\rho(\mathbf{r})] \tag{2}$$

The associated density ρ(r) must essentially be a ground state density for it to have minimal energy functional.

2.2 The Kohn-Sham (KH) Equations

Hohenberg-Kohn's theorems are accurate, however they aren't very helpful when performing actual calculations. DFT was transformed into a practical tool by the Kohn-Sham equation. They transformed the challenging issue of electrons interacting collectively in external effective potential V_{ext} into electrons that are not interacting in Vext, and the total energy for an interacting electron ground state in fixed potential, $V(\vec{r})$, is:

$$\mathbf{E}[\rho(r)]=\mathbf{V}[\rho]+\mathbf{U}[\rho+\mathbf{G}[\rho] \tag{3}$$

Where universal density functional G[ρ] holds exchange-correlation.

It can be expressed as

$$\mathbf{E}[\rho(r)]=T_s[\rho]+\mathbf{V}[\rho]+\mathbf{U}[\rho]+E_{xc}[\rho] \tag{4}$$

In a many-body system with non-interacting electrons, the kinetic energy is given by $T_s[\rho]$, whereas V[ρ] is the external potential created by the core's positive charge, U[ρ]is the coulomb potential, and $E_{xc}[\rho]$ is the energy resulting from exchange-correlation effects.

2.3 Exchange-correlation potential

The KS scheme's results showed that the energy functional's limiting energy may be used to determine the least energy state, and this can be done by finding an agreeable solution

to a set of single-particle equations. One major issue with the KS approach is that it is impossible to precisely locate E_{xc}(exchange-correlation energy). E_{xc} provides a precise solution to a many-body problem if it is determined with accuracy. Since there isn't presently an exact solution, approximations are used to estimate Exc, with Local Density Approximation(LDA) and Generalized Gradient Approximation (GGA) being the most popular choices.

3 Challenges for DFT

The exchange-correlation E_{xc} functionals must develop and advance for DFT to be effective, which can be done by optimising against larger data sets and employing improved functional arrangements that are more flexible and contain more elements. Recent improvements have also given smoothness a higher priority, which helps to solve issues with grid-size convergence and self-consistent field iterations. We shall discuss a few DFT difficulties in this area, ranging from those that seem to be "solved" to those that are currently being investigated.

3.1 Strong correlation

It has been known since DFT's inception that typical approximations are inadequate for strongly correlated systems. This can be investigated, as well as connected to typical approximation localization or delocalization errors when integer or half-integer electron quantities are found in different locations. By dissolving the symmetry of equally spaced atomic chains into many solutions, one of which will have the least amount of energy, this issue can be solved.

3.2 Uniformly simple functionals

The need to maintain some level of simplicity is one of DFT's main challenges. One of the most important characteristics of the theory, namely simplicity, is lost when DFT functionals get as complex as full configuration interaction. This is especially true in terms of the computer

environment. However, this simplicity must not come at the expense of precision or turn into a wholly empirical methodology. One of DFT's first significant stumbling blocks in chemistry was the accurate description of binding energies and geometries of simple molecules.

3.3 Barriers to dispersion and reaction

It is essential to explain weakly interacting atoms or molecules as well as the transition states of chemical reactions in addition to a molecule in equilibrium geometry in order to give a thorough understanding of chemistry. Local Density Approximation(LDA) or Generalized Gradient Approximation (GGA) functionals consistently underestimate how difficult it is to change from one state to another, making it difficult to represent response barriers with these models. Although efforts are being made to solve these issues, transition states, covalent bonding, and van der Waals attraction are all difficult to accurately and successfully describe.

3.4 Errors in delocalization and static correlation

Another crucial issue is the implementation of DFT, which is shown by large inaccuracies for one-electron systems. A single electron system plays no special role in DFT; in fact, as the self-interaction error has long demonstrated, one electron can interact with itself. Naturally, the exact functional does not involve self-interaction; the exchange energy perfectly cancels the coulomb energy of a single electron. Despite most recent developments, even the simplest systems can contain errors in most recent functionals.

4 Advancements

Accurate and universal density functionals have been the focus of recent developments in Kohn-Sham DFT (KS-DFT). Numerous atom, molecule, and solid properties have been successfully described by KS-DFT, and very large systems can be accurately addressed at a reasonable computing cost. Here we will focus on the evolution of new functionals in DFT in the past.

4.1 Approximation of the random phase

With the use of DFT fluctuation dissipation in the form of coupling constant and frequency, the exchange correlation energy (E_{xc}) may be determined. The effects of neglecting the exchange kernel of TDFT are the time-dependent TD-Hartree or the direct random-phase approximation (RPA). Direct RPA overcorrelates systems by neglecting additional contributions at higher levels that lessen correlation because it only looks at bubble diagrams in the many-body expansion of the energy. It also has problems with self-interaction since even when only one electron is involved, it produces low correlation energies and incorrect molecule dissociation energies.

4.2 Weak Interactions

Strong progress has been achieved in overcoming the issues brought on by weak van der Waals interactions over the past 20 years. Due to their semi-local character, traditional functionals are good at manipulating covalent, ionic, and metallic interactions, but they struggle with longer, weaker bonds and are unable to provide weak binding that decreases as a function of R^6 (R is the distance between two atoms). The standard functionals must be modified in one of three ways in order to take these effects into account. Any type of substance, from molecules to solids, may benefit from these functionals.

4.3 Gaps of solids

A significant drawback in conventional approximations is their inability to predict the band gaps of semiconductors and insulators. Germanium becomes a metal as a result of the LDA's two-fold underestimation of the difference between bulk Si and Ge, whilst GGAs do somewhat better but also underestimate.In this instance, the orbital dependent part of the functional is taken into consideration as in Hartree-Fork approach to address shortcomings of other E_{xc} functionals, as opposed to employing pure Kohn-Sham theory.

5 Future Aspects

Warm dense matter has many applications, ranging from modelling the interiors of planets to inertial confinement fusion, a brand-new area for DFT that has experienced an explosion in interest over the past ten years. Warm dense matter has significant temperatures on the electronic scale of about 105 K, but not to the extent that the Thomas-Fermi hypothesis or classical performance is superseded. This field is so "new" that the thermal LDA input, the temperature-dependent exchange-correlation energy of a uniform gas, is only now being computed with astounding accuracy.

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