Basic concepts of Density Functional Theory: Electronic structure calculation

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Abstract. We are looking for a material which possesses the required properties as demanded for technological applications. For this we have to repeat the preparation of the appropriate materials and its characterizations. So, before proceeding to experiments, one can study on computer generated structure and predict the properties of the desired material. To do this, a concept of Density Functional Theory comes out.

1. Introduction

The first principles approach to condensed matter theory is widely used. It starts from the very basic principles that materials are made of atoms. These atoms are again made of a positively charged nucleus and a number of negatively charged electrons. The interactions between atoms are determined by the interactions of the constituent electrons and nuclei that form the basic interaction. Thus if we can model interactions accurately, then most of the complex physical properties can be understood. Thus the *ab initio* calculation or first-principles calculation do not depend upon any external parameters except the atomic numbers of the constituent atoms to be modelled and cannot therefore be biased by preconceptions about the final result. Such calculations are reliable and can be used with confidence to predict the behaviour of nature.

2. Concepts of Density Functional Theory:

Density functional theory (DFT) is the basic theory of electronic structure calculations in Condensed Matter Physics. It was so challenge to approximate functional and computational cost. In 1990's there are widely used functional that give a quite reasonable accuracy with the affordable computational cost. In simple language, Density functional theory is a completely different in terms of its approaching any interacting problem that by mapping it exactly to a non-interacting problem that gives an alternative way to tackle the problem. Thus DFT is a ground-state theory in which the charge density is the relevant physical quantity. DFT is very successful in describing structural and electronic properties in materials science and chemical science.

Density functional theory is developed based on the Hohenberg-Kohn theorem. There are two parts in Hohenberg-Kohn Theorem.

Hohenberg-Kohn Theorem –I:

This theorem states that the external potential V_{ext}(r) is determined (within a trivial additive constant) by the electron density ρ(r).

It implies that for a given density there will be a single V_{ext}(r). In other words, there cannot be two V_{ext}(r) for a given ρ(r). Thus, this theorem demonstrates that the electron density specifies uniquely the Hamiltonian operator.

In consequence, an alternative statement of the first Hohenberg Kohn theorem is that any ground state expectation value corresponding to an observable $\hat{O}$, is a functional of the density,

$$O[\rho] = \left\langle \psi[\rho] \middle| \hat{O} \middle| \psi[\rho] \right\rangle$$

Hohenberg-Kohn Theorem –II:

The second Hohenberg Kohn theorem states that the functional $F_{HK}[\rho]$ that delivers the ground state energy if and only if the input density is the true ground state density.

In other words,

For a trial density $\tilde{\rho}(r)$ such that $\tilde{\rho}(r) \geq 0$ and $\int \tilde{\rho}(r) dr = N$

$$E[\rho] \leq E\left[\tilde{\rho}\right]$$

where $E\left[\tilde{\rho}\right]$ is the energy functional.

$$E\left[\tilde{\rho}\right] = \int \tilde{\rho}(r) V_{ext}(r) dr + F_{HK}\left[\tilde{\rho}\right]$$

2.1 Kohn-Sham equations

We know that a solid consists of heavy positively charged particles (nuclei) and lighter negatively charged particles (electrons). The nuclei are much heavier and therefore much slower than the electrons. We can consider the nuclei are at fixed positions. So, the nuclei become the external potential to the electrons. This is the Born-Oppenheimer approximation. In the further discussion, we use the atomic units (that is $e = m_e = \hbar = 1$; $4\pi\epsilon_o = 1$). Now, after Born-Oppenheimer approximation, we can see the Solid is generally a system of interacting electrons in the field of fixed ions described by the Hamiltonian,

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right) + \sum_{i=1}^{N} V_{ext}(r_i) + \sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{1}$$

where "r_{ij}" is the separation between i^{th} and j^{th} electrons;

$V_{ext}(r_i) = -\sum_{I=1}^{M}\frac{Z_I}{r_{iI}}$ is the external potential acting on i^{th} electron due to the M nuclei and "r_{iI}" is the separation of ith electron and I^{th} nucleus.

A stationary electronic state is then described by a wave function Ψ (r_1, r_2, ...r_i......r_N) satisfying the many electron Schrödinger equation,

$$\hat{H}\psi = E\psi$$

$$[\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}]\psi = E\psi$$

that is

$$\tag{2}$$

Hohenberg and Kohn proved that the total energy of a system in the presence of the static external potential is unique functional of the charge density.

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ext}[\rho]$$

$$E[\rho] = F_{HK}[\rho] + \int \rho(r)V_{ext}(r)d^3r \tag{3}$$

Here the term,

$$T[\rho] + V_{ee}[\rho] = F_{HK}[\rho]$$

is same for all solid and thus it is universal. This does not depend on the particular system under consideration and is called Hohenberg-Kohn functional.

In the non-interacting case, $V_{ee} = 0$,
Thus the ground state energy $E[\rho]$ has a kinetic contribution and a contribution from the external potential.

$$E[\rho] = T_o[\rho] + V_{ext}[\rho] = T_o[\rho] + \int \rho(r)V_{ext}(r)d^3r \tag{4}$$

Again, the ground state wave function of the non-interacting system can be written as a Slater determinant with the orbitals satisfying the single particle Schrodinger equation,

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(r) \right]\phi_m^o(r) = \varepsilon_m^o\phi_m^o \tag{5}$$

The ground state density is then given by a sum over occupied states,

$$\rho(r) = \sum_m^{occup} \left|\phi_m^o(r)\right|^2 \tag{6}$$

where the orbital ϕ_m^0 are normalized so that the density satisfies the correct condition to the number of particles N.

Thus, we can write the ground state energy for this non-interacting case as

$$\sum_m^{occup} \varepsilon_m^o = T_o[\rho] + \int \rho(r)V_{ext}(r)d^3r \tag{7}$$

Now, for the interacting case, we can represent the energy functional $E[\rho]$ for a many electron system in the form,

$$E[\rho] = T_O[\rho] + \int \rho(r)V_{ext}(r)d^3r + \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}d^3r_1 d^3r_2 + E_{XC}[\rho(r)] \tag{8}$$

Where

$$\frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}d^3r_1 d^3r_2 = V_H[\rho]$$ is the Hatree energy

and $E_{XC}[\rho(r)]$ is the exchange correlation energy that contains all the contributions not taken into account in the kinetic energy functional of non-interacting electron gas, the external and the Hatree energy respectively.

Thus, we can write the analogous equation [equation (5) for non-interacting case] for the interacting electron system as

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(r) \right]\phi_m(r) = \varepsilon_m\phi_m \tag{9}$$

where the single particle wave functions $\phi_m(r)$ are the N lowest energy solutions of the above equation (9) called the Kohn Sham equations and $\phi_m(r)$ are the Kohn Sham orbital that reproduce $\rho(r)$ of the original many-body problem.

$$V_{eff} = V_{ext}(r) + \int \frac{\rho(r^/)}{\left|r - r^/\right|} d^3 r^/ + \frac{\delta E_{XC}[\rho]}{\delta \rho(r)}$$

That is

$$V_{eff} = V_{ext}(r) + V_H(r) + V_{XC}(r) \tag{10}$$

where

$V_H(r) = \int \frac{\rho(r^/)}{\left|r - r^/\right|} d^3 r^/$ is the Hatree potential.

$V_{XC}(r) = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)}$ is the exchange correlation potential.

2.2 Easy Steps for Computational DFT

We recall the representation of total energy [equation (8)] of the interacting electrons system,

$$E[\rho] = T_o[\rho] + \int \rho(r) V_{ext}(r) d^3 r + \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{\left|r_1 - r_2\right|} d^3 r_1 d^3 r_2 + E_{XC}[\rho(r)]$$

So, we have from equation (10),

$$V_{eff} = V_{ext}(r) + V_H(r) + V_{XC}(r)$$
$$V_{ext} = V_{eff}(r) - V_{XC}(r) - V_H(r)$$

Incorporating this expression in the above equation, we can write as

$$E[\rho] = \sum_m^{occup} \varepsilon_m^o - \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{\left|r_1 - r_2\right|} d^3 r_1 d^3 r_2 - \int V_{XC}(r)\rho(r) d^3 r + E_{XC}[\rho(r)] \tag{11}$$

Equation (11) gives the final expression for the ground state energy of the system of interacting electrons. This is the expression used in computational calculation to determine the ground state energy functional for the interacting system of electron.

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