DENSITY FUNCTIONAL THEORY

- Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases.

- With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density.

Function is rule that transforms one number to another number

eg $2 \xrightarrow{x^3} 8$

Functional (function of a function) is a rule that transforms a function into a number

f(x) = x^3

$\int_0^2 f(x)dx = \frac{16}{4} = 4$

"In DFT the function is the electron density which is a function of space and time"

- It is difficult to solve Schrödinger equation for N-electron systems

- The multiple determinant calculations require very large basis sets due to the poor convergence of the correlation energy when the inter-electronic distance becomes very small. However, DFT can produce accurate results with relatively small basis sets.

- *DFT is thus "A method of obtaining an approximate solution to the Schrödinger equation of a many-body system"*

- *In DFT we consider electron density functional and not wave function**

 Uses:

     Used to Investigate the structural, magnetic and electronic properties of molecules materials and defects.

❖ Despite the improvements in DFT, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially:

1. *van der Waals forces (dispersion)*

2. *charge transfer excitations*

3. *transition states*

4. *global potential energy surfaces and some other strongly correlated systems*

5. *calculations of the band gap in semiconductors. (under estimates band gap)*

- Its poor treatment of dispersion renders DFT unsuitable (at least when used alone) for the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules).

- The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic.

DFT calculations an overview

1) Reduce as far as possible the number of degrees of freedom of the system (B.O Approximation)

2) Electron density is used in DFT as the fundamental property (unlike Hartree-Fock theory which deals directly with the many-body wavefunction)

3) The electron density is only a function of x, y, z -only three variables (unlike using N electron wavefunction which depends upon 3N coordinates)

4) Using electron density speeds up the calculation

5) Electron density of any system determines all ground-state properties of the system

6) if we know the electron density functional, we know the total energy of our system.

7) From the electron density it is possible to derive an effective one-electron-type Schrödinger equation

HOHENBERG-KOHN THEOREMS

Note:

❖ Hohenberg-Kohn theorem employs the ground-state density.

❖ Electrons interact with one another and with an external potential.

❖ External potential is the attraction to the nuclei.

❖ Integration of the density: number of electrons.

THE FIRST H-K THEOREM

- It demonstrates that "*the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates*".

- It lays the groundwork for reducing the many-body problem of N electrons with 3N spatial coordinates to 3 spatial coordinates, through the use of functionals of the electron density.

- This theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states

THE SECOND H-K THEOREM

The ground state energy can be obtained variationally: the density that minimizes the total energy is the exact ground state density

- It defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

- In principle: choose different densities and those that provide the lower energies are closer to correct.

- The second Hohenberg-Kohn theorem has two drawbacks. Firstly, it assumes that there is no degeneracy in the ground state, and secondly the density has unknown form.

The uniform electron gas model

- "The uniform electron gas is defined as a large number of electrons N in a cube of volume V, throughout which there is a uniform spread of positive charge sufficient to make the system neutral".

- Although it does bear some resemblance to electrons in metals, its widespread use is due to its simplicity – it is completely defined by one variable, the electron density ρ.

- The electron densities of atoms and molecules are often far from uniform, so functionals based on systems which include an inhomogeneous density should perform better.

KOHN-SHAM DFT

  ➢ The kinetic energy has a large contribution to the total energy. Therefore, even the 1% error in the kinetic energy prevented DFT from being used as a quantitative predictive tool.

- The many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. For this, consider an imaginary system of not interacting electrons where the ground state electron density is the same as a real system.(K-S Systems)

- Real and fictitious system have the same positions and atomic numbers of the nuclei so they have same density

- Ground state density of interacting system is equal to that of some noninteracting system that is exactly soluble, with all the difficult parts (exchange and correlation) included in some approximate functional of the density.

- The theory begins by considering the non-interacting reference system: N non interacting electrons moving in external potential V_s, each in one of N orbitals, ψ_i. Such a system will be defined by the Hamiltonian

  The energy of the molecule may be given as

$$E = T + V_{ne} + V_{ee} + V_{xc}$$

Or

$$F[\rho(r)] = E_{KE}[\rho(r) + E_H[\rho(r) + E_{XC}[\rho(r)]$$

$Where$

$F[\rho(r)]$ $is\ the\ electron\ density\ functional$

$E_{XC}[\rho(r)]is\ the\ echange\ correlation\ energy$

- The K-S equations are very similar to the Hartree–Fock equations. In fact, setting the exchange-correlation potential to the HF exchange potential yields the HF equations.

- Drawing too many similarities to HF is dangerous, however. Firstly, the KS orbitals are simply a way of representing the density; they are not (as in HF) an approximation of the wavefunction.

- The above analysis is only appropriate for closed shell molecules. Because the KS equations so closely follow the restricted HF equations, both the restricted open shell and unrestricted methodologies are readily available.

- Just as in HF theory, the KS equations are solved by expanding the orbitals over a basis set.

- The major advantage of DFT is that the basis set requirements are far more modest than the more conventional correlated methods

- In DFT the basis set only needs to represent the one electron density the inter-electron cusp is accounted for by the effective potential. In the more traditional methods, the basis set describes the entire N-electron wave function, requiring an accurate description of the cusp which is sensitive to the basis set.

- The exchange-correlation part of the total-energy functional remains unknown and must be approximated.

APPROXIMATION OF EXCHANGE- CORRELATION FUNCTIONALS

1) LOCAL-DENSITY APPROXIMATION

In *local-density approximation (LDA),* the exchange-correlation energy functional $E_{XC}[\rho]$ depends only on the density at the coordinate where the functional is evaluated.

$$E_{xc}[n(r)] = \int \varepsilon_{xc}^{\text{hom}}(n(r))n(r)d^3r$$

$$\varepsilon_{xc}^{\text{hom}}(n(r)) \rightarrow \text{Exchange} - \text{Correlatio n Energy of Homogeneou s}$$
$$\text{Electron Gas of Density } n(r)$$

- The exchange-correlation energy is decomposed into exchange and correlation terms linearly

$$E_{xc} = E_x + E_c$$

So that separate expressions for E_x and E_c are sought.

We have

$$E_X^{LDA} = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int[\rho(r)]^{\frac{4}{3}}dr$$

- The uniform electron gas functional is used for the E_x.
- Only limiting expressions for the correlation density are known exactly, leading to numerous different approximations for E_c.

2) GENERALIZED GRADIENT APPROXIMATION

LDA treats all systems as homogeneous. However, real systems are inhomogeneous. Generalized gradient approximation (GGA) takes this into account by including the derivative information of the density into the exchange-correlation functionals.

$$E^{GGA}_{xc}[\rho] = \int f(\rho(r), \nabla(\rho(r))dr,$$

- In comparison with LDA, GGA tend to improve total energies, atomization energies, energy barriers and structural energy differences
- GGA expand and soften bonds, an effect that sometimes corrects and sometimes overcorrects the LDA prediction

DFT AT A GLANCE

- In practice, Kohn-Sham theory can be applied in several distinct ways depending on what is being investigated.

- In solid state calculations, the local density approximations are still commonly used along with plane wave basis sets, as an electron gas approach is more appropriate for electrons delocalized through an infinite solid.

- In molecular calculations more sophisticated functionals are needed, and a huge variety of exchange-correlation functionals have been developed for chemical applications.

HYBRID FUNCTIONAL

They are a class of approximations to the exchange–correlation energy functional in density functional theory (DFT) that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (ab initio or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used versions is B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr

*Widely used is B3LYP which is a **hybrid functional** in which the exchange energy, in this case from Becke's exchange functional, is combined with the exact energy from Hartree–Fock theory. The adjustable parameters in hybrid functionals are generally fitted to a training set' of molecules.*