

In density Functional Theory, we want to find the electron density of the system because this is what gives the most important information about it such as the allowed energy levels, etc. . In order to do this we repeatedly solve something called the “Kohn-Sham” equations which look like Schrodinger equation and the purpose of solving that equation is to find the Kohn-Sham Orbitals from which electron density can be found. The process of iteratively solving this one equation consists of the following steps:

S1. We guess the electron density

S2. We solve the Kohn Sham equation with this assumed electron density and, as a result obtain the Kohn Sham orbitals and hence a **NEW** electron density. Why this newly obtained electron density and the one that we used to solve the Kohn-Sham equations are different is a personal problem, solved only by further exploration of Density Functional Theory and its intricacies.

S3. With this new electron density we keep repeating step 2 until:

3.1 - A specified number of steps are completed, or,

3.2 - A newly obtained electron density and the previous one are very close, the closeness of whom can also be specified.

The Kohn Sham equation look like the Schrodinger equation and the purpose of solving it iteratively is to arrive at a correct electron density for the system. While solving it, one of the term that are required is that of the “Potential Energy” of the system which is constructed of three terms:

1)Potential due to the Kinetic Energy of the electrons around the nucleus(As per the Bohn-Oppenheimer approximation, the nuclei don’t move and the electrons do owing to the large difference in their masses)

2)The Hartree Fock Potential due to the classical electrostatic potential as a result of the electron density. In the Kohn Sham equations, this term is calculated by assuming a pool of **non-interacting** electrons, revolving around the nuclei with electron density same as that of an interacting system.

3)Exchange-Correlation potential due to :

i)Exchange energy due to the repulsion between parallel spin electrons

ii)Correlation energy due to attraction between anti-parallel spin electrons

**The resultant “exchange-correlation” energy due to these two terms is not a simple arithmetic sum

This third term gives rise to the concept of exchange correlation functionals which are methods that give an approximate value for the exchange-correlation energy since this term is very difficult to calculate for many-body systems which are of the greatest importance.

They are so called because they are functionals, i.e., functions of functions. In this case functions of electron density (which in turn is a function of the position of the electrons).

The different exchange correlational functionals are:

Local Density Approximation(LDA)

This approximation assumes that the exchange correlation energy in a particular small volume containing electrons is present only because of the electron density in that particular volume, and not due to surrounding such volumes. The exchange correlation energy of the whole system is then calculated by a simple integral.

$$E_{XC} = \int_r \rho(r) \epsilon_{XC}(\rho(r)) dr$$

Where

$\rho(r)$ - Electron density in that volume(assumed to be constant throughout)

$\epsilon_{XC}(\rho(r))$ - exchange-correlation energy per electron, expressed as a function of the electron density

This approximation works well for systems where the electron density across the entire system varies smoothly but it fails otherwise.

LDA is a family of functionals. Each has minor improvements in the parameters of the exchange-correlation energy density part that goes in the integral. In order of development they are Slater exchange(LDA-X), Vosko-Wilk-Nusair (VWN), Ceperley-Alder (CA), Perdew-Zunger (PZ81), and finally Perdew-Wang 91 (PW91). PW91 is a hybrid functional

which was last in line of LDAs but the first one to incorporate the gradients of the electron density, a feature on which the family of GGAs stand.

Generalized Gradient Approximation(GGA)

This approximation is an improvement over LDA because now the gradient of the electron density is also taken into consideration. The exchange correlation energy per electron is now a functional dependent on two functions - the local electron density and the gradient of the electron density at that point. Using this term the exchange - correlation energy of the whole system is calculated as:

$$E_{xc}^{GGA} = \int \epsilon_{xc}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d^3r$$

More specifically, GGA is a class of exchange-correlation functionals each having its own merits and demerits. The above is the most simplest of GGAs known as **Perdew Wang-91** aka **PW91**.

Perdew-Burke-Ernzerhof(PBE)

It is an improvement which provides a better approximation of the exchange-correlation energy than even GGA. In reality, it is a type of GGA. In addition to the same improvements in PW91 over LDA, PBE seems to capture the electron density more “accurately” ,i.e., the gradient term used in the integral is more accurate. PBE treats the local electron density and the gradient descent terms differently than PW91 and hence is able to capture non local interactions such as those due to dispersion(brief creation of dipoles due to shifting of electron density).

Revised PBE(PBEsol)

This functional also comes under the broad family of GGAs.

PBE is said to underestimate lattice constants and bulk moduli of solids and hence PBEsol was developed and is extensively used for solid state calculations because it solved the problem by adjusting parameters related to the exchange part of the functional.

Tao-Perdew-Staroverov-Scuseria (TPSS)

This approximation also comes under the broad family of GGAs. It improves upon PBE by including additional terms in the exchange-correlation energy term that comes in the integral

to account for higher order gradients. As a result, it is able to better capture non local interactions such as due to dispersions.

Heyd-Scuseria-Ernzerhof (HSE06)

This is a hybrid functional. It is however still considered a GGA. The “hybrid” is because the exchange-correlation energy term in the integral now has a portion of the exact exchange energy from a previously developed and then rejected Hartree Fock Theory. It hence better incorporates the interactions between opposite spin electrons(exchange interactions). It is used extensively for systems with significant charge transfer or localized electrons.

Becke's Three-Parameter Hybrid (B3LYP)

This is a hybrid functional. The exchange correlation energy density term includes:

- exchange energy from Hartree Fock Theory
- exchange energy from B88(a GGA)
- Correlation energy from Lee-Yang-Parr(an LDA)

Due to these contributions it is able to make an even more accurate prediction of the exchange correlation energy term in the Kohn-Sham equation.

Perdew-Burke-Ernzerhof (PBE0)

It is also a hybrid functional. The exchange correlation energy density term includes:

- PBE exchange functional
- Exchange energy from Hartree Fock Theory

This is an improvement over PBE really as it solves the rare case where PBE sometimes overestimates the band gap in some cases(Delocalized systems and metals).

Gaussian and Slater-type hybrid (GOS)

GOS functionals are formulated by taking a combination of Gaussian type orbitals(The probability density of electrons has a bell shaped curve) and Slater Type orbitals(a more realistic distribution of electron density around the nucleus - probability density of electrons resembles the curve of $1/x$ in the 1st quadrant). The Kohn Sham equations are solved by keeping this assumption.

Minnesota Functionals (M06, M06-2X)

This is a family consisting of two functionals - M06 and M06-2X. It is a hybrid functional of GGAs and Meta-GGAs(These are enhanced GGAs which also include gradients that describe

the Kinetic energy of electrons.

M06 was developed to correct the self interaction error(The error wherein the functional incorrectly describes the interaction between repulsive electrons) in pure GGAs by including a part of energy due to the Hartree Fock potential.

M06-2X was developed as an improvement over M06. It has a higher proportion of energy due to the Hartree Fock potential as compared to M06.