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Project Report

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<u>Project Title</u>

"Study of Density Functional Theory"

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1. Quantum Many-Body Problem

● Introduction :

A significant part of condensed matter physics and chemistry would be solved if the electronic structure of atoms, molecules and solids could be determined exactly. This however a formidable task for two main reasons. Firstly, electrons in matter must be treated using laws of quantum mechanics rather than classical physics - the quantum length scale is set by Plank's constant h, and onset of quantum effects occurs when the de Broglie wavelength of a particle, λ, given by

$$\lambda = \frac{h}{p}$$

is comparable to the average inter-particle separation.

The second problematic issue concerns the number of electrons that are involved - the coupling of the electron interactions due to debroglie wavelength overlap renders an analytic solution impossible for systems with more than one electron, and the complexity grows dramatically with increasing electron number. It is for these reasons the electronic structure of matter is known as the quantum many-body problem.

The properties of any (non- relativistic) time independent quantum system can be determined by solving the Schrodinger equation,

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,l} \frac{Z_l e^2}{|r_j - R_l|} + \frac{1}{2} \sum_{j \neq j'} \frac{e^2}{|r_j - r_j'|} - E \right\} \Psi = 0$$

where $\Psi \equiv \chi(x) = \varphi(r)\sigma(w)$ and $E \equiv E(R_1, R_2, \ldots, R_m)$, such that solution must satisfy Pauli's Principle i.e upon exchange of spatial and spin coordinates of two electrons $\chi(x)$ reverses its sign.

Th Hamiltonian above is simplified version of actual version, where simplification is done with Born-Oppenheimer approximation [1].

Few electron systems - the H2 molecule
The power of Schrodinger Equation in chemistry were calculations of the properties of the simplest molecule H2. Its experimental binding energy and inter-nuclear separation are D = 4.75 eV , R = 0.740 A

Electron Wavefunction estimates were:
1. Hitler and London 1927, Ansatz gave results D = 3.14eV and R = 0.87A.

2. Mullikan 1928, Results D = 2.65eV and R = 0.76A, close results for inter-nuclear separation but far off for binding energy.

3. Hartree-Fock ansatz, with result D = 3.63eV and R = 0.74A, much better than previous one .

4. The most complete early study of H_2 was taken by James and Coolidge 1993. They made the very general variational ansatz and it gave very close estimates ,
D = 4.70eV and R = 0.740 A.

Conclusion: For sufficiently small molecules, wave-function methods give excellent results.

● **Hartree-Fock Theory**

The Hartree-Fock method [2] which builds upon single particle approximation was earlier proposed by Hartree [3]. The Hartree product approximation does not account for exchange interactions thus violates antisymmetry principle under exchange of particle coordinates. This problem was rectified by Hartree-Fock approximation [] by writing waveefunction as an antisymmetrized product of orbitals.

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} [\varphi_1(x_1)\varphi_2(x_2)\dots\varphi_N(x_N) - \varphi_1(x_2)\varphi_2(x_1)\dots\varphi_N(x_N) + \dots]$$

With this approach the system's Hamiltonian is the sum of Hamiltonians of each electron inside system. Schrodinger equation for electron 'k' is written as

$$\left[-\frac{\hbar^2}{2m}\nabla_k^2 + W(r_k)\right]\chi_j(x_k) = E_j\chi_j(x_k)$$

where $w(r_k) \equiv V_c(r_k) + V_H(r_k)$ called "central potential for electron k"

$$V_c(r_k) = \begin{cases} -\dfrac{Ze^2}{r_k} & \text{, system with a nuclei} \\ -\sum_l^m \dfrac{Z_le^2}{|R_l - r_k|} & \text{, system with 'm' nuclei} \end{cases}$$

$$V_H(r_k) = \int \sum_{i \neq k} |\chi_j(x_k)|^2 \frac{e^2}{|r_i - r_k|} d^3r_i \rightarrow \text{"Hartree Potential"}$$

◆ In Hartree potential, single electron feels effect of others only as average.
◆ Hartree-Fock approach assumes that complete wavefunction $\chi(x)$ for N electrons system, can be approximated using Slater Determinants thus satisfying Antisymmetry Principle.
◆ Z electrons in the atoms gives Z schrodinger equations, each with Z eigenstates consistent with requirement to form Slater Determinants.

● **Hartree-Fock : Iteration Scheme**

Assume an approximate central potential $W^{(1)}(r_k)$ representing $W(r_k)$.

1. Electron wavefunctions are computed employing $W^{(1)}(r_k)$.
2. With first-order wavefunctions $\{\varphi^{(n)}(r_k)\}$ at hand, calculate charge densities :

$$e^2n(r_k) = e^2\left|\varphi_k^{(1)}(r_k)\right|^2$$

3. From these charge densities, calculate second-order atomic potential $W^{(2)}(r_k)$.

4. Plug $W^{(2)}(r_k)$ in step-1 & repeat untill $\left\| W^{(n+1)}(r_k) - W^{(n)}(r_k) \right\| \leq \epsilon$

● Slater Determinants

In 1951 Slater gave the N*N determinant representation of Hartree-Fock function.

After Iteration is finished take first N lowest energy eigenfunctions of each electron to form Slater determinant.

$$\Psi = \frac{1}{\sqrt{N!}} \mathrm{Det} \begin{bmatrix} \varphi_{j1}(r_1) & \cdots & \varphi_{jN}(r_1) \\ \vdots & \ddots & \vdots \\ \varphi_{j1}(r_N) & \cdots & \varphi_{jN}(r_N) \end{bmatrix}$$

Advantage of representing resultant wavefunction in determinant form is that the most important Pauli's anti-symmetry principle is not violated.

● Limitations of Wavefunctions based approximations :

➢ Many electron encountering an Exponential Wall

For a general molecule consisting of M atoms with total of N interacting electrons , where M >>10, say. We see that number of parameters required is $M = p^{3N}$, 3<p<10.

Now following the variational ansatz energy needs to be minimized in the space of these M parameters. Call M' the maximum value feasible with best available computer software and hardware, and N' the corresponding maximum number of electrons. Then from above equation we find   N' $= (1/3)\frac{\ln M'}{\ln p}$

Say M' $\sim 10^9$ and p = 3, then N' ~6, I.e with M' number of parameters only 6 electron wavefunction can be computed.

Lets say N=100 then M~10^{150}, a huge number of parameters, and minimization of energy w.r.t to these M parameters is nearly impossible not even by recent most advanced computers.

So, with increase in N , M increases exponentially and feasibility of handling these number of parameter vanishes.

➢ Recording of many electron wave-function

Lets assume somehow accurate approximation to wavefunction Ψ is obtained and we wish to record it to reproduce it at later time.

Question is "How many bits are needed?"

Lets take q bits per variable, then for N electron, total number of bits needed is $B = q^{3N}$.

For q=3, and N = 1000, $B = 10^{1500}$ a huge number, even the number of baryons in the accessible universe is estimated as 10^{80}.

- **Thomas Fermi model**

One of the earliest tractable schemes for solving the many body-problem was proposed by Thomas and Fermi [4]. A very crude theory of electronic energy in terms of the electron density distribution, $n(r)$. Quite useful for describing some qualitative trends e.g total energies of atoms, but for questions of chemistry and material science, which involve valence electrons it was useless.

However, theory had one feature , it considered interacting electrons moving in an external potential $v_{ext}(r)$ and provided a one to one implicit relation between $v_{ext}(r)$ and density distribution $n(r)$.

$$n(r) = \gamma[\mu - v_{eff}(r)]^{3/2} \quad , \quad \gamma = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^2 \quad , \quad v_{eff}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|}dr'$$

Where $n(r)$ expression is based on expression $n = \gamma(\mu - v_{ext})^{3/2}$ for density of a uniform degenerate electron gas in a constant external potential $v_{ext}(r)$. And second term in V_{eff} expression is classically computed electrostatic potential generated by electron density distribution $n(r')$.

First expression ignores gradient of V_{eff}, means theory would apply best for systems of slowly varying density.
Thomas-Fermi theory suffers many deficiencies, probably the most serious defect is that it does not predict bonding between atoms, so molecules and solids cannot form in this theory. The main source of error comes from approximating the kinetic energy in a very crude way. Another shortcoming is the oversimplified description of electron-electron interactions, which are treated classically and so do not take account of quantum phenomenon such as exchange-interaction.

Theory did not become significantly more useful even after some exchange correlation corrections. But it suggested the hypothesis that a knowledge of the ground state density $n(r)$ for any electronic system (with or without interactions) uniquely determines the system.

2. Density Functional Theory

Using hypothesis suggested by Thomas-Fermi theory, Hohenberg and Kohn [5] gave two remarkable powerful theorems establishing electron density as the central quantoty describing electron interactions and so devising the formally exact ground state method known as density functional theory (DFT).

- **Hohenberg- Kohn Theorems : Formulation of DFT**

Theorem-1: Ground state density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely.

Means, ground state electron density $n(r)$ determines all properties including the energy and wave-function of ground state.

Why this is an important result ?
We can think about solving Schrodinger Equation by approximating $n(r)$, a function of three variables , rather a function of 3N variables, wave-function.
So, for a nanocluster of 100 Pd atoms, theorem reduces problem of approximating a wave-function of 23,000 variables, to a problem of approximating just 3 variables.

From Theorem1 , $n(r)$ determines both N and $v_{ext}(r)$ for system, $\mathbf{N = \int n(r) d^3 r.}$
N and $v_{ext}(r)$ gives complete information of Hamiltonian H from which we can derive <u>properties of system</u> (such as frequency dependent electric polarizability, many body eigenstates) through solution of TISE or TDSE.
So, ground state energy $E \equiv E[n(r)]$ is a functional of ground state density $n(r)$.
Also be expressed as

$$E[n(r)] = E_{known}[n(r)] + E_{xc}[n(r)]$$

where

$$E_{known} \equiv T + C_{n-n} + C_{n-e}$$

& E_{xc} : Exchange Coorelation functional {includes all quantum mechanical effects that aren't included in known term}.

Theorem-2:
"It states that the electron density that minimizes the energy of the overall energy functional is the true electron density corresponding to the full solutions of the Schrödinger equation"

Assuming E_{xc} is known, Hohenberg and Kohn devised a iterative method [3] using variational principle to calculate minimal energy solutions $E_{min}[n(r)]$.

● **Hohenberg and Kohn Variational Principle**

H-K variational principle [5,6] says instead of taking trial wavefunctions as in Rayleigh Ritz method we take trial densities $\tilde{n}(r)$ and try to minimize Energy functional from HK theorem-1 and Theorem-2 , for ground state energy,

$$E[n(r)] = \underbrace{\int V_{ext}(r) n(r) dr}_{\substack{\text{net electrons−nuclei(s)} \\ \text{interaction potential} \\ \text{for system}}} + F[n(r)]$$

where $F[n(r)] = (\Psi|K.E + U|\Psi)$ is "<u>universal Energy functional</u>" composed of just K.E and x-c terms thus entirely independent of external potential $V_{ext}(r)$ of system.

Method Involves:

1) Take class of trial densities $\{\tilde{n}_X(r)\}$ for X = A,B,C,.....,K,... such that $\int \tilde{n}_X(r)dr = N$, actual number of electrons in the system.

2) Fix a trial density $\tilde{n}_K(r)$ say, and take Trial wavefunctions $\{\widetilde{\psi}_{\tilde{n}_K}^{\alpha}(r)\}$ associated with $\tilde{n}_K(r)$ such that

$$N * \left|\widetilde{\psi}_{\tilde{n}_K}^{\alpha}(r)\right|^2 = \tilde{n}_K(r) \quad \& \quad \int \tilde{n}_K(r)dr = N$$

means, trial wavefunction is normalized.

3) For fixed electron density $\tilde{n}_K(r)$, minimize energy functional w.r.t $\boldsymbol{\alpha}$.

$$E[\tilde{n}_K(r)] = \min_{\boldsymbol{\alpha}}(\widetilde{\psi}_{\tilde{n}_K}^{\alpha}|H|\widetilde{\psi}_{\tilde{n}_K}^{\alpha}) = \int \tilde{n}_K(r)v(r)dr + F[\tilde{n}_K(r)]$$

where,

$$F[\tilde{n}_K(r)] \equiv F[\{\widetilde{\psi}_{\tilde{n}_K}^{\alpha}\}] = \min_{\boldsymbol{\alpha}}(\widetilde{\psi}_{\tilde{n}_K}^{\alpha}|T+U|\widetilde{\psi}_{\tilde{n}_K}^{\alpha})$$

4) Apply Rayleigh Ritz principle to get $\widetilde{\psi}_{\tilde{n}_K}^{\beta}$, minimizing $F[\{\widetilde{\psi}_{\tilde{n}_K}^{\alpha}\}] \equiv F[\tilde{n}_K]$.

5) We have in hand minimized $F[\tilde{n}_K]$. To get ground state energy E_g, minimize $E[\tilde{n}_X(r)]$ over all $\{\tilde{n}_X(r)\}$.

$$E_g \sim \min\{E[\tilde{n}_X(r)]\} = \min\{\int v(r)\,\tilde{n}_X(r)dr + F[\tilde{n}_X(r)]$$

True ground state can be obtained if electron density $\tilde{n}_X(r)$ is exact
Ground state density $\mathbf{n(r)}$.

Note:- In Step3 , minimization of F, leads us right back to problem of minimizing 3N dimensional Trial wavefunction $\widetilde{\Psi}$. So, this problem still persists but achievement is the formulation of variational principle in terms of trial densities $\tilde{\mathbf{n}}_{\mathbf{K}}(\mathbf{r})$ i.e we can think in terms of taking a 3 variable Trial function.

● Kohn-Sham Equations

The 3N-dimensional many body wavefunction minimization problem was solved in Kohn-Sham equations[7] where $\chi(x_1, x_2, \ldots x_{3N-1}, x_{3N},)$ trial wavefunction is replaced by $\boldsymbol{\varphi_i}$, a single particle wavefunction.

Self-consistent Kohn-Sham Equations :

1. Single electron Schrodinger Equation,

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r) - \epsilon_j)\varphi_j(r) = 0\right)$$

where j denotes spatial coordinates and spin quantum number.

2. Electron density distribution,

$$n(r) = \sum_{j=1}^{N} \left| \varphi_j(r) \right|^2$$

3. Effective potential,

$$V_{eff}(r) = V(r) + \int \frac{n(r')}{|r - r'|} dr' + V_{xc}(r)$$

where $V_{xc}(r)$ is local exchange correlation energy potential given by

$$V_{xc}(r) = \left. \frac{\delta E_{xc}[\tilde{n}(r)]}{\delta \tilde{n}(r)} \right|_{\tilde{n}(r)=n(r)}$$

Then Ground state energy is given by

$$E[n(r)] = \sum_j \epsilon_j + E_{xc}[n(r)] - \int V_{xc}(r)n(r)dr - \frac{1}{2} \int \frac{n(r')n(r)}{|r - r'|} dr'$$

These $V_{xc}(r)$ and $E_{xc}[n(r)]$ are mysterious corrections that embodies all underlying unknown quantum many body effects.

The practical usefulness of ground-state DFT depends entirely on whether approximations for the functional $E_{xc}[n(r)]$ could be found which are sufficiently simple and sufficiently accurate.

● **K-S Iteration Scheme:**

Since the Kohn-Sham equations are self-consistent so an iteration method is needed to solve it. Methods involves following iterative steps :

1. Define initial ground state trial density $\tilde{n}(r)$.
2. Plug $\tilde{n}(r)$ in V_{eff} and solve N single electron Schrodinger's equations

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(r) \right) \varphi_j(r) = \epsilon_j \varphi_j(r) \quad \text{for } j \in \{ j_1, j_2, \ldots j_N \}$$

3. Calculate mean electron density

$$n_{KS}(r) = \sum_{j=1}^{N} \left| \varphi_j(r) \right|^2$$

   Sum runs over lowest energy eigenfunctions for each electron.

4. Repeat step-2 &3 untill $|n_{KS}(r) - \tilde{n}(r)| < \varepsilon$

After iteration is finished, take first N lowest energy eigenfunctions of each electron and form Slater determinant to get an approximate many body wavefunction.

$$\Psi = \frac{1}{\sqrt{N!}} \text{Det} \begin{bmatrix} \varphi_{j1}(r_1) & \cdots & \varphi_{jN}(r_1) \\ \vdots & \ddots & \vdots \\ \varphi_{j1}(r_N) & \cdots & \varphi_{jN}(r_N) \end{bmatrix}$$

3. Exchange and Correlation

● The Exchange-Correlation Hole

Region around an electron where its less likely to find another electron due to exchange-correlation effects. This region is created because electrons try to avoid each other in various ways.
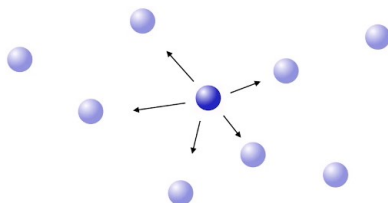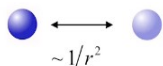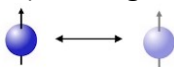

Fig-4 Electrons trying to avoid each other to get "personal space"
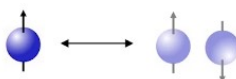
Electrons avoid each other in three ways :

1. Through classical Coulomb interaction (like charges repel)

$\sim 1/r^2$

2. Through the Pauli principle (exchange interaction between parallel spins)

3. Through non classical correlation effects (between both parallel and anti-parallel spin)

The Exchange-correlation Hole (Mathematical description):

Expectation value of electron-electron interaction is

$$(\Psi|V_{ee}|\Psi) = \frac{1}{2} \iint \frac{P(r,r')}{|r-r'|} drdr'$$

where Ψ is normalized anti-symmetric ground state wavefunction of the system. The pair density $P(r,r')$ gives probability of simultaneously finding an electron at the point **r** within volume element dr and another electron at r' in volume element dr' , among other $N-2$ electrons in the system.

Then electron density is given by,

$$n(r) = \frac{1}{N-1} \int P(r,r')dr'$$

Since $\int n(r)dr = N$, this leads to condition,

$$\iint P(r,r')drdr' = N(N-1)$$

In a classical description the motions of electrons are not correlated, so classical pair density is simply a product of density at point r and r',

$$P^{classical}(r, r') = n(r)n(r')$$

In reality , electrons obey Fermi statistics and so are kept apart quantum mechanically by Pauli-Exclusion principle, and also from other non-classical interactions mentioned below.
Therefore each electron creates a depletion, or hole, of electron density around itself as a direct consequence of exchange correlation effects.
Taking into account hole density, pair density is

$$P(r, r') = n(r)n(r') + n(r)n_{xc}(r, r')$$

Where quantum effects are accounted for by the exchange-correlation hole density $n_{xc}(r, r')$, surrounding each electron located at position **r** .

X-C hole density can be written as $n_{xc} = n_c + n_x$, and have properties :

1. $n_X(r, r') \leq 0$ { 2. $\int n_X(r, r')dr' = -1$ 3. $\int n_X(r, r')dr' = -1$ } $\rightarrow$ [*Sum Rule*]

This implies that exchange-correlation hole itself has a deficit of exactly one electron, therefore an electron and its hole constitute an entity with no net charge.

● **Exact Definition of Exchange and Correlation Energy**

An exact definition of the exchange-correlation energy $E_{XC}[n(r)]$ in DFT can be derived using a method known as "adiabatic connection". The basic concept is that while keeping the density fixed , the non interacting system is connected to the interacting system via a coupling-constant λ, which represents the strength of the electron-electron interaction. $\lambda = 0$ implies the non-interacting system and $\lambda = 1$is the fully interacting system. The exchange-correlation energy is given by

$$E_{XC}[n(r)] = \frac{1}{2}\int n(r)dr \int \frac{n_{XC}(r, r')}{|r - r'|}dr'$$

The exchange-correlation hole density $n_{XC}(r, r')$ is actually averaged over a coupling -constant dependent hole $n_{XC}^{\lambda}(r, r')$, given by,

$$n_{XC}(r, r') = \int_0^1 n_{XC}^{\lambda}(r, r')d\lambda$$

4. Exchange-Correlation Approximations :

X-C functionals essentially try to model the exchange-correlation hole. This is done with varying degrees of sophistication depending on approach taken. However all functionals are written in general from,

$$E_{XC}[n(r)] = \int n(r)\,\epsilon_{XC}(n(r))dr$$

where $\epsilon_{XC}(r)$ is the exchange-correlation energy per particle, or energy density, given by

$$\epsilon_{XC}(r) = \frac{1}{2}\int \frac{n_{XC}(r,r')}{|r-r'|}dr'$$

Functionals can be characterized by the way in which hole density $n_{XC}(r,r')$ surrounding each electron is sampled in order to construct $\epsilon_{XC}(r)$.

Exchange Correlation functional are classified into 3 categories :
1- Local
2- Semi-Local
3- Non-Local

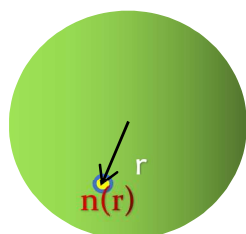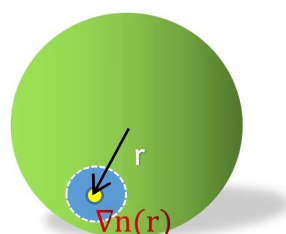Below picture illustrates some electronic density distribution.

Figure-1   Figure-2

Local functional:
The exchange-corr energy density $\epsilon_{xc}(n)$ at point r, depends on electron density n(r) at same point r (Figure-1), i.e we need only local information to construct $\epsilon_{xc}(n)$.
E.g : Local Density Approximation (LDA)

Semi-Local Functional:
$\epsilon_{xc}(n, \nabla n(r))$ depends on density and/or orbitals and their gradients at r. So we need some information in small neighbourhood around r (Figure-2) to construct functional.
E.g : GGA, meta-GGA, Hybrid Functionals

Non-Local Functional:
$E_{xc}[n(r)]$ depends on density and/or orbitals everywhere throughout the system not just at or near point r.
Eg : ADA and WDA

● **Various approximations of exchange-correlation functional:**

➢ *Local Density Approximation - LDA (Local)*
In the local density approximation LDA [6,8], the value of E_{xc} is approximated by the exchange-correlation energy of an electron in an homogeneous electron gas of the same density n(r), i.e

$$E_{xc}^{LDA}[n(r)] = \int \epsilon_{xc}(n(r))n(r)dr$$

Where $\boldsymbol{\epsilon_{xc}}$ is the exchange -correlation energy per particle of an uniform electron gas of density $n(r)$.
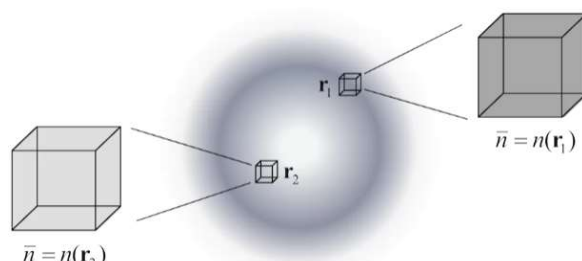
Physical Meaning of LDA :

Figure-3 Strongly in-homogeneous system, with electron cloud resembling spherical shells

➢ We treat small volume elements at r_1 and r_2 as little piece of a homogeneous electron gas with same density as in the real system at those points.
➢ ϵ_{xc}^{hom} energy density is evaluated at local $n(r)$
➢ So, we treat system locally as homogeneous electron gas.

This V_{xc} is plugged into V_{eff} in K-S equation, thereby completing missing term. Now, this K-S is solved using above Iteration scheme to get approximated ground state energy. The $\epsilon_{xc}(n)$ can be split into exchange and correlation potentials
$$\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$$
The exchange part $\epsilon_x(n)$, in atomic units, is $\epsilon_x(n) = -0.458/r_s$, where r_s is the radius of a sphere containing one electron.
Accurate values for $\epsilon_c(n)$ have been determined by Perdew and Zunger [9] which uses accurate Quantum Monte Carlo (QMC) data of homogeneous electron gas generated by Ceperley and Alder [10].

Limitations:
LDA gives ionization energies of atoms, dissociation energies of molecules and cohesive energies with a fair accuracy of typically 10–20%. However the LDA gives bond lengths and thus the geometries of molecules and solids typically with an astonishing accuracy of 1%.
For systems where the density varies slowly, the LDA tends to perform well, and chemical trends are well reproduced. In strongly correlated systems where an independent particle picture breaks down, the LDA is very inaccurate.

Concept of Nearsightedness (*by Kohn*) : "$n_{xc}(r, r')$ is mostly determined by $n(r)$ i.e electron density at reference position r"
In other words, only input information of density within small neighbourhood of **r** is needed as shown in Figure-5.
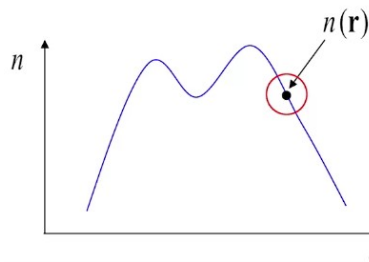
Figure-5 Inhomogenous density distribution.

> ### Generalized Gradient Approximation - GGA (Semi-Local)

As the LDA approximates the energy of the true density by the energy of a local constant density, it fails in situations where the density undergoes rapid changes such as in molecules. Following principle of Nearsightedness an obvious approach to improve the LDA is to include gradient corrections [11], by making E_{xc} a functional of the density and its gradient:

$$E_{xc}^{GGA}[n(r)] = \int d^3r \, \epsilon_{xc}(n(r))n(r) + \int d^3r \, F_{xc}[n(r), |\nabla n(r)|]dr$$

where F_{xc} is a correction chosen to satisfy one or several known limits for E_{xc} .

Commonly used functionals in condensed matter community
1. BLYP (Becke-Lee-Yang-Parr 1988)
2. Perdew and Wang (PW91)
3. PBE (Perdew-Burke-Ernzerhof 1996)

> ### Meta-GGA (Semi-Local)

The meta-GGA (MGGA) **[12,14]** include additional semi-local information beyond the first order density gradient contained in the GGA, such as higher order density gradients, or more popular is the inclusion of the kinetic energy density $\tau(r)$ which involves derivatives of the occupied Kohn-Sham orbitals,

$$\tau(r) = \frac{1}{2}\sum_{i}^{occ} \left|\nabla\psi_i(r)\right|^2$$

where $\int \tau(r) \, dr$ is equivalent to the usual non-interacting kinetic energy $T_s[n(r)]$. The MGGA may be written with the general form,

$$E_{XC}^{MGGA}[n(r)] = \int f[n(r), \nabla n(r), \nabla^2 n(r), \tau(r), \mu(r), \dots, \gamma(r)]$$
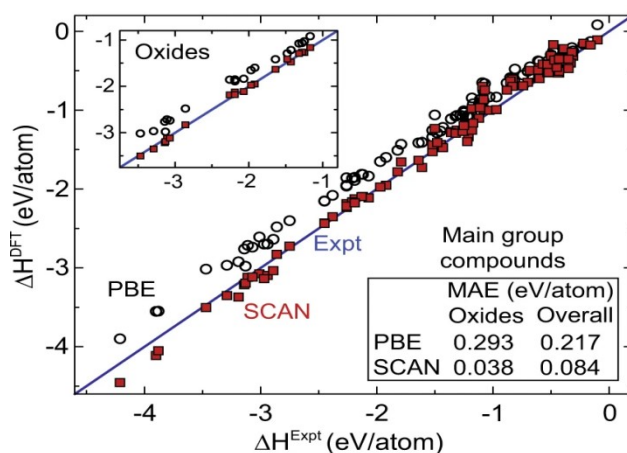
where $\mu(r)\dots\gamma(r)$ are other possible semi-local quantities (i.e. defined locally at **r**) that could be used in the construction of m-GGAs.

Examples:
1. TPSS (Tao-Perdew-Staroverov-Scuseria 2003)
2. SCAN (Strongly Constrained Appropriately Normed 2016)

Performance of GGA and Meta-GGA :

1. *Formation Enthalpy of Solids (main group binary compounds)*

- Mean absolute error (MAE) close to chemical accuracy (0.04 eV per atom)
- Study showed the results were less accurate for transition metal compounds(but still good)

2. *Binding Energy for different structures formed 6 H2O molecules.*
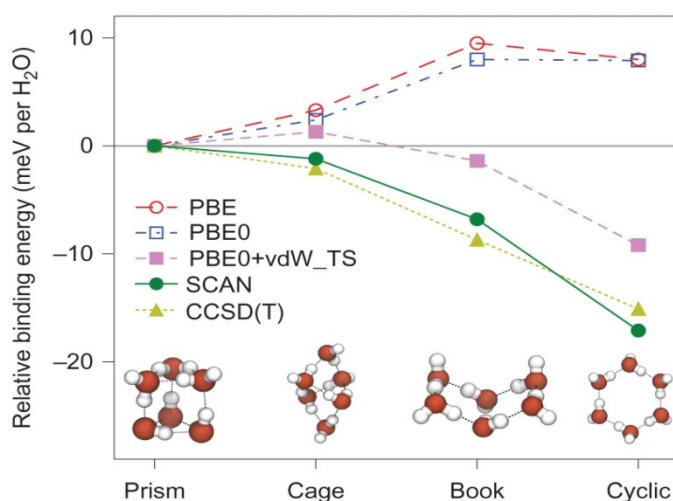
- SCAN compares very well with CCSD(T), which is a high level very expensive quantum chemistry method, and predicts correct ordering of water hexamer structures.

- PBE, PBE0 and (PBE0 +vdW_TS), with vander waals correction is not doing well.

> ### Hybrid Density Functional (semi-local)

The hybrid density functionals [13], which combine non-local exact (Hartree-Fock) exchange with conventional GGAs, the general form is,

$$E_{XC}^{hybrid} = \alpha(E_X^{HF} - E_X^{GGA}) + E_{XC}^{GGA}$$

where E_X^{HF} is the Hartree-Fock exchange energy evaluated with Kohn-Sham Orbitals and coefficient α determines the amount of exact exchange mixing , fitted semi-empirically.

The logic behind this prescription was put forward by Becke [80] who noted that the limits of the adiabatic connection integral for exact exchange- correlation energy could be approximated as a Linear Interpolation :

$$E_{XC} = \int_0^1 U^\lambda d\lambda = \frac{1}{2}U^0 + \frac{1}{2}U^1$$

Since $\lambda = 0$ corresponds to the exchange only limit, this could be well described using Hartree-Fock theory, while $\lambda = 1$ represents the most local part of the electron interactions, as a result of correlation, and so could be responsive to a local-type density functional treatment. As a result , Becke proposed the so called half and half functional,

$$E_{XC} = \frac{1}{2}E_X^{HF} + \frac{1}{2}E_{XC,\lambda=1}^{DF}$$

Where $E_{XC,\lambda=1}^{DF}$ is obtained from a density functional approximation such as LDA. It later emerged from semi-empirical fits to atomic and molecular data that the optimum amount of exchange mixing should be reduced to ≈ 0.25, so mixing parameters needed to be optimized , which is done by improving the interpolation of above integration.

Some of successful Hybrid functionals are:

1. PBE0 (1999) :

$$E_{XC}^{Hybrid} = \frac{1}{2}E_X^{exact} + \frac{3}{4}E_X^{GGA} + E_C^{GGA}$$

2. B3LYP (1994) :

$$E_{XC}^{Hybrid} = (1-a)E_X^{;DA} + aE_X^{exact} + bE_X^{B88} + cE_C^{LYP} + (1-c)E_C^{LDA}$$

where

$$\underbrace{a = 0.20 , b = 0.72 , c = 0.81}_{Fitted\ to\ a\ molecular\ data\ set}$$

Results:

Calculated for molecular datasets by Stratov, Scuseria, Tao & Perdew 2003 [14]

		Mean Absolute Error (MEA)	Formation Enthalpy (kcal)	Equilibrium bond length A	Cohesive energy (eV/atom)	Lattice constant
	LDA	121.85	0.0131	0.77	0.071
GGA	BLYP	9.49	0.0223	0.69	0.120
	PBE	22.22	0.0159	0.19	0.061
MGGA	TPSS	5.81	0.0142	0.20	0.054
	SCAN			0.19	0.03
HYBRID	PBE0	6.66	0.0097	0.46	0.038
	B3LYP	4.93	0.0104	0.84	0.084

Performance of hybrid functionals :

- Very good for energetics, especially of molecules.
- Good geometries/ lattice constants, but GGA/MGGA often better because some hybrids are optimized for molecules not solids.
- HF exchange energy can be expensive for solids because of the difficulty of computing the exact-exchange part within a plane-wave basis set. Therefore, hybrids are not used so much for solids but it turns out they give very good band gaps for solids.

5. Band Structure Calculation using Quantum Espresso

- ## Some basics of Quantum Espresso :

Quantum Espresso[15] is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale using DFT plane wave basis sets library of pseudo-potentials representing electron-ion interactions. Quantum espresso distribution is written in Fortran-95, Fortran -77 and C. Application executables are run through text input files based on Fortran namelists, thus requiring user to input only essential control variables.

The distribution comes with different packages designed for specific calculations, some of which that are widely used in Condensed matter physics and Materials Science particularly in study of Topological insulators are :

1. **PWscf** *:* It executes the self consistent calculation to find the ground state charge density using iterative diagonalization techniques using pseudo-potentials. It can also minimize forces to find the optimal structure from a given set of atomic positions.

2. **pHonon (ph.exe)** : A code which uses Density Functional Perturbation Theory to calculate the dynamical matrix at different ~q points in the Brillouin zone (BZ). The dynamical matrices are used by other executables to calculate the phonon dispersions. It can also calculate the electron-phonon coupling.

3. **Wannier90**: a code that calculates maximally localized Wannier functions in insulators or metals.Besides calculating maximally-localized Wannier functions, the code is able to construct the Hamiltonian matrix in this localized basis, providing a chemically accurate, and transferable, tight-binding representation of the electronic structure of the system.

4. **GIPAW** : The GIPAW code allows for the calculation of physical parameters measured in (i) nuclear magnetic resonance (NMR) spectroscopy in insulators (the electric-field-gradient (EFG) tensors and the chemical shift tensors), and by (ii) electronic paramagnetic resonance (EPR) spectroscopy for paramagnetic defects in solids or in radicals (the hyperfine tensors and the g- tensor). The code also computes the magnetic susceptibility of nonmagnetic insulators.

- ### *Band Structure of Strong Topological Insulator Bi2Se3*

Bismuth Selenide (Bi2Se3) is a strong topological insulator. The layers are stacked together via van der Waals interactions and can be exfoliated into thin 2D layers. Crystal Structure of Crystal Structure of Bi2Se3 is "Rhombohedral" with Unit cell parameters (Lattice parameters and angles):

$$a = b = 0.413 \, , c = 2.856 \, , \alpha = \beta = 90 \, , \gamma = 120$$
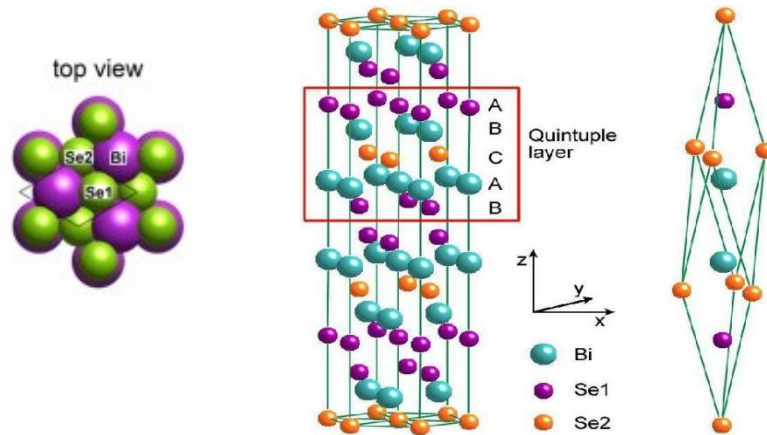

Figure: 6 Layer Quintuple crystal structure of Bi2Se3.

The crystal structure with Quintuple layer made of 6 layers of atoms as described in Figure-8 . Using the Kohn-Sham self consistent equations the ground state energy and Fermi-level of the Bi2Se3 are calculated with and without spin orbit coupling.
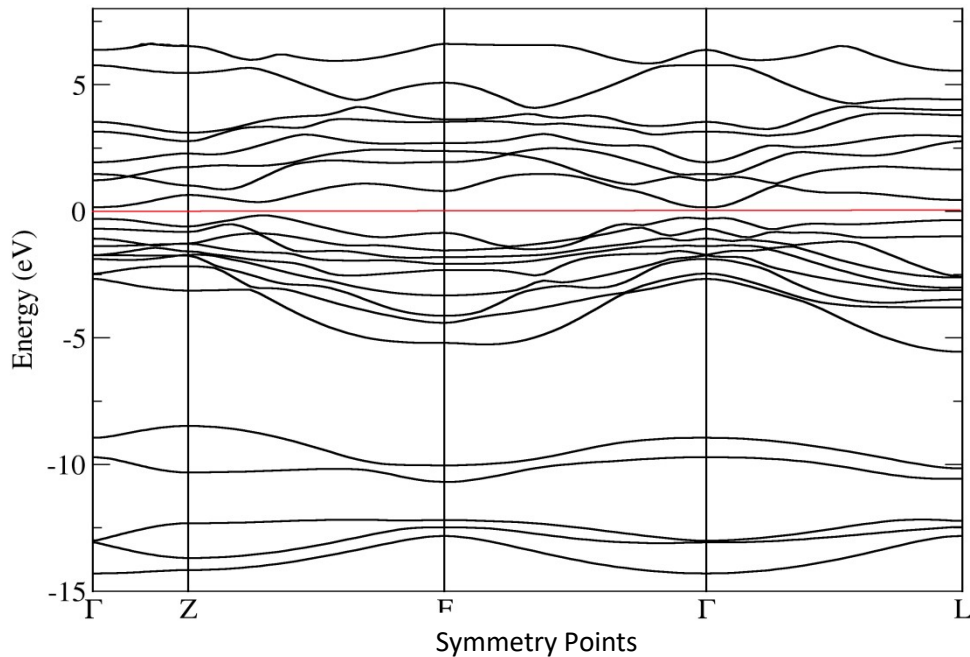

Figure: 7 Band Structure of Bi2Se3 without spin-orbit coupling (SOC), along specified symmetry points.

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