Density Functional Theory (DFT)

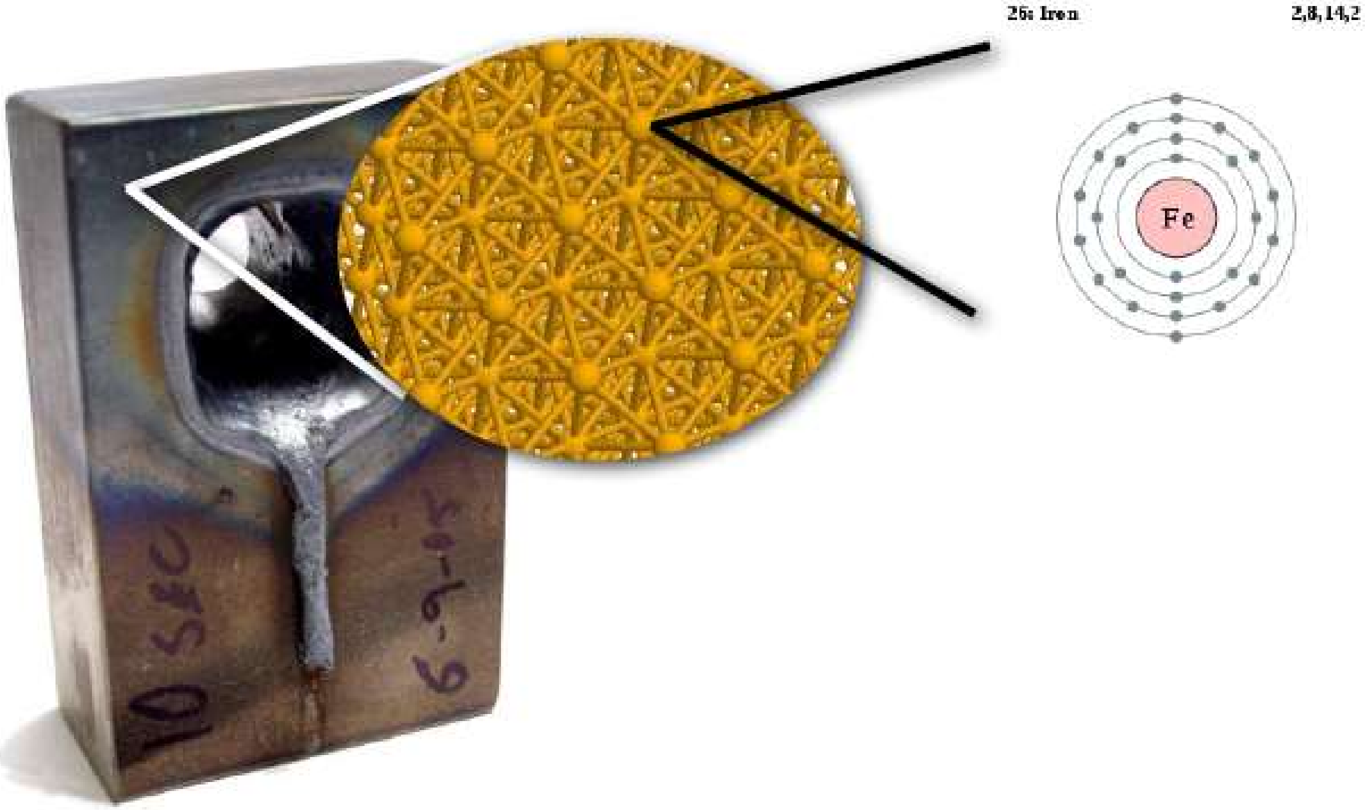
Content

- Introduction to quantum mechanical modeling:
  - Hartree-Fock and Density function theory (DFT)
  - Plane wave based DFT calculations
  - Equilibrium properties and surfaces from DFT calculations
  - Atomistic modeling of defects in materials
  - Applications
- Introduction to Monte Carlo Methods:
  - Kinetic, Lattice, applications.

Motivation

If we understand **electrons, then** we understand ***everything***

A simple iron atom



All materials essentially consist of electrons and nuclear charge.

Due to electron and its interaction with other electrons which results in various mechanical, electronic, magnetic etc. properties.

In order to define electron and their interaction Schrodinger equation is best tool.

If Schrodinger equation of many electron problem can be solved accurately and efficiently then almost any property of the materials can be determined accurately.

Unfortunately there is neither a accurately nor efficient method to solve these problems.

Phase Transformations

- DFT can predict various phase transformations that takes place under mechanical strain.
- Crystal structure changes even when dimension of the system is altered for example ZnO in Wurtzitic in bulk but it is Graphitic in nanowire this can be predicted by DFT;
- Calculating cohesive energy per atom of the system we can predict the phase transformations.
- Phase transformation are determined using X-ray and neutron diffraction.

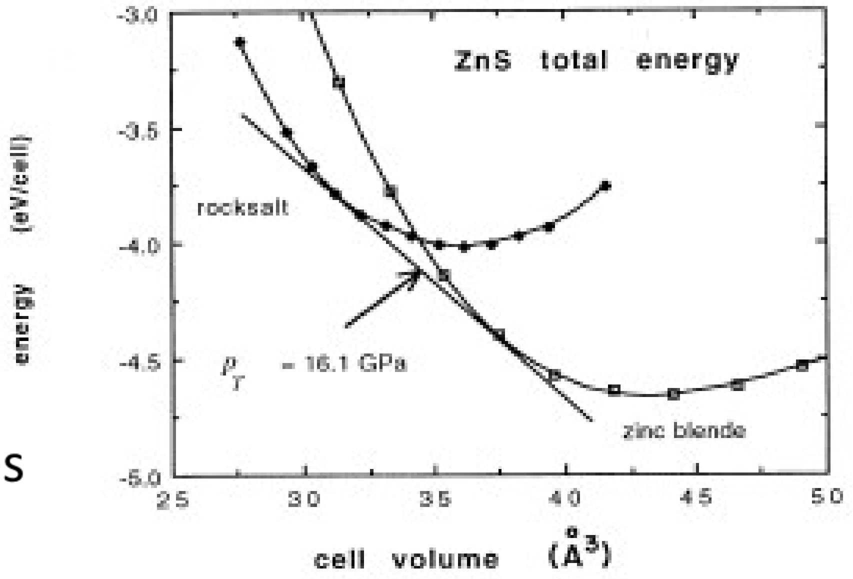
- ZnS exist in the B3 (zinc blende) at equilibrium and B1 (rocksalt) crystal structures at high pressure.
- Transformation takes place when P of both crystal structure is same.
- Now to calculated pressure at what pressure Zinc Blend structure of ZnS changes to rocksalt we use Birch–Murnaghan equation of state that relates pressure to volume and energy.

$$P = -\left(\frac{\partial E}{\partial V}\right)$$

Where P is pressure, E is energy per unit cell, V volume .

Slope of the curve give pressure at various volume of unit cell.

Common tangent to two curves give the pressure of phase transformation since at that point pressure is same for two crystal



Ref: J. E. Jaffe, R. Pandey and M. J. Seel, Ab initio high pressure structural and electronic properties of ZnS, PHYSICAL REVIEW B 47, 6299 (1993)

Thus calculated value of phase transformation is 16.1 Gpa. Experimental value of pressure of phase transformation is 15-18 Gpa

Mechanical properties

- DFT can predict various mechanical properties of given material.
  - Elastic Modulus:
  - Compressibility:
  - Thermal expansion coefficients:
- Experimentally mechanical properties can be determined using tensile test, hardness test (Vicker and Rockwell).
- Thermal expansion can be determined using X-ray diffraction.

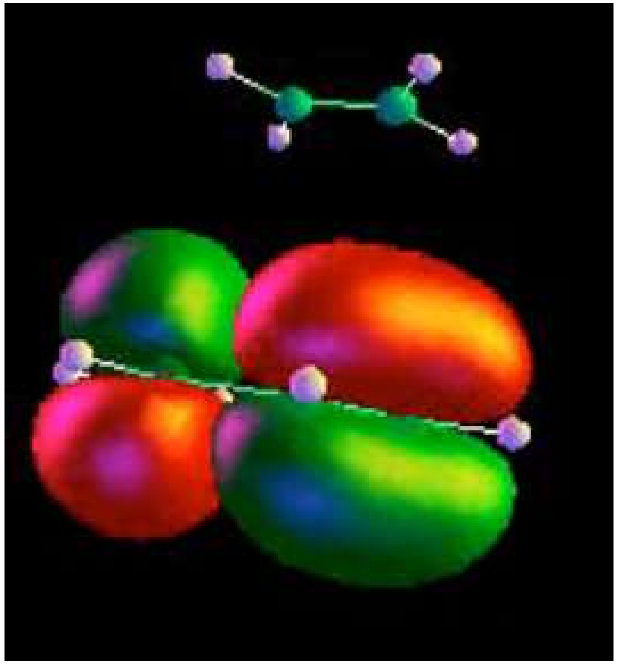
- Phase diagram can be made by finding crystal structure at various composition and temperature.

- Experimentally various alloy composition have to be made and crystal structure should be found.

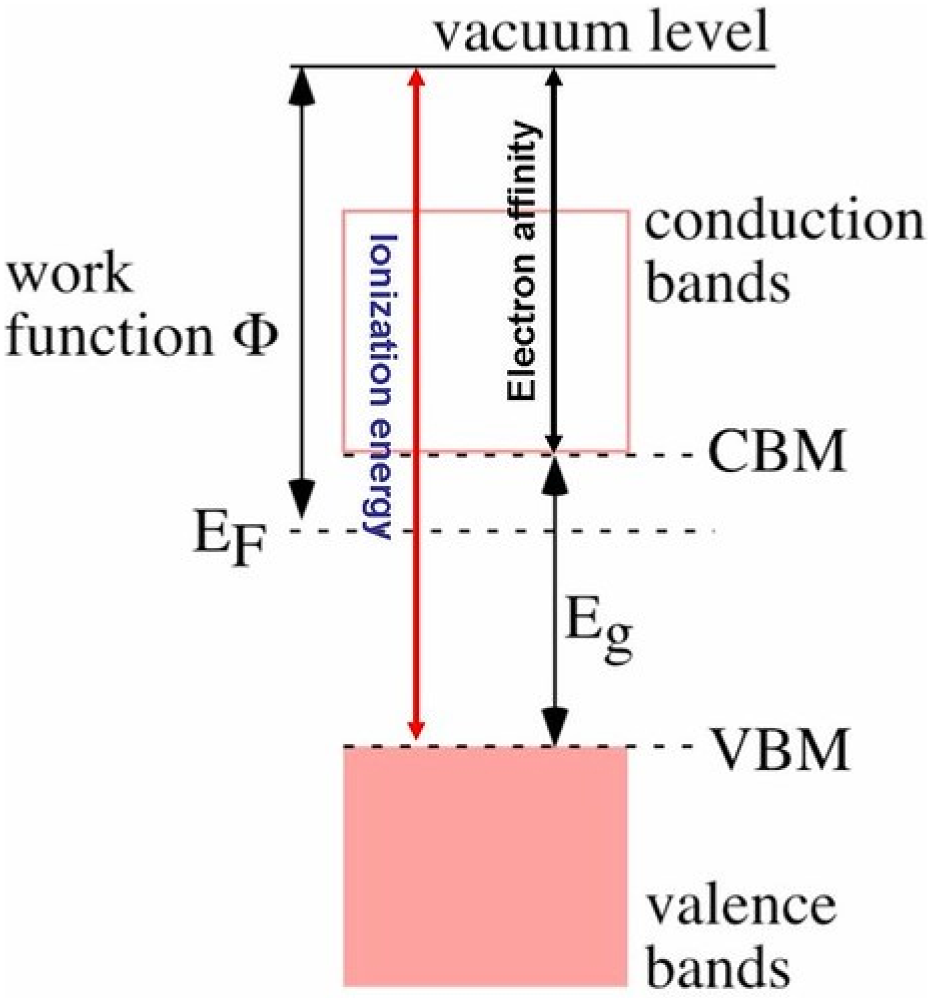
Electronic, Electrical and Optical properties

- Band structure, Dipole moment of molecule, interface, calculated.
- Conductivity of materials can be found.
- Ionization energies and electron affinity can be estimated.
- Optical spectra can be estimated. Luminescence and fluorescence of materials can be found using DFT.

- Band offset can be calculated at hetero-junctions. Band structure can be plotted using technique as Auger effect
- Conductivity can be measured Four-probe method
- Ionization energy and affinity is measured using Low Energy Electron Ionization and Chemical Ionization Mass Spectrometry.
- Band gap, luminescence and fluorescence can be measured using UV-Visible spectroscopy.



1,3-butadiene + ethylene→cyclohexene



Schematic energy diagram in an n-type semiconductor

Ref:http://electrons.wikidot.com/dharma

- Atoms are made by massive, point like nuclei (protons+neutrons)
- Surrounded by tightly bound, rigid shells of core electrons
- Bound together by a glue of valence electrons (gas vs. atomic orbitals)

DFT provides

- Microscopic understanding
- Predictive power
- Minimize experiments
- Challenges:
  - length scale
  - Time scales
  - accuracy

Classical mechanics is based on Newton's law (1687)

$$\vec{F} = \frac{d(m\vec{v})}{dt}$$

The configuration or state of a system is given by a point (x, p) in the space of coordinates and momentum. Everything else of the system determined by function Y(x,v).

In quantum mechanics, the position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision.

$$\Delta x \Delta p > \frac{\hbar}{2}$$

Uncertainty principle

Similarly,

$$\Delta E \Delta t > \frac{\hbar}{2}$$

In quantum mechanics, each particle is represented by a wave function $\Psi(x,t)$. A **wave function** is a mathematical description of the quantum state of an isolated quantum system.

The probability of finding the particle at that position at that time is $\psi * \psi$.

Comparison of classical and quantum harmonic oscillator-GIF image enclosed

Constraints on wave function

The wave function must satisfy certain constrains,

- Must be a solution of the Schrödinger equation,
- Must be normailizable. Implies that the wave function approaches zero as x approaches infinity.
- Must be a continuous function of x.
- The slope of the function in x must be continuous. i.e. $\frac{\partial \psi(x)}{\partial x}$ must be continuous.

Note: these constraints are applied to the boundary conditions on the solutions, and in the process to determine the energy eigenvalues.

The wave function represents the probability amplitude for finding a particle at a given point in space at a given time.

The actual probability of finding the particle is given by the product of the wave function with its complex conjugate.

$\Psi(x,y,z,t)$=probability amplitude

$\Psi^* \Psi$ =probability

$\int \psi^* \psi dr = 1$ → normalization.

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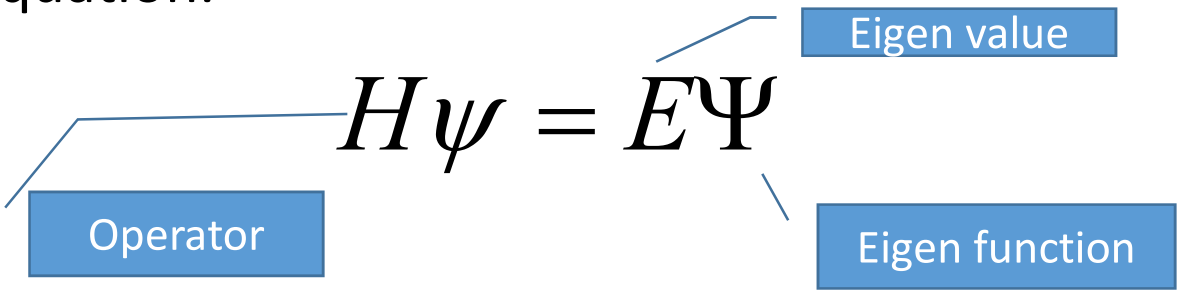
Eigen values and Eigen functions

- The wavefunction for a given physical system contains the measurable information about the system.
- To obtain specific values for physical parameters, for example energy, you operate on the wavefunction with the quantum mechanical operator associated with that parameter.
- The operator associated with energy is the Hamiltonian, and the operation on the wavefunction is the Schrodinger equation.



Eigen value

$$H\psi = E\Psi$$

Operator

Eigen function

This type of equations are called as eigenvalue equation

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SK1 Santhy K, 11-03-2020

$$H\psi = E\Psi$$

Multiply the above equation with complex conjugate of the wave function, then

$$\Psi^* H\psi = \Psi^* E\Psi$$

$$\Psi^* H\psi = E\Psi^*\Psi$$

Integrating and rearranging the equation, we get

$$E = \frac{\int \Psi^* H\Psi dr}{\int \Psi^* \Psi dr}$$

dr is spatial coordinate (x, y, z in a Cartesian coordinates system)

We know that, $\int \Psi^* \Psi dr = 1$

Therefore

$$E = \int \Psi^* H\Psi dr = \left\langle \Psi^* \mid H \mid \Psi \right\rangle$$

The SchrÖdinger Equation

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

$$\hat{H} = \left.\boxed{-\sum_{n} \frac{\hbar}{2M}\nabla_n^2 \; - \; \sum_{i} \frac{\hbar}{2m_e}\nabla_i^2}\right\}\text{KE}$$

$$\left.\boxed{\begin{array}{l} +\dfrac{1}{4\pi\epsilon_0}\dfrac{1}{2}\displaystyle\sum_{n\neq m}\dfrac{Z_n Z_m}{|R_n - R_m|} \\ +\dfrac{1}{4\pi\epsilon_0}\dfrac{1}{2}\displaystyle\sum_{i\neq j}\dfrac{e^2}{|r_i - r_j|} + \dfrac{1}{4\pi\epsilon_0}\displaystyle\sum_{i,n}\dfrac{Z_n e}{|r_i - r_j|} \end{array}}\right\}\text{PE}$$

$$\hat{H} = -\overbrace{\sum_n \frac{\hbar}{2M}\nabla_n^2}^{\hat{T}_R} - \overbrace{\sum_i \frac{\hbar}{2m_e}\nabla_i^2}^{\hat{T}_r}$$

$$+\underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{n\neq m}\frac{Z_nZ_m}{|R_n-R_m|}}_{\hat{V}_R}$$

$$+\underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i-r_j|}}_{\hat{V}_r}+\underbrace{\frac{1}{4\pi\epsilon_0}\sum_{i,n}\frac{Z_n e}{|r_i-r_j|}}_{\hat{V}_{R\ r}}$$

Wave function is a function of coordinates of all electrons and ions with respect to time.

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

$_1, r_2, \ldots . R_1, R_2, ..$

$(\{r_i\}, \{R_i\}, t)$

(r, R, t)

$$\hat{H} = \hat{T}_R + \hat{T}_r + \hat{V}_R + \hat{V}_r + \hat{V}_{R\ r}$$

Density functional theory in a nut shell:
Reduce 3N-dimensional problem
to a 3-dimensional one

Born-Oppenheimer approximation

The nuclei are much heavier than electrons

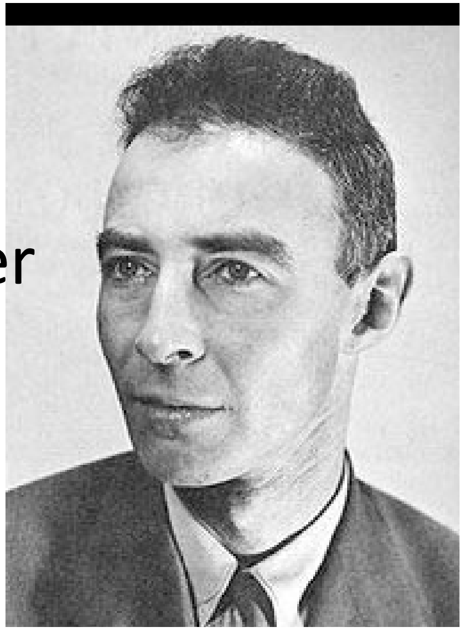
→ they move much more slowly

→ the nuclei can be considered frozen in a single arrangement (molecular conformation)

→ the electrons can respond almost instantaneously to any change in the nuclear position

Born

Oppenheimer



Born-Oppenheimer approximation

$$\hat{H} = \underbrace{-\sum_{n}\frac{\hbar}{2M}\nabla_n^2}_{=0} - \sum_{i}\frac{\hbar}{2m_e}\nabla_i^2$$

$$\underbrace{+\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{n\neq m}\frac{Z_nZ_m}{|R_n - R_m|}}_{=\text{constant}}$$

$$+\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} + \frac{1}{4\pi\epsilon_0}\sum_{i,n}\frac{Z_ne}{|\boldsymbol{R}_n - r_j|}$$

Particle	Relative Mass	Relative Charge	Charge / C	Mass / kg
Protons	**1**	**+ 1**	**$+ 1.6 \times 10^{-19}$**	**1.67×10^{-27}**
Neutrons	**1**	**neutral**	**0**	**1.67×10^{-27}**
Electrons	**0.0005**	**- 1**	**$- 1.6 \times 10^{-19}$**	**9.11×10^{-31}**

$$\hat{H} = \hat{T}_R + \hat{T}_r + \hat{V}_R + \hat{V}_r + \hat{V}_{R,r}$$

Simplified as

$$\hat{H} = \hat{T}_r + \underbrace{\hat{V}_r}_{\text{Also called as Coulomb interaction}} + \underbrace{\hat{V}_{R,r}}_{\text{Also called as external potential}}$$

Wave function

In chemistry, a **molecular orbital** (**MO**) is a mathematical function describing the wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region.

Wave function of H_2 molecule

- GIF image enclosed

When atomic orbitals interact, the resulting molecular orbital can be of three types: bonding, antibonding, or nonbonding.

Bonding MOs:

- Bonding interactions between atomic orbitals are constructive (in-phase) interactions.
- Bonding MOs are lower in energy than the atomic orbitals that combine to produce them.

Antibonding MOs:

- Antibonding interactions between atomic orbitals are destructive (out-of-phase) interactions, with a nodal plane where the wavefunction of the antibonding orbital is zero between the two interacting atoms
- Antibonding MOs are higher in energy than the atomic orbitals that combine to produce them.

Nonbonding MOs:

- Nonbonding MOs are the result of no interaction between atomic orbitals because of lack of compatible symmetries.
- Nonbonding MOs will have the same energy as the atomic orbitals of one of the atoms in the molecule.

Linear Combination of Atomic Orbital-LCAO

The molecular wave function (ψ) is approximated as a linear combination of atomic orbital. i.e. MO are expressed by combining simple function called as basis function. These functions comprise a basis set(ϕ).

Using LCAO approximation,

$$\Psi = c_1\phi_1 + c_2\phi_2$$

Where ϕ_1 and ϕ_2 are basis functions of atoms 1 and 2, c_1 and c_2 are weighting coefficients to be adjusted to get the best ψ.

Variational Principle

- The energy computed from a guessed wave function Ψ is an upper bound to the true ground-state energy E_0. Full minimization of E with respect to all allowed N-electrons wave functions will give the true ground state.

Therefore,
$$E = \frac{\int (c_1\phi_1 + c_2\phi_2)\widehat{H}(c_1\phi_1 + c_2\phi_2)dr}{\int ((c_1\phi_1 + c_2\phi_2))^2 dr}$$

$$E = \frac{c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1c_2S_{12} + c_2^2 S_{22}}$$

where

$$\int \phi_1\widehat{H}\phi_1 dr = H_{11} \qquad \int \phi_1^2 dr = S_{11}$$

$$\int \phi_1\widehat{H}\phi_2 dr = H_{12} = \int \phi_2\widehat{H}\phi_1 dr = H_{21} \qquad \int \phi_2^2 dr = S_{22}$$

$$\int \phi_2\widehat{H}\phi_2 dr = H_{22} \qquad \int \phi_1\phi_2 dr = S_{12} = \int \phi_2\phi_1 dr = S_{21}$$

Therefore , $E_0 < E$

Electrons obey the Pauli exclusion principle and fermi statistics

- Wave function changes sign when the coordinates of two electrons are interchanged
- Wave function is zero if two electrons are in the same state.
- Wave function is written to be an antisymmtrized product (Slater determinant)

The ground state wave function is approximated by a Slater determinant:

$$\Psi(x_{1,}x_2 \ldots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & . & . & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & . & . & \phi_N(x_2) \\ . & . & . & & . \\ . & . & & . & . \\ \phi_1(x_N) & \phi_2(x_N) & . & . & \phi_N(x_N) \end{vmatrix}$$

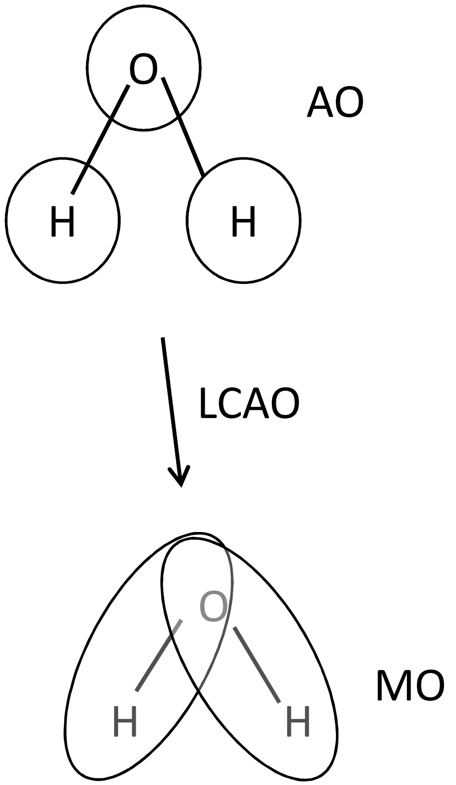
- Minimize the energy with respect to Slater determinant leads to the Hartree-Fock equations

$$[\widehat{T}_i+\widehat{V}_{ion}+\underbrace{\widehat{V}_H}_{\text{Coulomb potential / Hartree potential}}+\underbrace{\widehat{V}_X}_{\text{Exchange potential}}]\phi_i(r)=\varepsilon_i\phi_i(r)$$

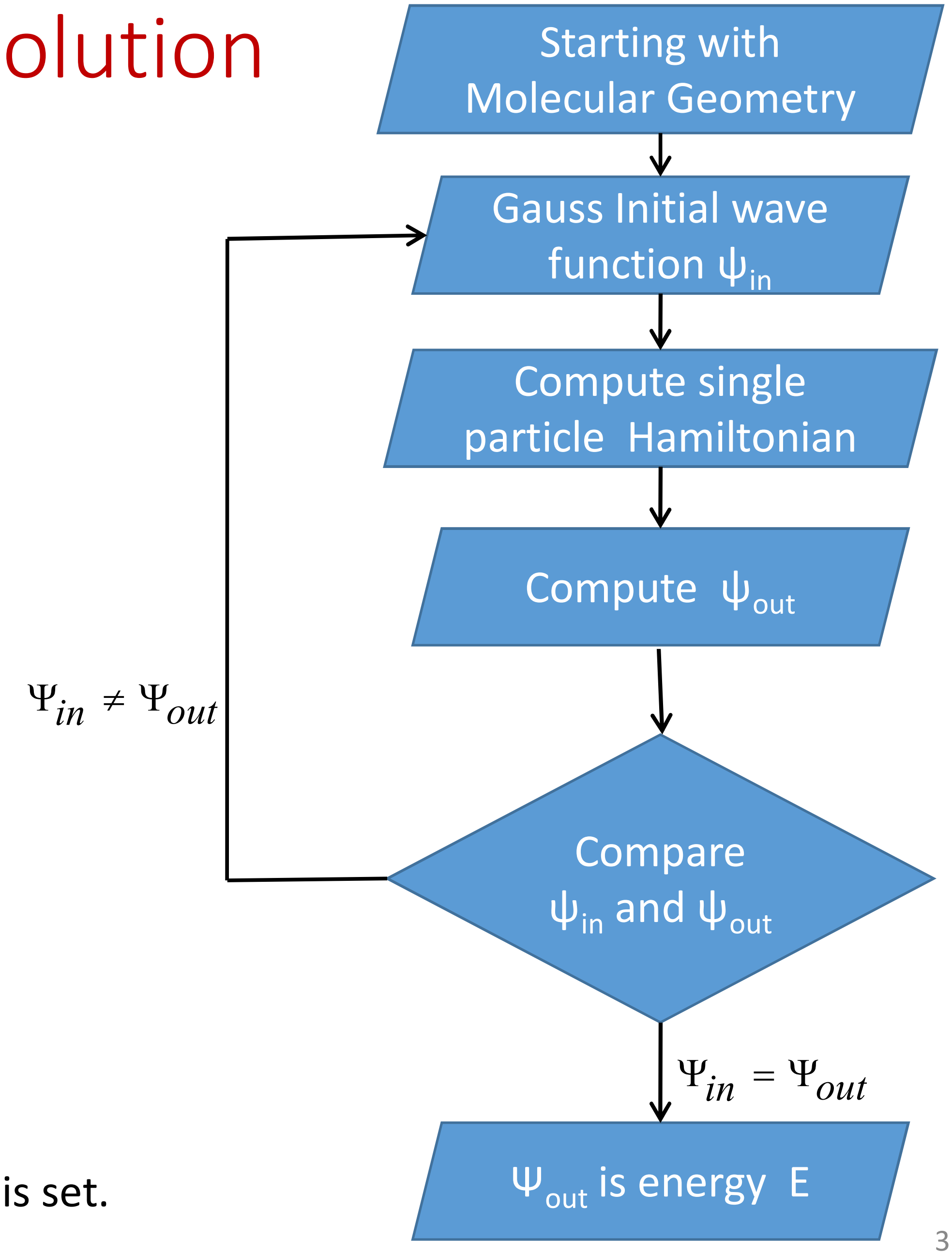
$$\widehat{V}_X=-\frac{1}{2}\left[\sum_j\int\frac{\phi_j^*(r_j)\phi_i(r_j)}{|r_i-r_j|}dr_j\right]\frac{\phi_j(r_i)}{\phi_i(r_i)}$$

- Considering Pauli exclusion principle, Hartree method give rise to an effective potential called exchange interaction.
- Still neglect the correlation effect, so large deviation from the experiment results.

Self-consistent solution



Atomic orbitals are expresses by basis set.



Starting with Molecular Geometry

Gauss Initial wave function ψ_{in}

Compute single particle Hamiltonian

Compute ψ_{out}

Compare ψ_{in} and ψ_{out}

$\Psi_{in} \neq \Psi_{out}$

$\Psi_{in} = \Psi_{out}$

Ψ_{out} is energy E

Hartree Fock Method

- ϕ given by Slater determinant
  - Each electron moves in an average electric field produced by all the other electrons
  - Explicitly $e^- - e^-$ repulsion is not included
- Result:
  - e-/e- repulsion is overestimated
  - Energy results are generally not accurate
- Iterative solution process is time consuming

- produced is often “close enough” that some useful information can be obtained

Limitation of Hartree Fock Method

There are four sources of error in ab initio calculations:

1. The Born-Oppenheimer approximation
2. The use of an incomplete basis set
3. Incomplete correlation
4. The omission of relativistic effects

Additionally time consuming process.

Density Functional Theory (DFT)

- Hohenberg-Kohn-Sham proposed a new approach to the many body interacting electron problem.
- All ground state properties are determined by the ground state density
- Hohenberg-Kohn theorems (1964)
    - Two statements constitute the basis of DFT
    - Do not offer a way of computing in practice
- Kohn-Sham ansatz (1965)
    - Turn DFT into practical method

Hohenberg-Kohn theorem

- Theorem I: density as a basic variable

The ground state energy E of an N-electron system is a functional of the electronic density ***ρ, and E is*** *a minimum when evaluated with the exact ground state density*

- A function whose argument is also a function is called a *functional.*

$\rho \rightarrow \psi \rightarrow r$

- The energy is minimized with respect to variations in ρ, subject to the constraint of charge conservation:

$$N = \int \rho(r)dr \qquad \rho = 2\sum_i \Psi_i^*(r)\Psi_i(r)$$

  - HF-SCF Theory is 4*N dimensional*
  - Electron density is 3*N dimensional (*Get rid of one dimension (spin))
  - Easier to deal with electron density than with wave functions
  - DFT is also an iterative process, as was HF

- Theorem II: Variational for the energy in term of density
- The functional *E[ρ(r)] has its minimum when electron density is* at the equilibrium electron density *n_0(r)*
- The minimum of the energy *E_0 is exactly equivalent to the true* ground-state energy

$$E_0 \equiv \min E\left[\rho(r)\right] \equiv E\left[\rho_0(r)\right]$$

$$[\widehat{T}_i + \widehat{V}_{ion} + \widehat{V}_H + \widehat{V}_{XC}]\rho(r) = E\rho(r)$$

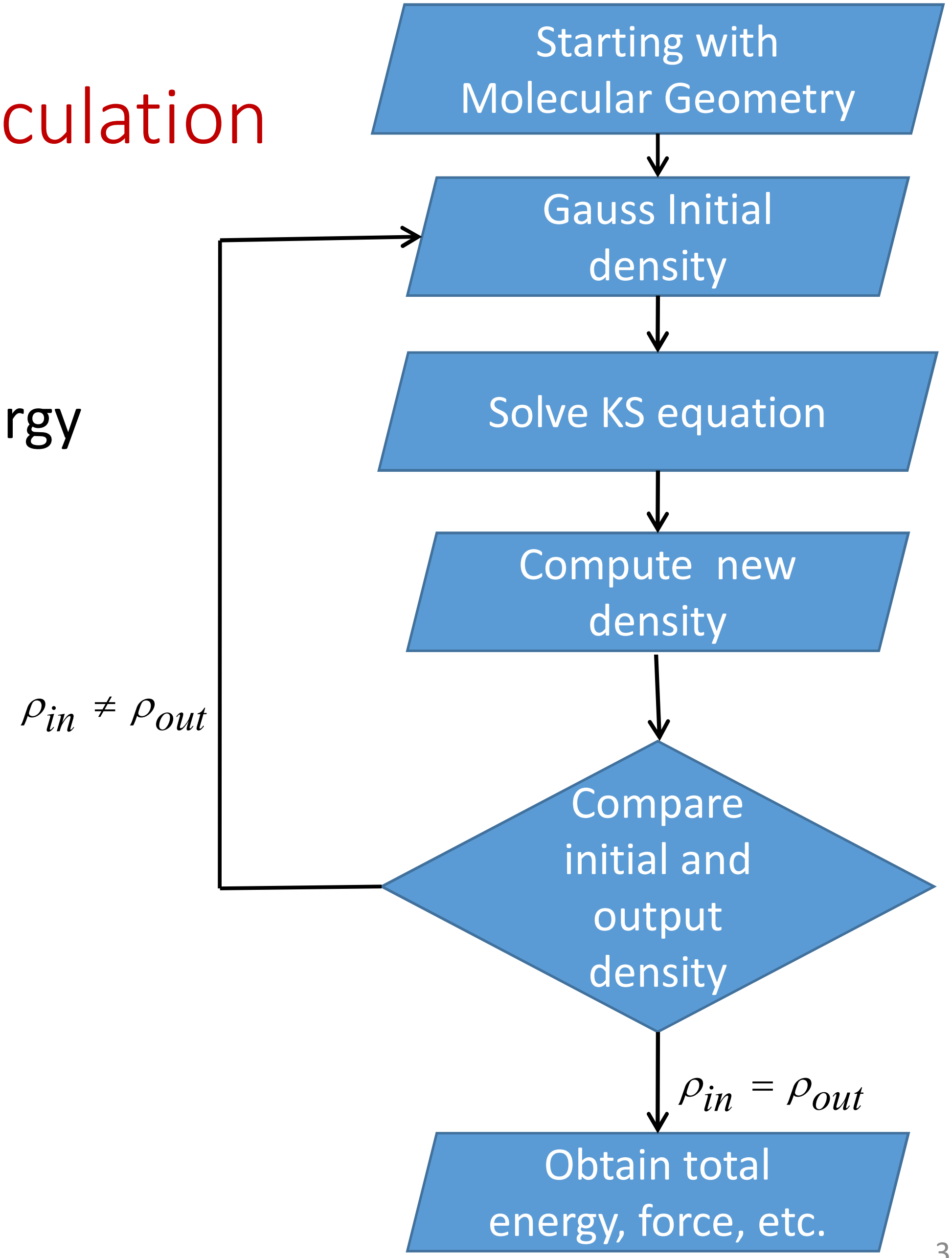
- Exact theory but unknown functional *E_{xc}[ρ]*

- Exchange
  - Keep electrons of same spin away from each other (Pauli exclusion)
- Correlation
  - Keep electrons away from each other due to Coulombic forces
- Finding E_{xc} *functional is the great challenge, but approximate* functionals work:
  - LDA
  - GGA
  - Hybrid functional
  - EXX

Self Consistent Calculation

The output gives,

- Ground state total energy
- Forces acting on atom
- Charge density
- Band structure and density of states



Starting with Molecular Geometry

Gauss Initial density

Solve KS equation

Compute new density

Compare initial and output density

$\rho_{in} \neq \rho_{out}$

$\rho_{in} = \rho_{out}$

Obtain total energy, force, etc.