

## Must-Remember Note – DFT

This note summarizes some DFT concepts and simulation strategies using simple words. It helps you understand and remember the concepts and quickly search the concepts when you do a DFT simulation.

### 1. Schrödinger Equation (Ref: LeSar Ch 4.1)

Schrödinger equation is the basis for all quantum mechanical calculations of the electronic structure of a material. We solve this equation for wavefunction  $\Psi$

$$H\Psi = E\Psi$$

- $H$  – Hamiltonian operator
- $E$  – energy

### 2. DFT – Density Functional Theory (Ref: LeSar Ch4.1.1)

In DFT, energy  $E$  is written as a function of the electronic density  $\rho(r)$ , which is a function of the position, thus the energy is a functional of density.

### 3. Kohn-Sham Method (LeSar Ch 4.4)

Kohn-Sham Method is advanced DFT (It was developed later). This method does two important things:

- Simplify an n-electron (interacting) system to a one-electron (non-interacting) system plus an external energy (i.e. XC energy  $E_{XC}$ ) that includes all the corrections to the approximate total energy.
- Any energy term for the system (e.g. kinetic energy, interaction energy etc.) can be written as functions of electron density.

### 4. XC Functional or XC Energy $E_{XC}$ (XC for Exchange-Correlation) (Ref: LeSar Ch 4.5)

XC Functional or XC Energy  $E_{XC}$  describes the interaction between electrons in a system.

- Consider same- and opposite-spin effects.
- Two types: LDA (Local Density Approximation) and GGA (Generalized Gradient Approximation)
- Crystal structures – Choose LDA; Surface or molecule – Choose GGA.

### 5. Basis Set (LeSar Ch 4.6)

Basis set is used to determine wavefunction  $\Psi$ .

- SIESTA uses a linear combination of atomic orbitals basis set.
- A larger or more complicated basis set leads to a more accurate simulation, but it takes a longer computational time.
- In SIESTA, single zeta (SZ) is a minimum basis set for some quick simulation tests (but not accurate enough).
- Double zeta (DZ) is more accurate, because it considers the radial flexibility of an atomic orbital.
- DZP, P stands for Polarization (electron spin effect). It considers the angular flexibility of an atomic orbital.
- Choosing DZP as a basis set is accurate enough for any simulations.

### 6. Pseudopotential (Ref: LeSar Ch 4.7)

Pseudopotential describes the interactions of the valence electrons with the core region including nuclei and electrons very close to the nuclei.

### 7. k-Point Sampling (June Gunn Lee's book "Computational Materials Science: An Introduction" pp161 – 169)

Generate a grid of k-points spaced evenly throughout the Brillouin Zone (or along each reciprocal lattice vector).

- Any crystal structure can be represented in two spaces: real space (primitive cell or unit cell in  $x, y, z$ ) and reciprocal space (Brillouin Zone in  $k_x, k_y, k_z$ ).
- Many physical properties of crystals as well as the geometry of the three-dimensional patterns resulting from a diffraction event (e.g. X-ray diffraction) are represented using the reciprocal lattice.
- Diffraction occurs in inverse proportion to the spacing between objects causing diffraction.
- Any point in the Brillouin Zone can represent a  $k$ -point, there are an infinite number of discrete  $k$ -vectors well qualified to be a wave function.
- The wave function and other properties (e.g. band structure) vary smoothly over the Brillouin Zone, so we can just sample a finite number of  $k$ -points that represent each small region.
- Each  $k$ -point contains rich information: Wave length ( $\lambda=2\pi/k$ ), and kinetic energy ( $E = k^2/2$ ); All the incoming energies on each  $k$ -point, it will form band structure.
- More  $k$  points lead to a more accurate simulation, but it costs more computational time.

### 8. Mesh Cutoff

In SIESTA, mesh cutoff is an energy (default 100 Ry), which corresponds to a finite 3D grid for the calculation of electron density  $\rho(r)$  and potentials. Note that electron density is a function of position. We need to define the spacing of this 3D grid to map the electron density.

- Larger mesh cutoff  $\Rightarrow$  smaller spacing  $\Rightarrow$  more dense 3D mesh  $\Rightarrow$  more accurate simulation but longer computational time.

### 9. DFT Simulation Procedure

Whatever materials or properties you would want to study using DFT simulations, you need to do the three steps below:

- Step 1: Optimize  $k$ -point density, mesh cutoff, basis set, and XC functional. Find the lowest total energy of a system.
- Step 2: Using the optimized parameters, run geometry optimization (i.e. select "geometry optimization" for the "Run type" in SIESTA).
- Step 3: Using the optimized parameters but increasing  $k$ -point density (at least twice or more), run electronic band structure calculation to determine if the material is a semiconductor, metal or insulator with the band gap size.