Experiment No:03

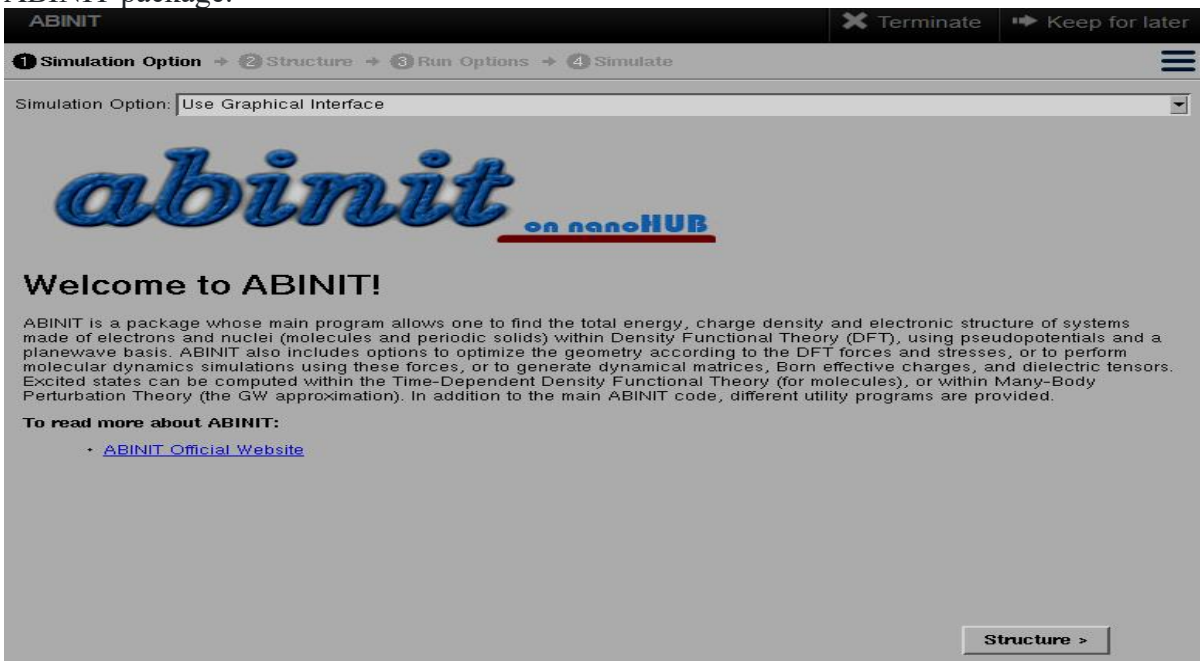
To study the effect of density functional theory calculations parameters like K points, energy cutoff etc. on the calculated physical properties.

Abstract

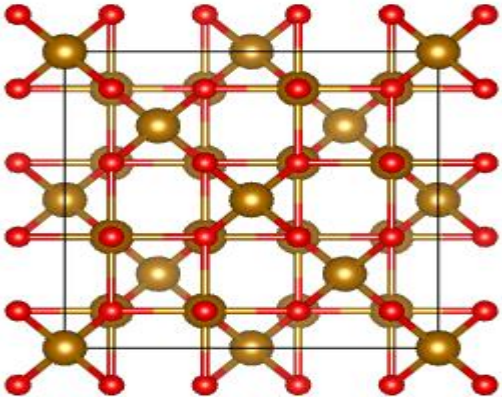
Density Functional Theory (DFT) calculations were performed to investigate the impact of computational parameters on the physical properties of Iron Oxide **(ii/iii)** (Magnetite Fe3O4).Systematically varied k-points grids (2*2*2) to (6*6*6) energy cutoff values (90-360ev) to hartree and exchange correlation functionals (LDA) to assess their influence on bandstructure and dielectric constant. Results shows that increasing k-points density and energy cutoff improves covergence, while the choice of exchange- correlation functionals significantly affects the calculated bandstructures.

Introduction:

ABINIT is a package whose main program allows one to find the total energy, charge density, electronic structure and many other properties of systems made of electrons and nuclei, (molecules and periodic solids) within Density Functional Theory (DFT), Many-Body Perturbation Theory (GW approximation and Bethe Salpeter equation) and Dynamical Mean Field Theory (DMFT). ABINIT also allows to optimize the geometry according to the DFT forces and stresses, to perform molecular dynamics simulations using these forces, and to generate dynamical matrices, Born effective charges and dielectric tensors. The present paper aims to describe the new capabilities of ABINIT that have been developed since 2009. It covers both physical and technical developments inside the ABINIT code, as well as developments provided within ABINIT package.



Physical Properties of (Fe3O4):



Fe3O4 occurs as a mineral with a chemical name Iron (II, III) oxide. It is also known as Magnetite or Magnetic oxide. It is stone iron-like, brownish to grey or black in colour. It is not transparent and has a characteristic greasy or metallic lustre.

3Fe(OH)2 → Fe3O4 + H2 +2H2O

Molecular Weight/ Molar Mass	231.533 g/mol
Density	5 g/cm³
Boiling Point	2,623°C
Melting Point	1,597°C

DFT properties of Fe3O4:

Title Fe3 O4

Lattice type F
Space group name F d -3 m
Space group number 227
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
8.38400	8.38400	8.38400	90.0000	90.0000	90.0000

File type: XYZ

Coordinates type: Cartesian coordinates in angstroms

Scaling factor (x,y,z in bohrs): 15,15,15

Primitive lattice vectors:

a: 1, 0, 0 b: 0, 1, 0 c: 0, 0, 1

K-point setup: user defined array of k-points

Parameters:

No. of k-points; 2

K-points: (1, 2, 3)

K-point normalization: 1

Weights of k-points: 2.0do

Driver Parameters:

Exchange Correlation Functionls: LDA

Plane wave cutoff energy (har): 90

Dielectric constant: 12.0

Self consistent field (SCF) iterations

Self consistent algorithm: pulay mixing of density

Number of pulay iterations for SC mixing: 5

Convergence criterion for SCF iterations: Tolerance on difference of total energy

Parameters for SCF iterations

Number of self consistent iterations: 25

Target energy change (har): 1.0e -10

Band structure definitions

Band ranges to plot: (16, 36)

k- path specified by k points boundries: (0, 0, 0) (0.5, 0.5, 0.5)

Divison along k path between boundries: 3

Post processing

Wavefunction to visualize: (1, 1, 1) (1, 1, 2)

Execution via MPI:

Number of cores: 4

Hours: 1.0

k- Points in DFT:

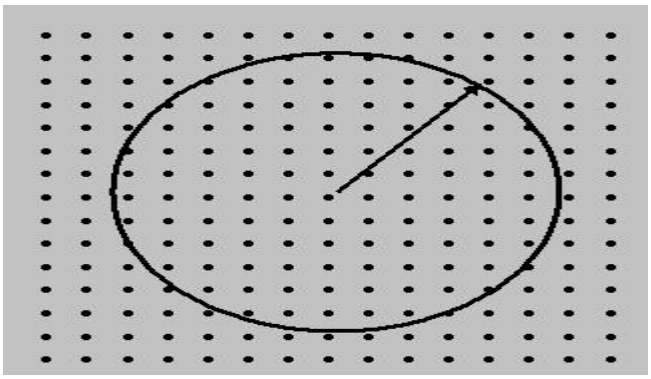
K-point sampling is a technique used in electronic structure calculations, particularly in the context of periodic systems like crystals. These calculations are often based on methods such as density functional theory (DFT) and are used to study the electronic properties of materials

```
Point     Cartesian coordinates     Fractional coordinates
              (units of 2pi/a)              (units of b1,b2,b3)
-----------------------------------------------------------
 Γ          (  0    0    0  )              (  0    0    0  )
 X          (  0    0    1  )              ( 1/2  1/2   0  )
 W          ( 1/2   0    1  )              ( 1/2  3/4  1/4 )
 K          ( 3/4  3/4   0  )              ( 3/8  3/8  3/4 )
 L          ( 1/2  1/2  1/2 )              ( 1/2  1/2  1/2 )
 k points along high symmetry lines
 40            ! number of points per line
line mode
fractional
 0    0    0    Γ
 0.5  0.5  0    X
 0.5  0.5  0    X
 0.5  0.75 0.25 W
 0.5  0.75 0.25 W
 0    0    0    Γ
```

Cutoff- energies in DFT:

The cutoff energy tells us about the cutoff on the number of plane wave functions being utilized as basis functions to represent the wavefunction. Theoretically, an infinite number of basis functions is required to produce an exact answer. In the case of the plane-wave representation, the energy cut-off is the kinetic energy of the

plane wave with highest plane-wave vector. The longer this cut-off is, the more waves will be used to represent the orbitals, the more accurate the description of the system will be



$$E_{cut} = \frac{1}{2}G_{max}^2$$

Materials and Methods:

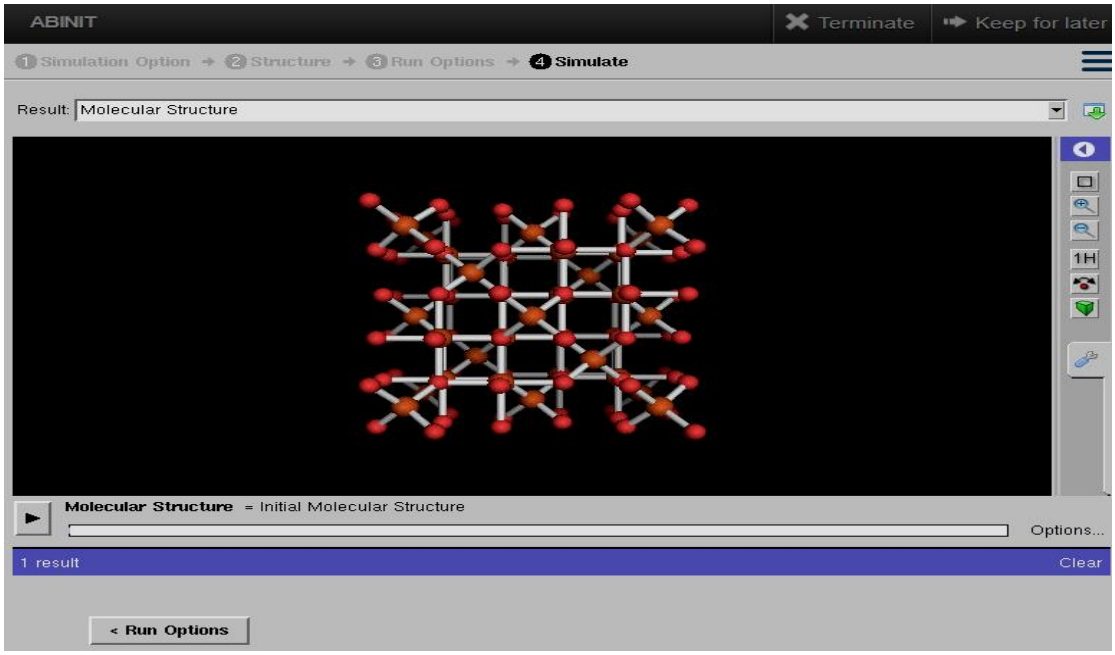
- XYZ file of Fe3O4
- VESTA software for conversion of CIF file into XYZ file
- Laptop or computer

Methods:

- I launch the **ABINIT** software for DFT calculations.
- Then, open a XYZ file of Fe3O4 (Magnetite) generate from **VESTA** software in ABINIT software for input.
- I determined the Fe3O4 space group and lattice parameters from cif file used in VESTA software.
- Then I, provide specific values of Fe3O4 to ABINIT software for taking output.
- Firstly I open structure in menu bar of ABINIT software then change the values of all parameters which are present in this menu.
- Then I, open the driver parameters and give the suitable values of plane wave cutoff energy, dielectric constant, no. of pulay iterations and No. Of self consistent (SC) iterations.

- Similarly I provide all suitable values for all parameters present in Bandstrcture menu, post processing menu and then Run options.
- Then, I simulate all input through simulate option in the menu bar of the software
- Finally I determined the output results of Fe3O4 for DFT calculations especially cutoff energy and K-points
- I used LDA functional and collect the data for 4 simulations, then compare with available literature of SiO2.
- I also draw a graph between cutoff energy values and k-points values.

Lab view:

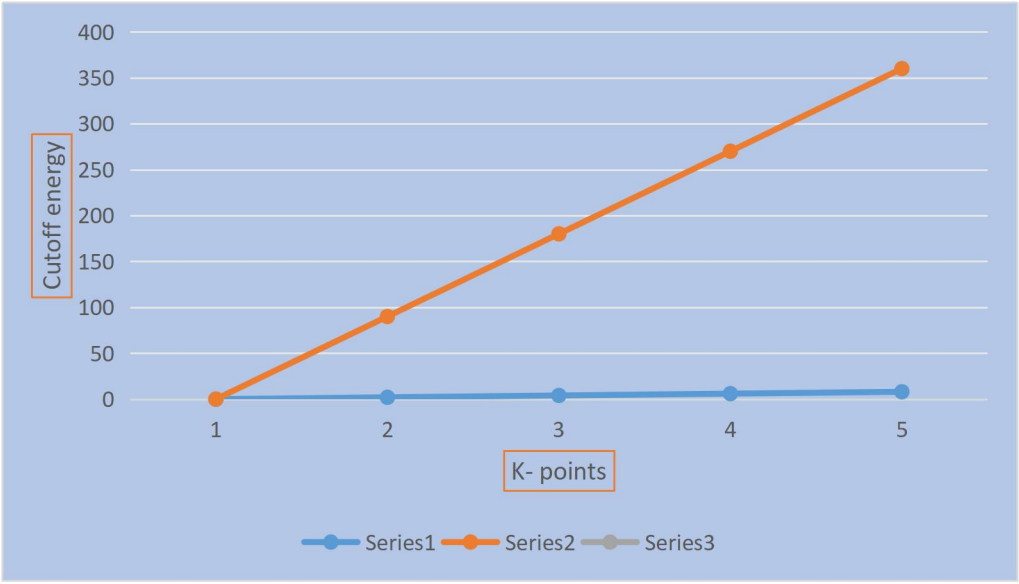


Observations:

Exchange correlation functional: LDA

Sr #	K- points	Cutoff- energies
1	2	90
2	4	180
3	6	270
4	8	360

Analysis



OUTPUT

Number of Data Sets (ndtset): 2

Definition of the unit cell
a cellscaling factor: 15 15 15
Primitive lattice vectors: 1 0 0 0 1 0 0 01

Definition of the atom types
No of totak K-points (typat): 2
Z- nuclei: 26 8

Convergence criterion for scf iterations (xc): 1
Definition of the atoms
No of atoms : 130

Definition of the planewave basis set
Total cutoff energy: 90

Definition of the SCF procedure
No of self consistent iterations (nstep): 25
toldfe1 1.0e-10
Dielectric constant of (diemac): 12.0
Usual self-consistent calculation
K-Path optimization (kptopt): 1 1
PrintTotal density (prtden): 1 1

Bandstructure Calculations
Iterarations for Self consistent field (iscf): 2 -2
Density (getden): 2 -1
K- Path optimization (kptopt) 2 -1

Print total volume (prtvol): 2 3
No of bands (nband): 2 36
K path specified by K points boundries (kptbounds): 2 0 0
0.5 0.5 0.5

Divisions along k path (ndivk): 2 3
Target wavefunction squared residual (tolwfr): 2 1.0d-12
Target Energy in hartree (enunit): 2 1

Conclusions:

This analysis investigated the effects of density functional theory (DFT) calculation parameters on the physical properties of Fe3O4. By changing the k- grid points of Fe3O4 ,cutoff energy varies linearly. .

Reference

- [1] phys.Rev. B85, 174416 (2012) - Fe3O4 bulk, 2*2*2, 90Ry
- [2] J. Phys: Condense. Matter 24, 266004 (2012) - Fe3O4 surface, 4*4*4, 180Ry
- [3] Phys. Rev. B91, 245115 (2015) - Fe3O4 bulk, 6*6*6, 270Ry.