Computational Material Science
Part II-1: introduction

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Outline

- Introduction of Computational Material Science (CMS)
- Density Functional Theory (DFT) and local-density approximation (LDA)
- Crystal structure, reciprocal lattice, and Brillouin Zone
- Band theory, band structure, k-points sampling, and density of state
- Plane wave, pseudopotential, LDA, and LSDA
- Transition-metal oxides, strong correlations, and LDA+U method
- Structure optimization
- Surface and molecule

Hands-on during the lectures

- unix or linux: operating systems
- VASP (Vienna Ab-initio Simulation Package): perform first-principles calculations
- Xmgrace (or gnuplot): plot the calculated density of states and band structures
- Vaspview: visualize the lattice structure, charge distribution, and spin density

References

- “Local Density Theory of Polarizability”, G. D. Mahan and K. R. Subbaswamy (1990).
- “Handbook of The Band Structure of Elemental Solids”, D. A. Papaconstantopoulos (1986).
- “Strong Coulomb Correlations in Electronic Structure Calculations”, V. I. Anisimov (2000)
- http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html

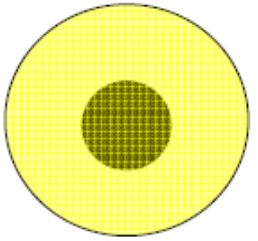
Review of CMS

- Atomic and electronic structure of solids
- Theoretical considerations
- Applications: ground state property calculations
- First-principles study on novel and nano materials
- limitations

Theoretical considerations

Ab-initio calculation = First-principles study
⇨ based on quantum mechanics

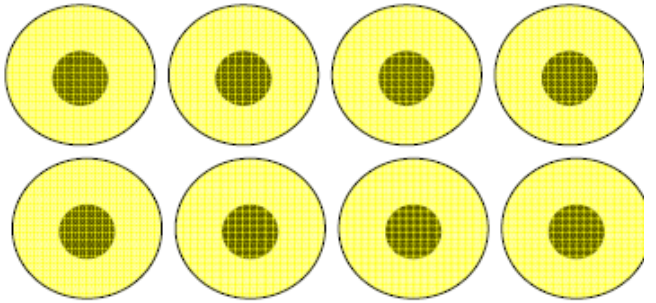
Simple example:
Schrodinger eqn. for 1 hydrogen atom



$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

$$\xrightarrow[\psi(r)=R(r)Y(\theta,\varphi)]{V(r)=-\frac{Ze^2}{r}}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}-\frac{\hbar^2 l(l+1)}{2\mu r^2}\right)\right]R(r)=0$$

Real solids



$$\textit{Ions}: \quad \left(\left\{\vec{R}_I\right\},\left\{\vec{P}_I\right\},\left\{Z_I\right\},\left\{M_I\right\}\right)$$

$$\textit{electrons}: \left(\left\{\vec{r}_i\right\},\left\{\vec{p}_i\right\},m\right)$$

$$H=\sum_{I=1}^{N}\frac{\vec{P}_I^{\,2}}{2M_I}+\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{i>j}\frac{e^2}{\left|\vec{r}_i-\vec{r}_j\right|}+\sum_{I>J}\frac{Z_I Z_J e^2}{\left|\vec{R}_I-\vec{R}_J\right|}-\sum_{I,i}\frac{Z_I e^2}{\left|\vec{R}_I-\vec{r}_i\right|}$$

$$=T_N+T_e+V_{ee}\left(\vec{r}\right)+V_{NN}\left(\vec{R}\right)+V_{Ne}\left(\vec{r},\vec{R}\right)$$

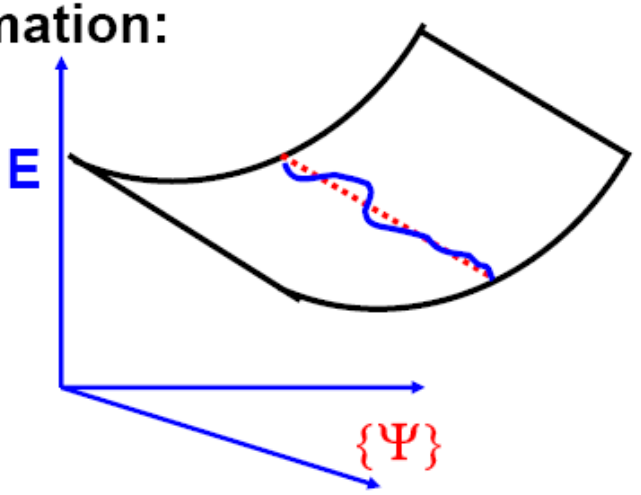
$$\Rightarrow\left[T_N+T_e+V_{ee}\left(\vec{r}\right)+V_{NN}\left(\vec{R}\right)+V_{Ne}\left(\vec{r},\vec{R}\right)\right]\Psi\left(x,\vec{R}\right)=E\Psi\left(x,\vec{R}\right)$$

$$x\equiv\left(\vec{r},s\right)$$

Adiabatic approximation

Born-Oppenheimer approximation:

Decupling I and *e* ($M_I >> m_e$)



$$\Psi\left(x,\vec{R}\right)=\psi\left(x,\vec{R}\right)\varphi\left(\vec{R}\right)$$

$$\begin{cases}\left[T_e+V_{ee}\left(\vec{r}\right)+V_{Ne}\left(\vec{r},\vec{R}\right)\right]\psi_n\left(x,\vec{R}\right)=\varepsilon_n\left(\vec{R}\right)\psi_n\left(x,\vec{R}\right)\\ \left[T_N+V_{NN}\left(\vec{R}\right)+\varepsilon\left(\vec{R}\right)\right]\varphi\left(\vec{R}\right)=E\varphi\left(\vec{R}\right)\end{cases}$$

Independent-particle approximation: Hartree-Fock method

- Many-electron wavefunctions = Slater-determinants

$$\Psi^a_{\alpha_1 \ldots \alpha_N}(q_1, \ldots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\alpha_1}(q_1) & \cdots & \phi_{\alpha_1}(q_N) \\ \vdots & & \vdots \\ \phi_{\alpha_N}(q_1) & \cdots & \phi_{\alpha_N}(q_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \phi_{\alpha_1}(q_1) \cdots \phi_{\alpha_N}(q_N)$$

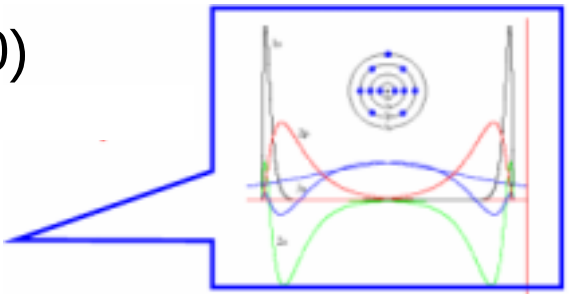
- Variational condition

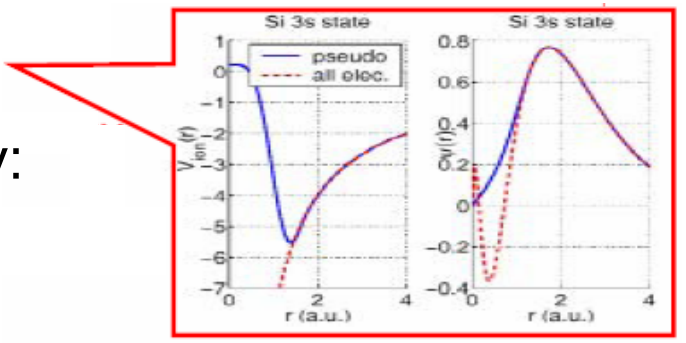
$$\delta \frac{\langle \Psi^a \mid H \mid \Psi^a \rangle}{\langle \Psi^a \mid \Psi^a \rangle} = 0$$

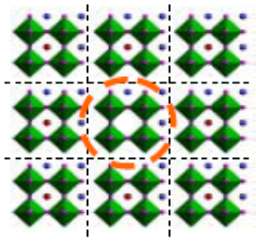
Variation with respect to the one-electron orbitals ϕ_α

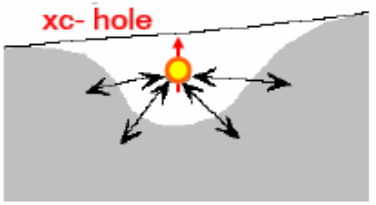
Key ideas (approximations)

- Periodic boundary condition:
  # of atom: O(10^{23}) -> O(10~1000)
- Density functional theory:
  Ψj(r) -> n(r)
- Plane wave vs atomic orbital
- All-electron vs pseudopotential:
  # of e in an atom:
  O(10~100) -> O(1~10)
- Exchange-correlation (xc) energy:
  mimic many-body effects





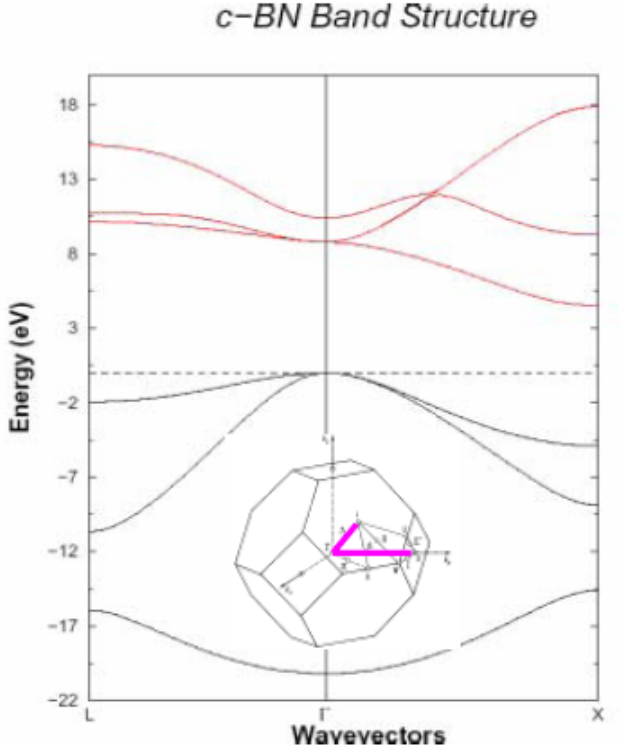


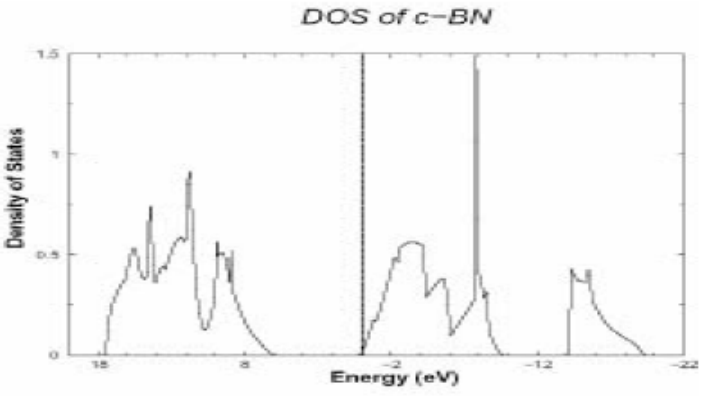


Applications to versatile materials

Band structure and density of state

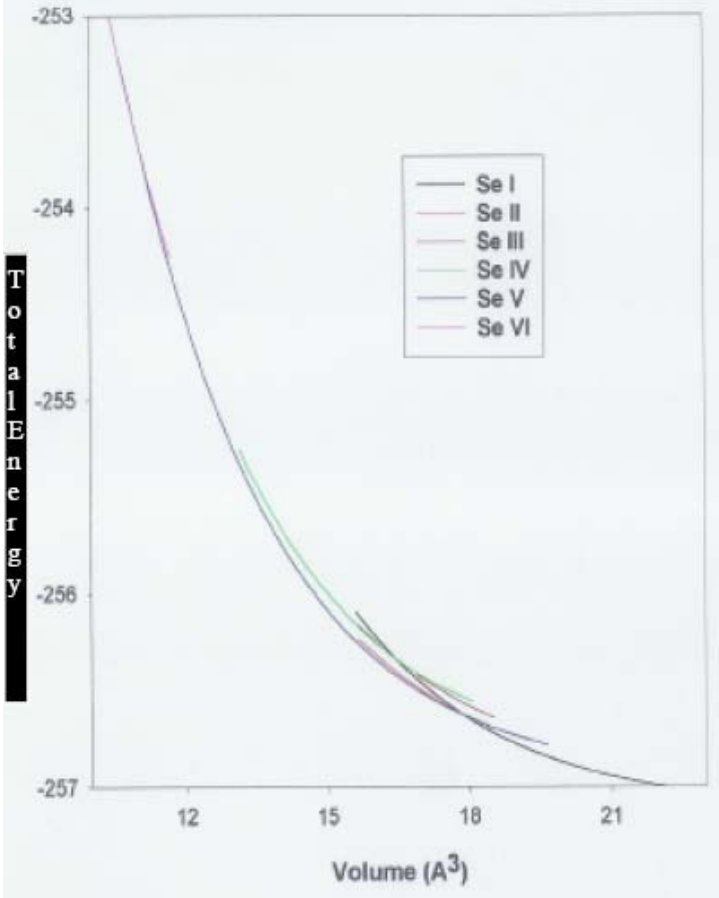
Electronic structures of semiconductors

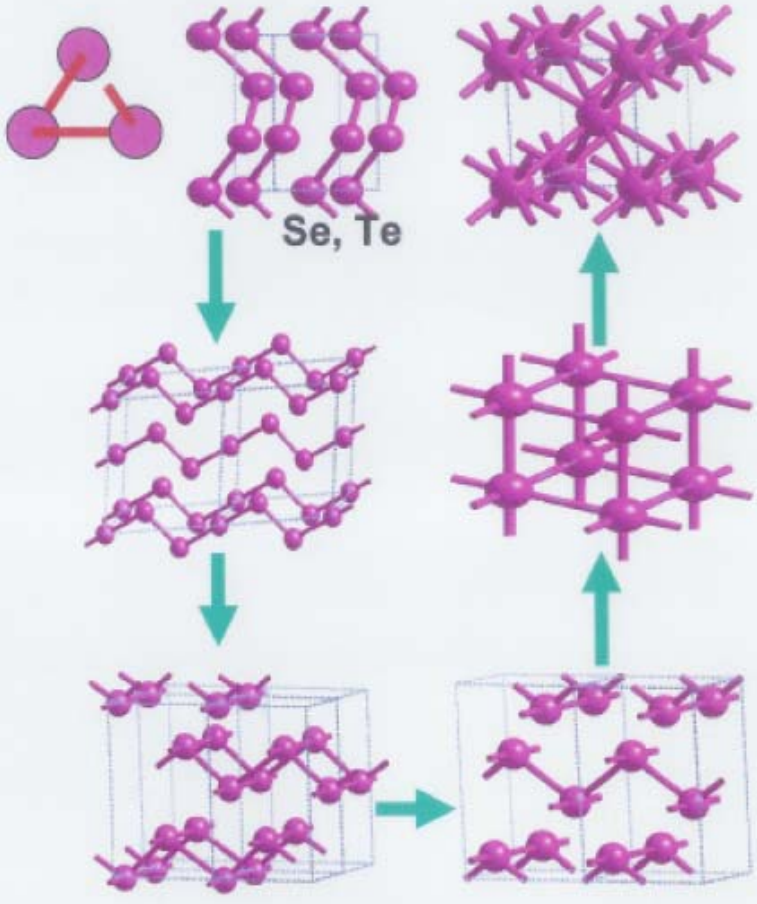




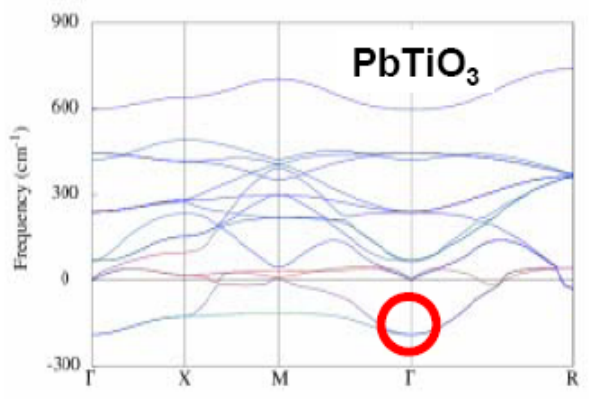
F-43m	a_0 (A)	B_0(GPa)	B_0'
LDA (GGA)	3.57 (3.62)	376.71 (365.43)	3.68 (3.49)
Expt.	3.62	369-400	4.0

Phase transitions in Se & Te under compression

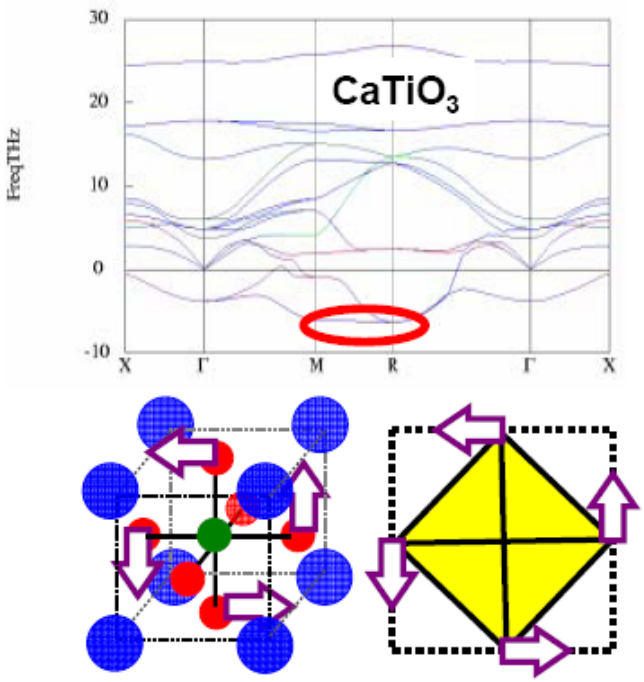




Phonon/Structural instability & ferroelectricity in perovskites:
Density Functional Perturbation Theory (linear response)



Cubic ➡ Tetragonal



Cubic ➡ Orthorhombic

Charge and spin density distribution

Jeng et al PRB (2003)

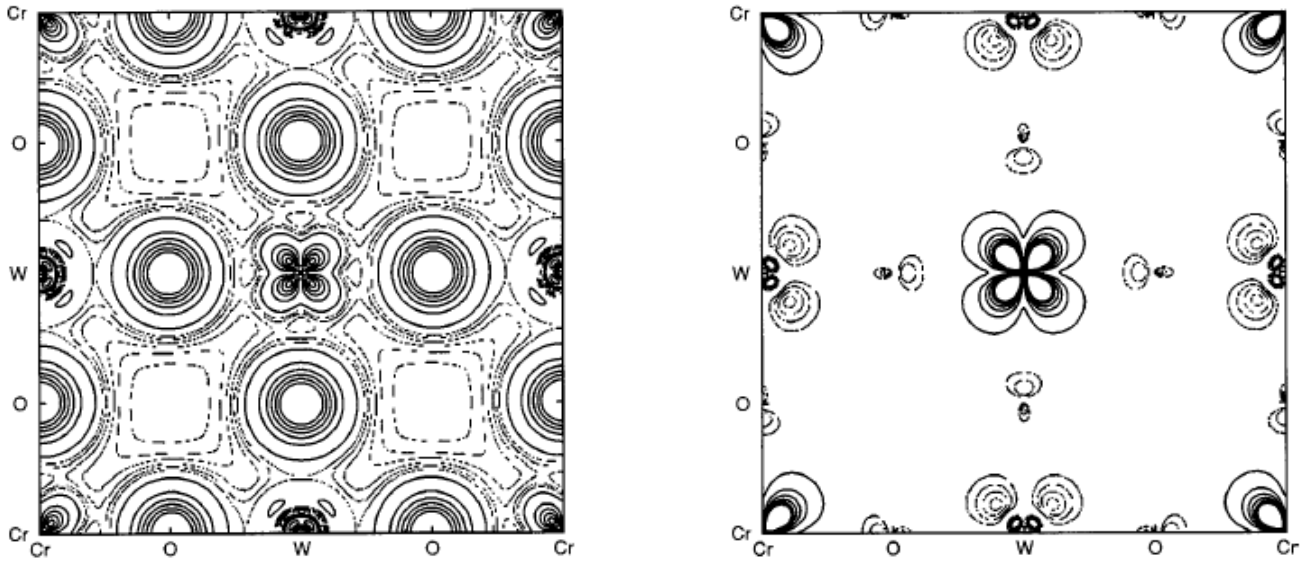


FIG. 4. Valence charge (upper panel) and spin (lower panel) densities of Sr_2CrWO_6 from the GGA. In the upper panel, the contours are along equal charge density lines from 0.015 to $0.065/a_0^3$ (broken lines) with step $0.01/a_0^3$, and from 0.1 to $0.85/a_0^3$ (solid lines) with step $0.15/a_0^3$. In the lower panel, they are from -0.005 to $-0.03/a_0^3$ (broken lines) with step $-0.005/a_0^3$, and from 0.01 to $0.16/a_0^3$ (solid lines) with step $0.03/a_0^3$.

Magnetocrystalline anisotropy

Jeng et al PRB (2002)

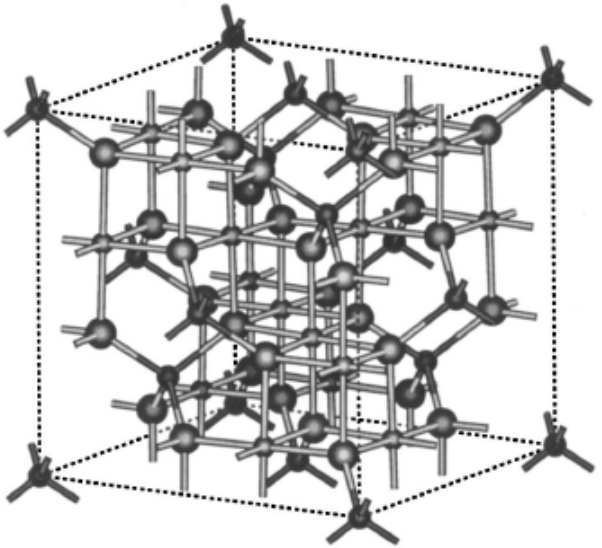


FIG. 1. Crystal structure of Fe_3O_4. Big balls denote oxygen atoms, small dark balls denote *A*-site (tetrahedral) iron atoms, and small light balls denote *B*-site (octahedral) iron atoms.

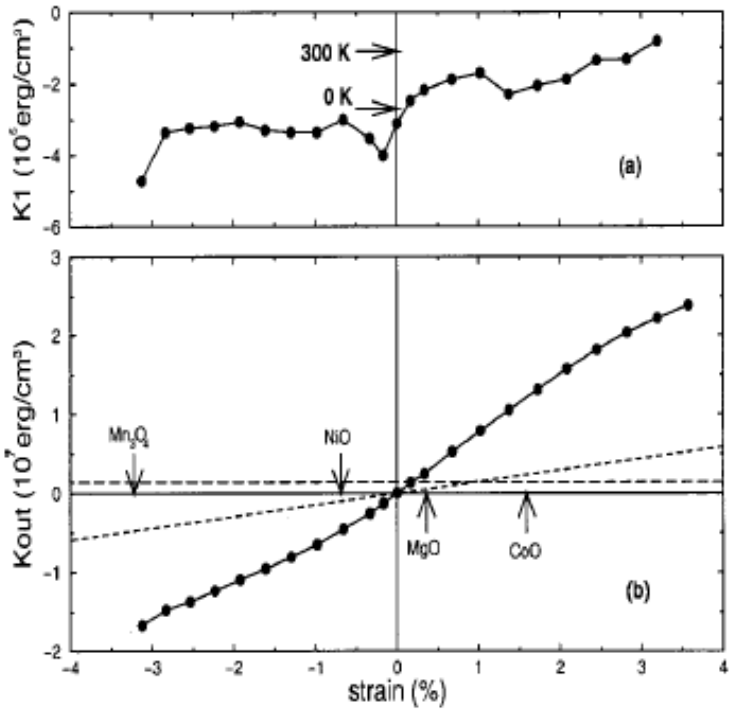
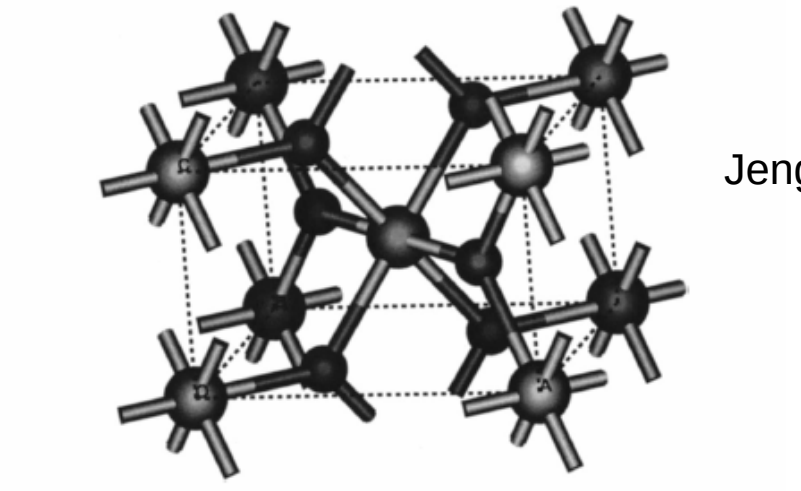


FIG. 8. The fourth-order anisotropy constant K_1 (a) and the out-of-plane anisotropy constant K_{out} (b) as a function of the lateral strain in the (001) plane of Fe_3O_4. The lines are a guide to the eye only. The arrows in (a) indicate the experimental K_1 value at 300 K and 0 K (see text). The arrows in (b) indicate the possible strain values if an Fe_3O_4 film is grown on Mn_3O_4, NiO, MgO, and CoO substrates, respectively.

Spin and orbital magnetic moment



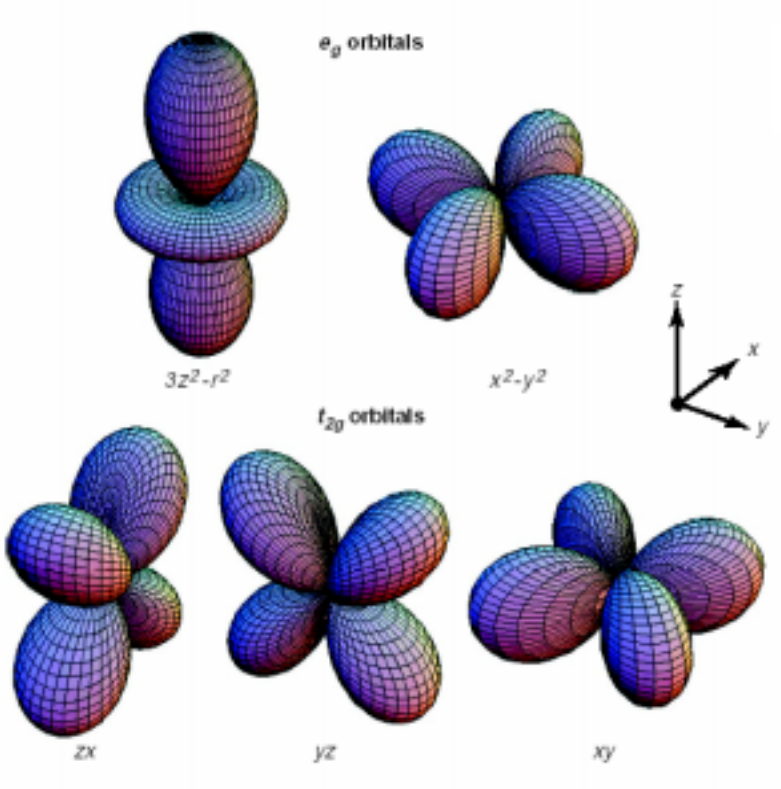
Jeng et al JAP (2002)

FIG. 1. Rutile structure of CrO_2. Big light balls denote Cr atoms and small dark balls denote O atoms.

TABLE II. Calcul and O in CrO_2 from the LSDA ($U=J=0$ eV) and from the LSDA+U. The on-site Coulomb energy U is in units of eV and the exchange parameter $J=0.87$ eV.

	Cr			O		
U (eV)	spin (μ_B)	Orbital (μ_B)	L/S (%)	spin (μ_B)	Orbital (μ_B)	L/S (%)
0	1.89	−0.037	−2.0	−0.042	−0.0011	2.6
2	1.94	−0.046	−2.4	−0.058	−0.0019	3.2
3	1.99	−0.051	−2.6	−0.079	−0.0025	3.2
4	2.03	−0.056	−2.8	−0.094	−0.0030	3.2
6	2.08	−0.067	−3.2	−0.111	−0.0040	3.6
9	2.12	−0.083	−3.9	−0.124	−0.0047	3.8

Projected density of state



Jeng et al PRB (2005)

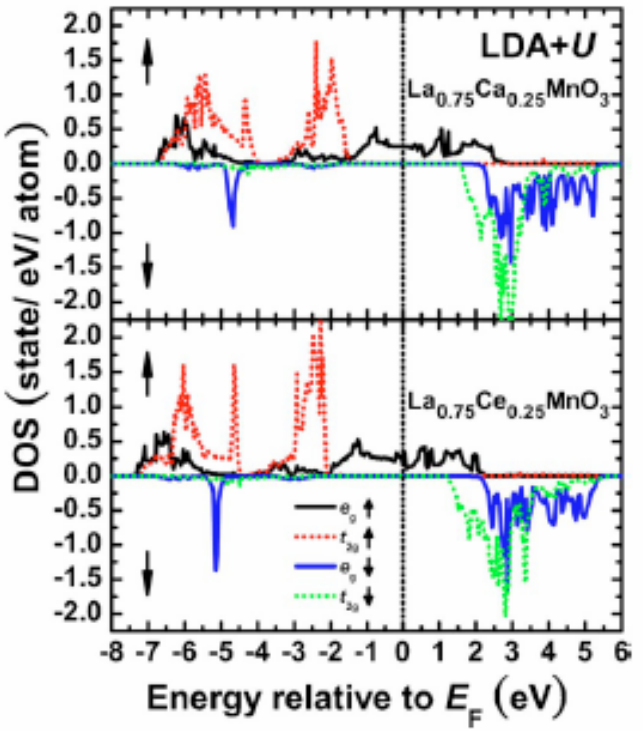


FIG. 2. (Color online) DOS of Mn 3*d* in LCaMO and LCeMO calculated by LDA+*U* method. The parameters used in these calculations are described in the text.

Magnetic orbital distribution

Jeng et al PRL (2004)

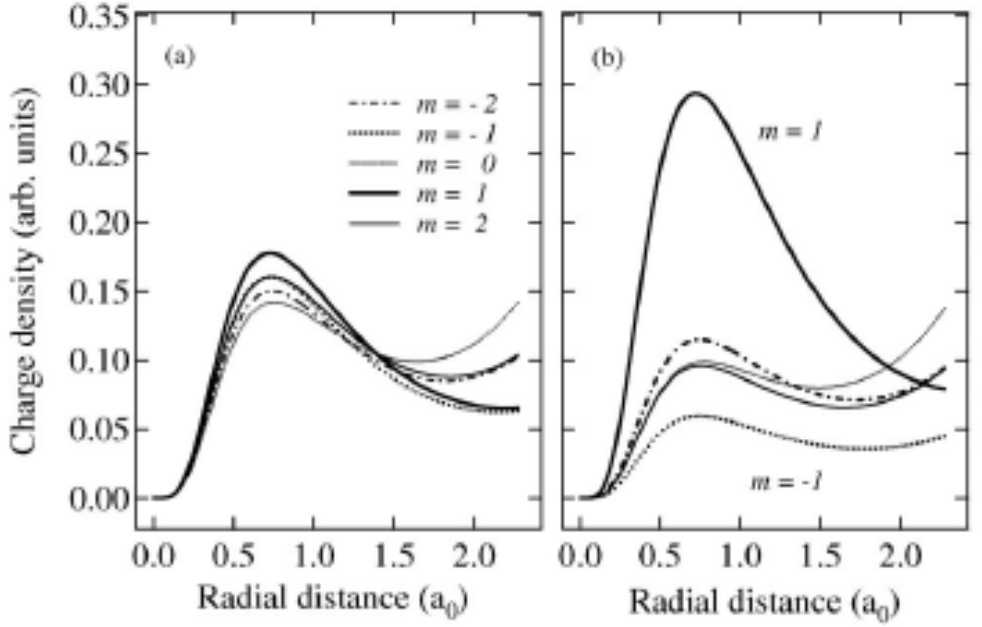


FIG. 2. Charge densities of cubic Fe_3O_4 versus radial distance in units of atomic radius a_0. The charge densities projected to different orbitals with magnetic quantum number m were obtained from (a) LDA and (b) LDA + U calculations.

Charge orbital ordering

Jeng et al PRL (2004)

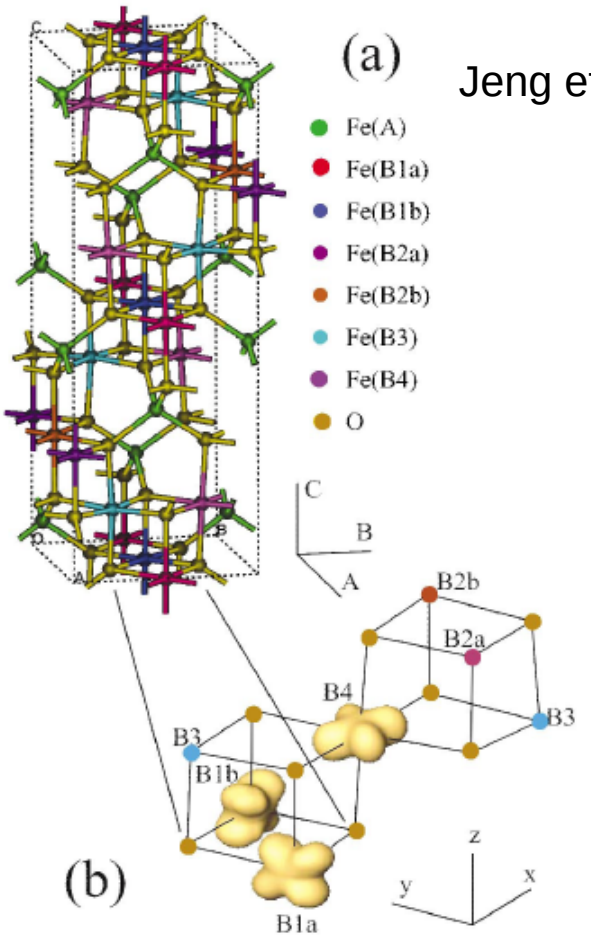


FIG. 1 (color). (a) Crystal structure of the monoclinic Fe_3O_4. (b) Orbital ordering in *B*-site sublattice. *x*-*y*-*z* and *a*-*b*-*c* are, respectively, the local and global coordinates.

Jeng et al PRL (2006)

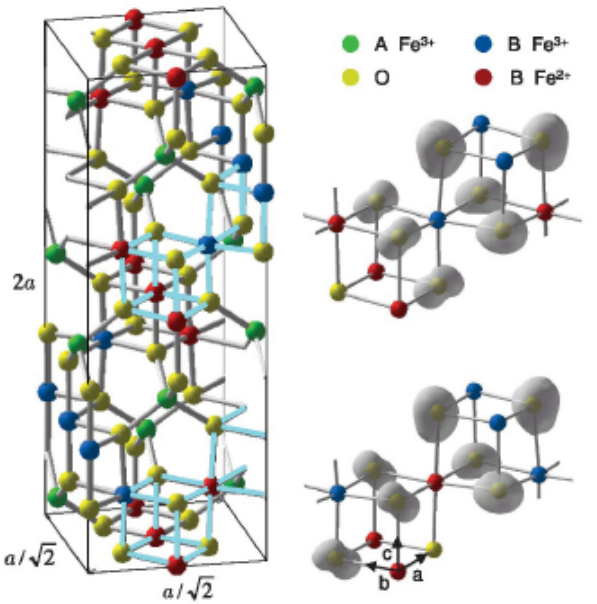


FIG. 2 (color). Left: monoclinic crystal structure of Fe_3O_4 in the low-temperature phase corresponding to a subcell of $\frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a$ with $P2/c$ symmetry. Right: 3D isosurfaces of unoccupied density of states of the O $2p$ integrated between the Fermi level and 1 eV above within the corresponding Fe_3O_4 cubes highlighted in the crystal structure. For simplicity, we denote the octahedral Fe site with nominal 2+ and 3+ valences as Fe^{2+} and Fe^{3+}, respectively.

Orbital ordering

Jeng et al PRL (2006)

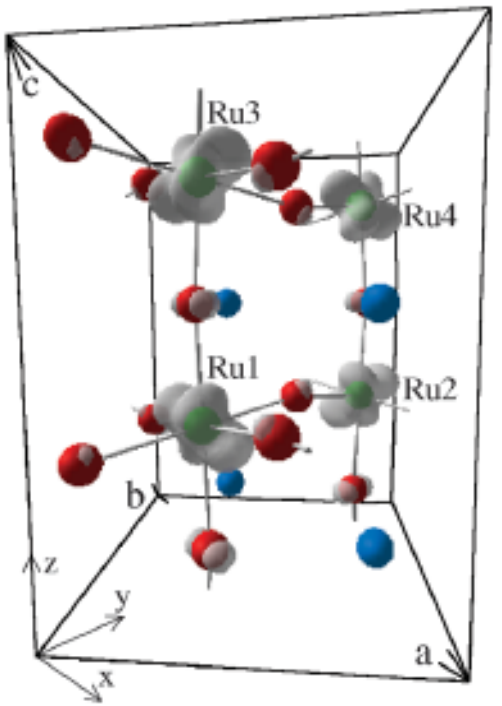
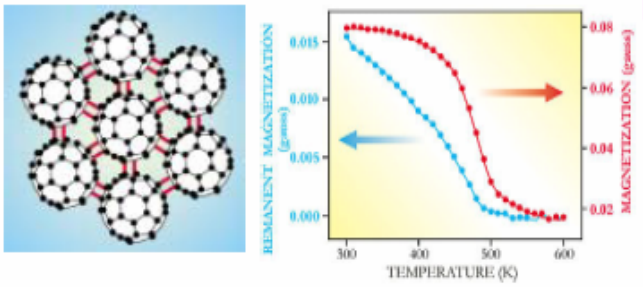


FIG. 4 (color). OO of $SrRuO_3$. Blue, green, and red balls are, respectively, Sr, Ru, and O ions. The origin has been shifted to $(-1/3, -1/3, -1/3)$.

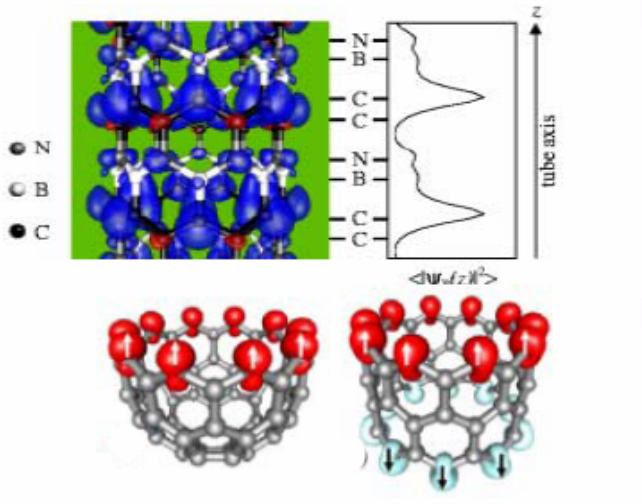
Novel magnetic materials



❑Magnetic carbon

in pure carbon system (polymerized C_{60}), Makarova *et al*. found a ferro-magnetic signal at room temperature.

(Nature **413** (2001))



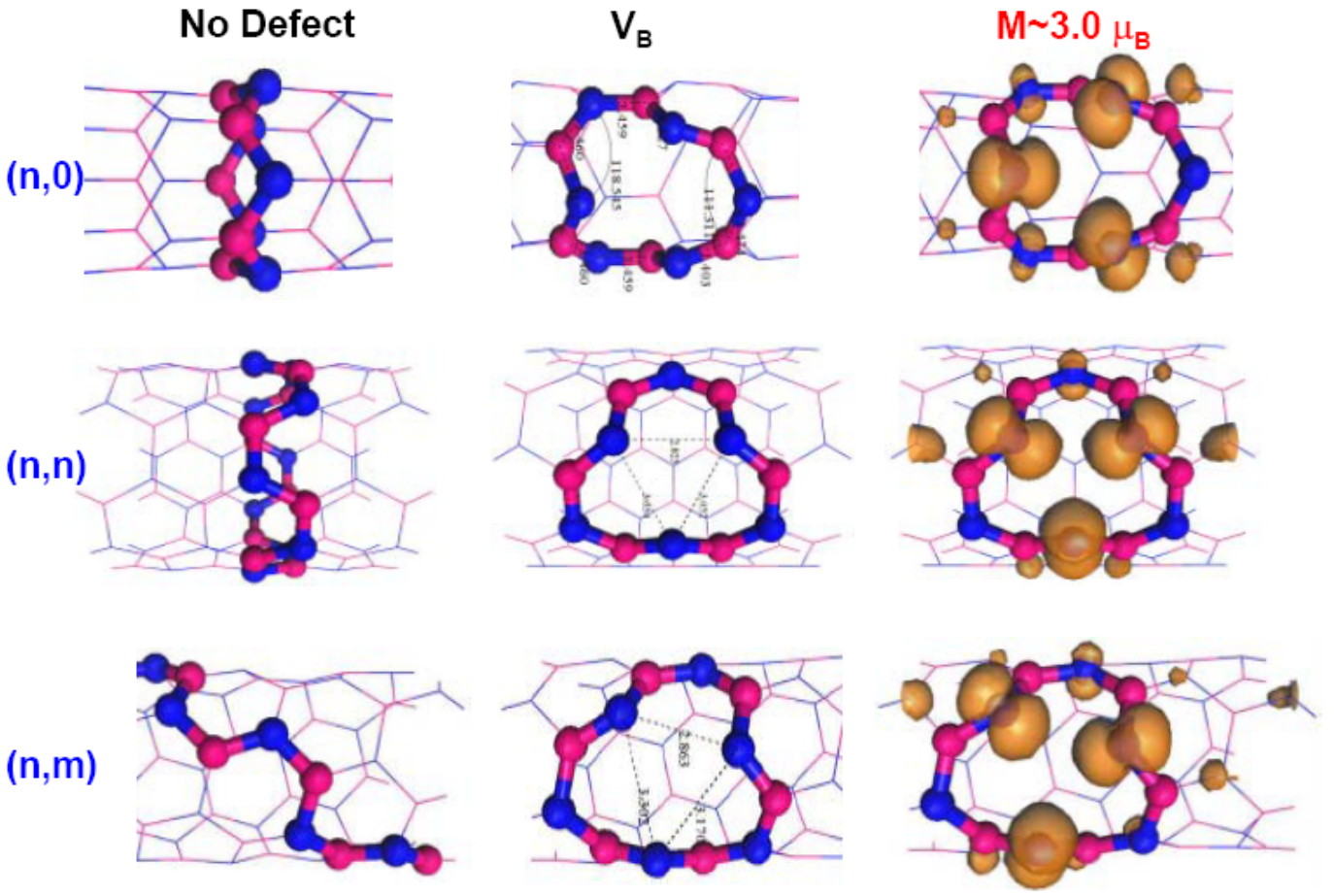
❑C/BN zigzag nanotubes

periodic arrangements of C/BN hetero-junctions can lead to the formation of a one-dimensional itinerant ferromagnetic state. (PRB **67** (2003))

❑Ferromagnetic fullerenes

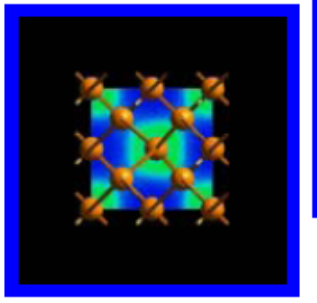
a moderate large m (~10 μB) at the open edge of defective C_{60}

(PRB 68 (2003))

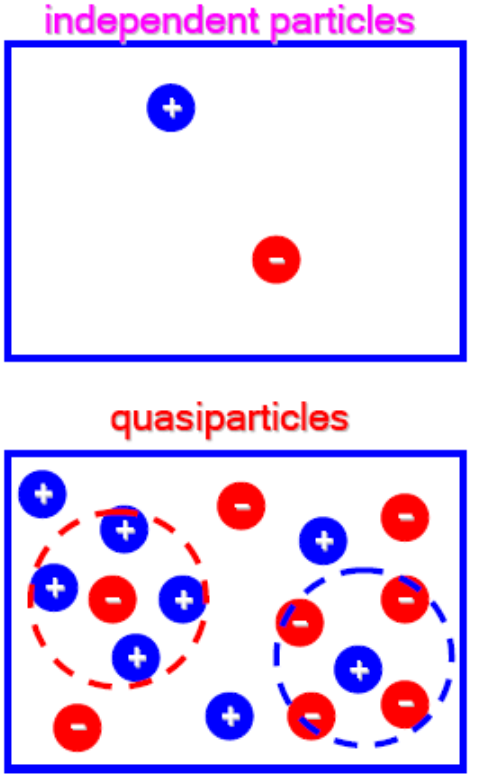

No Defect
V_B
M~3.0 μ_B
(n,0)
(n,n)
(n,m)

Ground state properties (LDA)

- **Ground-state properties (DFT)**
  Atomic structure (bond length, lattice constants)
  Phase stability
  Phonon
  Cohesive energy
  Band structure (v)
  Magnetization ...



- **Excitation (beyond DFT)**
  Optical spectrum
  Band structure (band-gap problem)
  Excitation ...

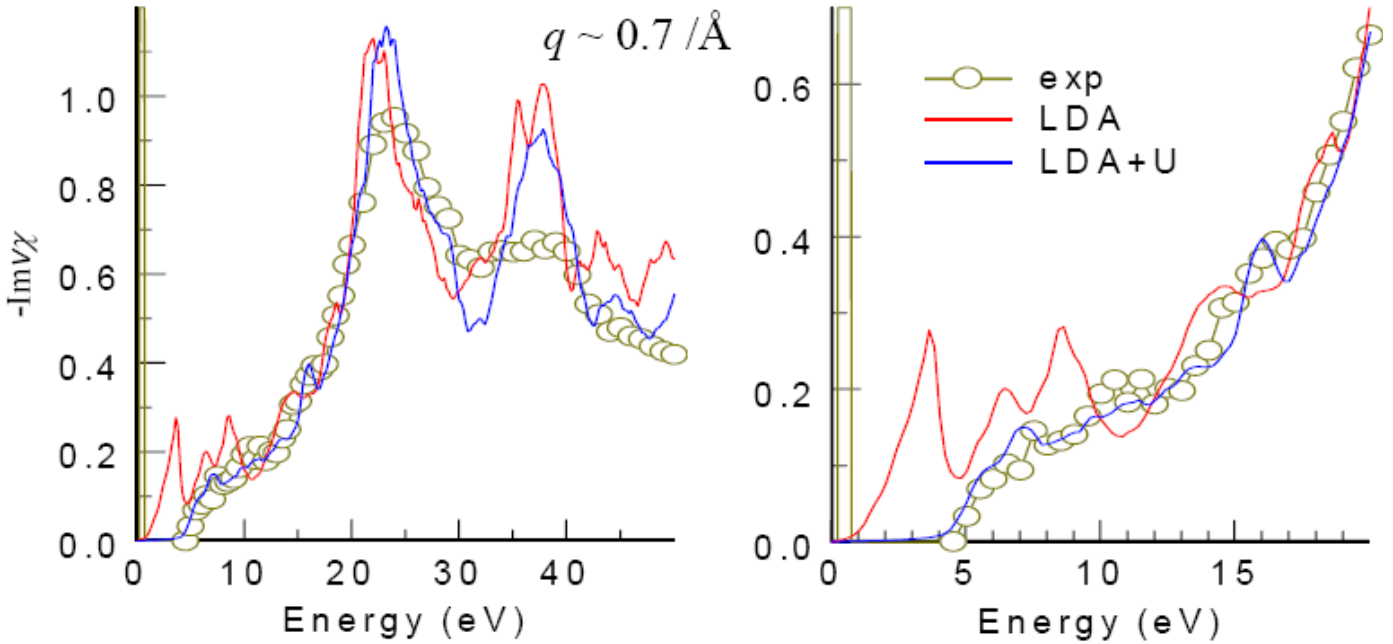


Beyond LDA

- LDA+U
- Self-Interaction Correction (SIC)
- GW Approximation (GWA)
- Optimized Effective Potential method (OEP)
- Time-Dependent Density Functional Theory (TDDFT)
- Quantum Monte-Carlo method (QMC)
- Dynamical Mean Field Theory (DMFT)
- . . . .

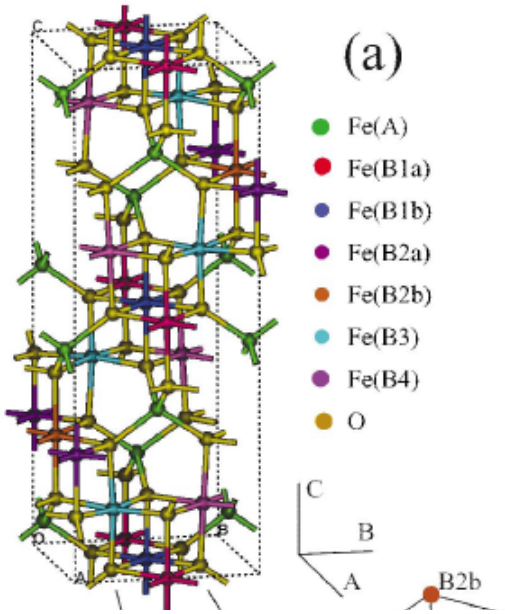
LDA+U for transition metal oxide NiO

➢ **Excitation : LDA, LDA+U vs. experiment** (inelastic X-ray scattering)



→ **LDA+U** ➔ **great improvement at small q**

LDA+U for low-T magnetite Fe3O4



Jeng et al, PRL (2004), PRB (2006)

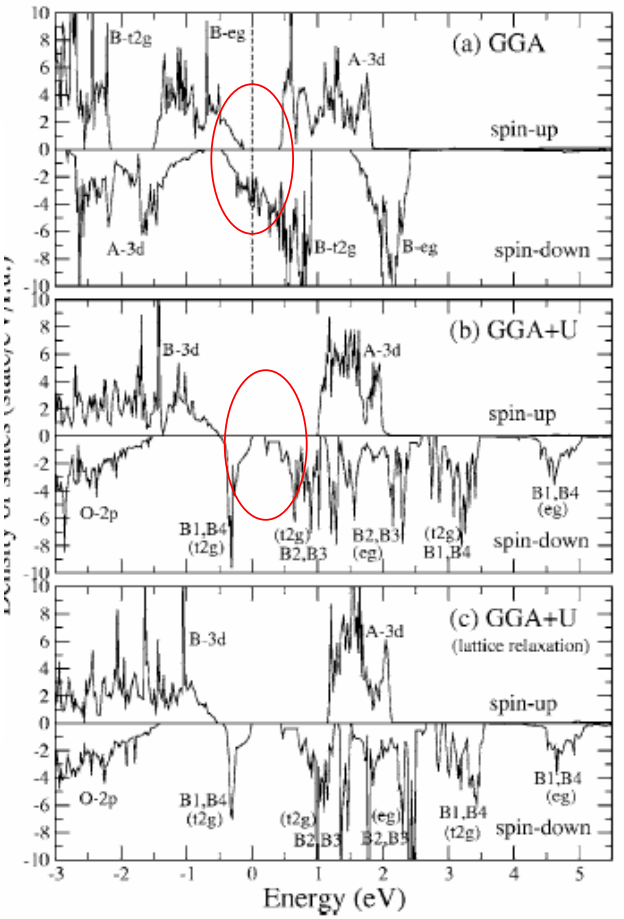
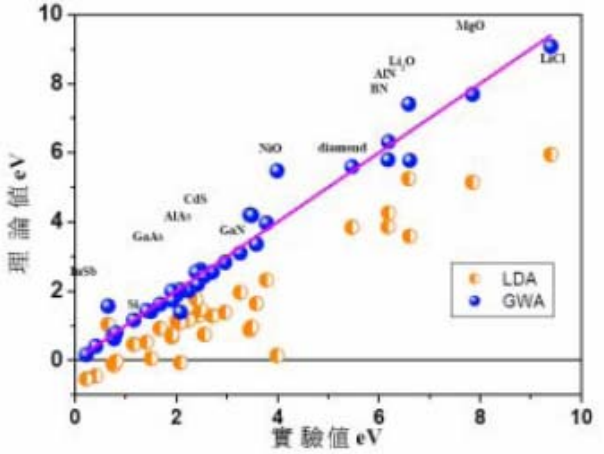


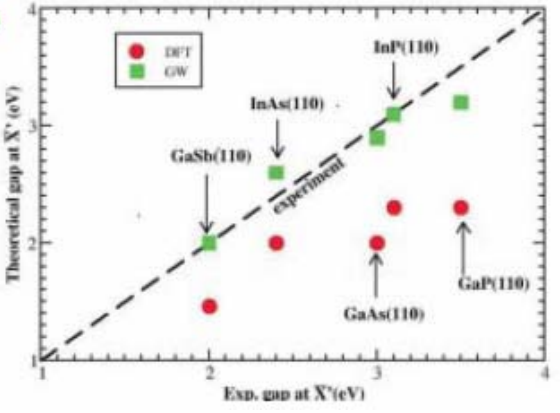
FIG. 2. Spin-resolved density of states of Fe_3O_4 in low-T monoclinic $P2/c$ structure from GGA (a), GGA+U (b), and GGA+U under lattice relaxation (c). The Fermi level is at zero energy.

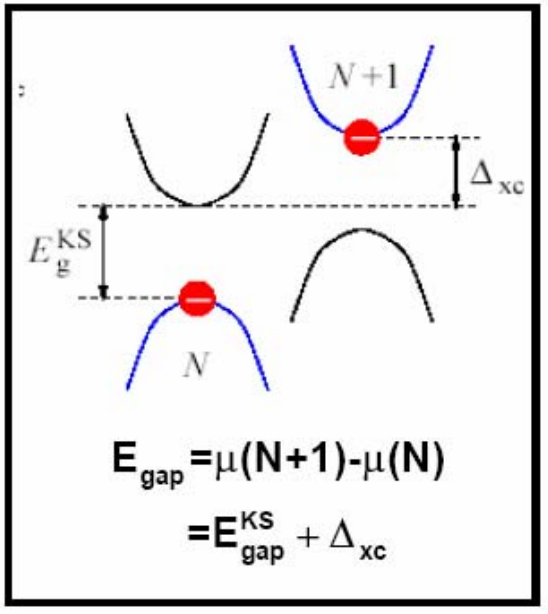
Band gap problem in semiconductors: GWA

Bulk



Surface





CMS II-1 Hands-on: Unix, vi, VASP, total energy, and convergence

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Unix

Login:guest ←account name

Password:******(abcdef) ←password

Change password: %passwd

Frequently used command

% pwd show the full path of the current directory

% cd ../Fe change directory

% ls *.f list all files with extension name of .f

% ls -l (long list)

% ls - l

```
-rwxrwxrwx   1  users  user  4564  Jun11  20:45   love
dr--r-----   2  users  user   547  Jun11  22:50   sub/
-rw-rw-r--   1  users  user  4135  Jun21  11:20   t1
  ↑  ↑  ↑       ↑      ↑      ↑      ↑              ↑
  u  g  o     owner  group  size   date   time     name
```

% chmod u+x filename

% chmod 741 filename

% ls -a (list hidden files, eg .csrch .login)

% ls -F (add * at the end of executable files, add / at the end of directories)

0	000	---
1	001	--x
2	010	-w-
3	011	-wx
4	100	r--
5	101	r-x
6	110	rw-
7	111	rwx

% mkdir dname

% rmdir dname, rm –rf dname

% rm filename (delete filename)

% mv filename1 filename2 (change name)

% cp [-i p r] filename target (copy)

i:to make sure

p:keep the original time

r:copy directory

% cat filename (>test)

Show the content of filename and put into another file (test)

% more filename, less filename

Show the content of filename page by page

% head –n filename

Show the first n lines of filename

% tail –n filename (>>test)

Show the last n lines of filename and put at the end of test

% grep –i string filename

Find all lines of filename containing string ignoring upper or lower cases

% grep ‘total energy’ filename

% find directory –name filename –print

Find filename in directory and list the full path

?,*,[ ],{ }

ls hw? →hw2,hw3,hw4
ls hw?? →hw11,hw12
ls hw* →hw2,hw3,hw4,hw11,hw12
ls hw[2-11] →hw2,hw3,hw4,hw11
ls hw{2,12} →hw2,hw12
ls test[a-c] →testa,testb,testc

alias

alias la ls-a ;
alias ch1 ‘cd /usr/john ; ls-l’
alias rm ‘rm –i’;
alias hm ‘history | more ’

unalias

Unalias ch1

alias: Show the available alias

Vi editor

% vi filename

There are 2 modes in vi editor : (1) insert mode, (2) command mode

i,a,o,I,A,O ⇨ insert mode To key-in characters

ESC ⇨ command mode To handle the file

h(←), j(↓), k(↑), l(→)

nG	go to the nth line
G	go to the last line
^g	show line number of the cursor
^f	next page
^b	last page

x	delete a character
dd	delete a line
ndd	delete n lines
u	undo the last commend
p,P	paste
/string	search for string
:q!	Quit
:wq	save and quit
:w filename	save as filename
:set nu	show line number
:1,$ s/string1/string2/g	replace string1 by string2
:n1,n2 w filename	write line n1 to n2 into filename
:r filename	read from filename

VASP

Vienna *Ab-initio* Simulation Package

- **VASP Home Page**
  http://cms.mpi.univie.ac.at/vasp/
- **Hands-on tutorial course on VASP**
  http://cms.mpi.univie.ac.at/vasp-workshop/
- **VASP Manual**
  http://cms.mpi.univie.ac.at/vasp/vasp.html

Total energy calculation: Si(Dia)

- Many properties depend on the total energy of the system
- Equilibrium Lattice constant
- Bulk module, Elastic constant
- Phase transition, surface reconstruction
- Bonding, Structure, …
- The most important point is to make sure your calculation is convergent (vs # of kpoints, cutoff energy, …)

Work list

- Setup bulk calculation for Si(Dia) using experimental lattice structure as input
- Increase the number of k-points (density of k-mesh) from (4 4 4), (8 8 8), …, till the calculated total energy is convergent
- increase the cutoff energy from default value to 1.2, 1.4, … times of default value to see the convergence of the total energy

Setup bulk calculation for Si(Dia)

- Make a working directory for Si
  %mkdir si
- Goto the working directory si
  %cd si
- Prepare the four input files
  INCAR: control parameters
  KPOINTS: BZ integration
  POSCAR: lattice structure
  POTCAR: pseudopotential
- Run the VASP code
  %vasp4620s&

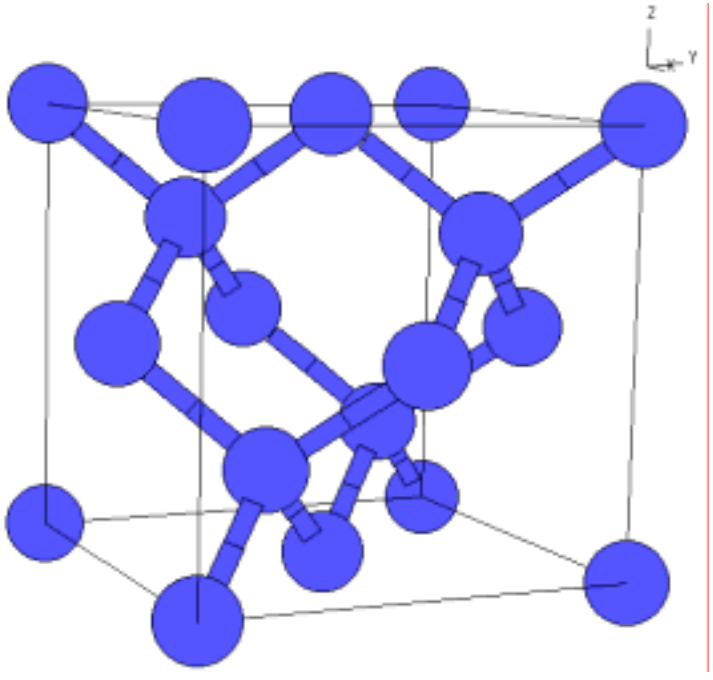
INCAR

SYSTEM = Si Diamond	Title
DOS related values	comment
ISMEAR = -5	Tetrahedron method
RWIGS = 1.1	Atomic radius

KPOINTS

Si Diamond	title
0	Automatic mesh
Mondhorst-Pack	Mondhorst-Pack type mesh
16 16 16	K-point density in BZ
0 0 0	Shift of the mesh

Diamond structure



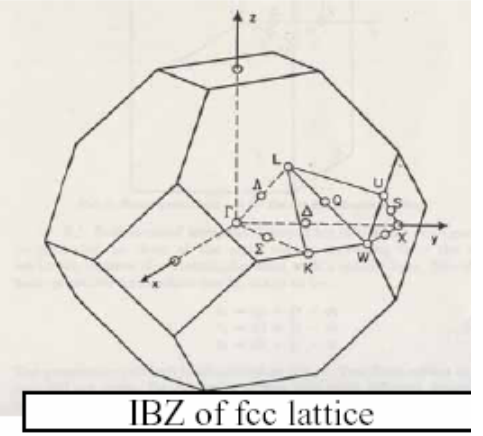
POSCAR

Si Diamond	Title
5.43	Lattice constant in A
0.0 0.5 0.5	a1 a2 a3
0.5 0.0 0.5	b1 b2 b3
0.5 0.5 0.0	c1 c2 c3
2	# of atoms in unit cell
Direct	Use a, b, c as the basis vectors
0.0 0.0 0.0 ! Si	Atomic positions (in a,b,c)
0.25 0.25 0.25 ! Si	Atomic positions (in a,b,c)

Example : fcc structure

$$\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3 \qquad \vec{k} = \frac{2\pi}{a}(x_1, x_2, x_3)$$

$\vec{a}_1 = \frac{a}{2}(\vec{j} + \vec{k})$	$\vec{b}_1 = \frac{4\pi}{a}\frac{1}{2}(-\vec{i} + \vec{j} + \vec{k})$
$\vec{a}_2 = \frac{a}{2}(\vec{i} + \vec{k})$	$\vec{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\vec{i} - \vec{j} + \vec{k})$
$\vec{a}_3 = \frac{a}{2}(\vec{i} + \vec{j})$	$\vec{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\vec{i} + \vec{j} - \vec{k})$



IBZ of fcc lattice

Point	Cartesian coordinates (units of 2pi/a)	Reciprocal coordinates (units of b1,b2,b3)
G	(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)

POTCAR

Copy POTCAR from potpaw Si directory

Ex: POTCAR of W

```
PAW W 19Jan2001
6.00000000000000000
parameters from PSCTR are:
 VRHFIN =W: 5p6s5d
 LEXCH  = CA
 EATOM  =   206.5370 eV,   15.1800 Ry

 TITEL  = PAW W 19Jan2001
 LULTRA =       F    use ultrasoft PP ?
 IUNSCR =       1    unscreen: 0-lin 1-nonlin 2-no
 RPACOR =   2.330    partial core radius
 POMASS =  183.850; ZVAL   =   6.000    mass and valenz
 RCORE  =   2.750    outmost cutoff radius
 RWIGS  =   2.750; RWIGS  =   1.455    wigner-seitz radius (au A)
 ENMAX  =  223.126; ENMIN  =  167.344 eV
 RCLOC  =   2.147    cutoff for local pot
 ..................

 Description
  l    E     TYP  RCUT    TYP  RCUT
  2   .000    23  2.500
 ..................
```

OUTCAR

```
vasp.4.6.9 24Apr03 complex
executed on            SP2/3/4 date 2005.03.16  15:42:04
running on    1 nodes
distr:  one band on    1 nodes,    1 groups
...........
I would recommend the setting:
  dimension x,y,z NGX =    11 NGY =   11 NGZ =   63
.............
 NGX is ok and might be reduce to  16
 NGY is ok and might be reduce to  16
 NGZ is ok and might be reduce to  82
..........
 Found     15 irreducible k-points:
 Following reciprocal coordinates:
          Coordinates               Weight
  .050000  .050000  .000000      4.000000
...............

 ion  position             nearest neighbor table
   1  .000  .000  .180-   2 2.44   2 2.44   2 2.44   2 2.44   3 2.82
   2  .500  .500  .090-   1 2.44   3 2.44   1 2.44   3 2.44   1 2.44   3 2.44
.........
 k-point  1 :   .0500 .0500 .0000  plane waves:   1255
 k-point  2 :   .1500 .0500 .0000  plane waves:   1249
.......
 E-fermi :    .7339     XC(G=0):  -7.2761     alpha+bet : -6.2180
   add alpha+bet to get absolut eigen values
```

grep E-fermi OUT*

```
k-point  1 :       .0500    .0500    .0000
 band No.  band energies     occupation
    1     -7.1007     1.00000
    2     -5.6294     1.00000
……..
   24      -.0812     1.00000
   25       .0452     1.00000
   26       .4166      .98757
   27       .4330      .98331
   28       .5655      .88306
   29      1.1510      .00159
   30      3.0240      .00000
   31      4.8957      .00000
   32      5.1413      .00000

 k-point  2 :       .1500    .0500    .0000
……
POSITION                                TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------
     .00000     .00000    2.80979         .000000     .000000     .044768
    1.41120    1.41120    1.44005         .000000     .000000     .023860

 external pressure =      783.50 kB   Pullay stress =       0.00 kB
…….
 external pressure =        0.54 kB   Pullay stress =       0.00 kB
…..
 direct lattice vectors                 reciprocal lattice vectors
   -1.532408821  1.532408821  1.532408821    0.000000000  0.326283687  0.326283687
    1.532408821 -1.532408821  1.532408821    0.326283687  0.000000000  0.326283687
    1.532408821  1.532408821 -1.532408821    0.326283687  0.326283687  0.000000000
```

```
........
 total charge

# of ion     s       p       d       tot
------------------------------------
  1        .391    .281   6.106   6.778
  2        .411    .433   6.211   7.054
  3        .411    .434   6.163   7.008
  4        .411    .433   6.211   7.054
  5        .391    .281   6.106   6.778
------------------------------------
tot        2.01    1.86   30.80   34.67

 magnetization (x)

# of ion     s       p       d       tot
------------------------------------
  1        .011    .003   2.867   2.880
  2       -.012   -.036   2.271   2.223
  3       -.001   -.036   2.462   2.425
  4       -.012   -.036   2.271   2.223
  5        .011    .003   2.867   2.880
------------------------------------
tot         .00    -.10   12.74   12.63
.............
```

```
-------------------------- Iteration   1(  1) ---------
   POTLOK:  VPU time   2.28: CPU time   2.28
   SETDIJ:  VPU time    .27: CPU time    .27
   EDDAV :  VPU time   8.15: CPU time   8.16
   DOS   :  VPU time    .00: CPU time    .00
   --------------------------
    LOOP:  VPU time  10.72: CPU time  10.77
..............

    LOOP+:  VPU time 271.30: CPU time 271.92

-------------------------- Iteration   2(  1) ---------

.................

General timing and accounting informations for this job:
 ========================================

                Total CPU time used (sec):     519.130
                      User time (sec):     518.960
                    System time (sec):       .170
                   Elapsed time (sec):     521.628

                 Maximum memory used (kb):      53852.
                 Average memory used (kb):      514.
```

grep LOOP OU*

OSZCAR

	N	E	dE	d eps	ncg	rms	rms(c)
DAV:	1	.335885869262E+02	.33589E+02	-.42225E+03	17288	.695E+02	
DAV:	2	-.429448425975E+01	-.37883E+02	-.34709E+02	14040	.191E+02	
DAV:	3	-.472026980215E+01	-.42579E+00	-.42552E+00	16554	.232E+01	
DAV:	4	-.472147266739E+01	-.12029E-02	-.12028E-02	15730	.115E+00	
DAV:	5	-.472148218577E+01	-.95184E-05	-.95179E-05	15418	.942E-02	.316E+00
DAV:	6	-.442946208768E+01	.29202E+00	-.98533E-01	14907	.126E+01	.817E-01
DAV:	7	-.440595084829E+01	.23511E-01	-.53654E-02	16133	.244E+00	.305E-01
DAV:	8	-.440083611401E+01	.51147E-02	-.18624E-03	14174	.672E-01	.115E-02
DAV:	9	-.440083792741E+01	-.18134E-05	-.94978E-06	7237	.266E-02	

1 F= -.44008379E+01 E0= -.43980580E+01 d E =-.440084E+01

E0: Cohesive energy:
Bulk total energy-atomic total energy

PROCAR

```
PROCAR new format
# of k-points:    1        # of bands:   9        # of ions:   2

 k-point    1 :    .00000000  .00000000  .00000000     weight = 1.00000000

band   1 # energy  -29.19030270 # occ.  2.00000000

ion      s     p     d      tot
  1   .162   .138   .025   .325
  2   .581   .089   .006   .676
tot   .743   .227   .031  1.001

band   2 # energy  -13.97365697 # occ.  2.00000000

ion      s     p     d      tot
  1   .181   .017   .001   .199
  2   .158   .418   .006   .582
tot   .339   .435   .007   .781
```

XDATCAR

```
2  2  50
  .5000000E+03  .1000000E-08  .1000000E-08  .1000000E-08  .5000000E-15
0.10000000000000005E-03
 CAR
bcc Fe

   .00000000  .00000000  .05500000
   .00000000  .00000000  .94500000

   .00000000  .00000000  .08205172
   .00000000  .00000000  .91794828

   .00000000  .00000000  .06383446
   .00000000  .00000000  .93616554

   .00000000  .00000000  .05825907
   .00000000  .00000000  .94174093

   .00000000  .00000000  .05727735
   .00000000  .00000000  .94272265

   .00000000  .00000000  .05571192
   .00000000  .00000000  .94428808

   .00000000  .00000000  .05710243
   .00000000  .00000000  .94289757
~
```

CHGCAR

$(((\ chg\ (i, j, k)\ ,\ i = 1, nx\ ), j = 1, ny\ ), k = 1, nz\ )$

```
bcc Fe
 10.0000000000000000
   1.000000    .000000    .000000
    .000000   1.000000    .000000
    .000000    .000000   1.000000
  1   1
Direct
  .000000  .000000  .057102
  .000000  .000000  .942898

  84   84   84
 .41098271954E+04 .38580593547E+04 .32056173636E+04 .23907855172E+04 .16323134731E+04
 .10440737881E+04 .64952106325E+03 .40394464342E+03 .25149651632E+03 .15428370958E+03
 .92653834837E+02 .55483939720E+02 .34042823873E+02 .21474147940E+02 .13548327933E+02
.........
augmentation occupancies   1  33
  .5244394E+00 -.3805205E+00  .8687841E-32  .9745050E-01 -.8804372E-32
.........
  .1622568E-01 -.1784093E-33 -.2752412E-18
augmentation occupancies   2  33
  .5478642E+00  .1011510E+00 -.1371290E-33 -.5095633E-01  .6053117E-33
 -.2851393E-33  .4943223E-01 -.2869968E-34  .1850662E-01  .3013137E-32
  .1147544E+00 -.1892876E-32 -.2537948E-33  .3431420E-01  .2348182E-33
  .1329580E+01  .0000000E+00 -.7399463E-33  .8218637E-01  .8516730E-33
 -.1488428E-16  .3152197E+00  .1110142E-31  .3496585E-33  .6753791E-01
  .1884802E-33  .4810138E-17  .2572049E-01  .0000000E+00  .9750446E-34
  .1262313E-01 -.6911072E-34 -.3365055E-19
```

K-point convergence test

- Use (4 4 4) k-mesh density in KPOINTS to calculate the cohesive energy
- Redo (8 8 8) record the cohesive energies
- Redo (12 12 12) … till a convergent cohesive energy is obtained

cutoff energy convergence test

- Use sufficient k-points KPOINTS to do the following calculations
- Find out the default cutoff energy (ENCUT) in OUTCAR
- Set a new line in INCAR to increase cutoff energy by 1.2 times larger and redo the calculation

  ENCUT = ???
- Set ENCUT 1.4 times larger … till convergent cohesive energy is obtained

Homework

please Email to jeng@phys.sinica.edu.tw

- K-point convergence test for Si(Dia) and C(Dia) using experimental lattice constant
- Cutoff energy convergence test for Si(Dia) and C(Dia) using experimental lattice constant