CMS II-7: structure optimization

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Atomic geometry relaxation

- Total energy and forces on atoms
- Hellmann-Feynman theory
- Steepest decent structure optimization algorithm
- Conjugate gradient structure optimization algorithm

Total energy calculation

$$E_T[n] = \int V_{ext}(\vec{r})n(\vec{r})d^3r + \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r d^3r' + T[n] + E_{xc}[n]$$

Coulomb energy

Exchange-correlation energy

Minimize E_T subject to the condition $N = \int n(\vec{r})d^3r$ ➡ $n(\vec{r})$

➡ $$\frac{\delta T[n]}{\delta n} + V_{ext}(\vec{r}) + \int \frac{n(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r + V_{xc}(\vec{r}) = \mu \quad ; \quad V_{xc}[\vec{r}] = \frac{\delta E_{xc}[n]}{\delta n}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i^{occ} |\psi_i(\vec{r})|^2$$ Kohn-Sham eq., PRB(1965)

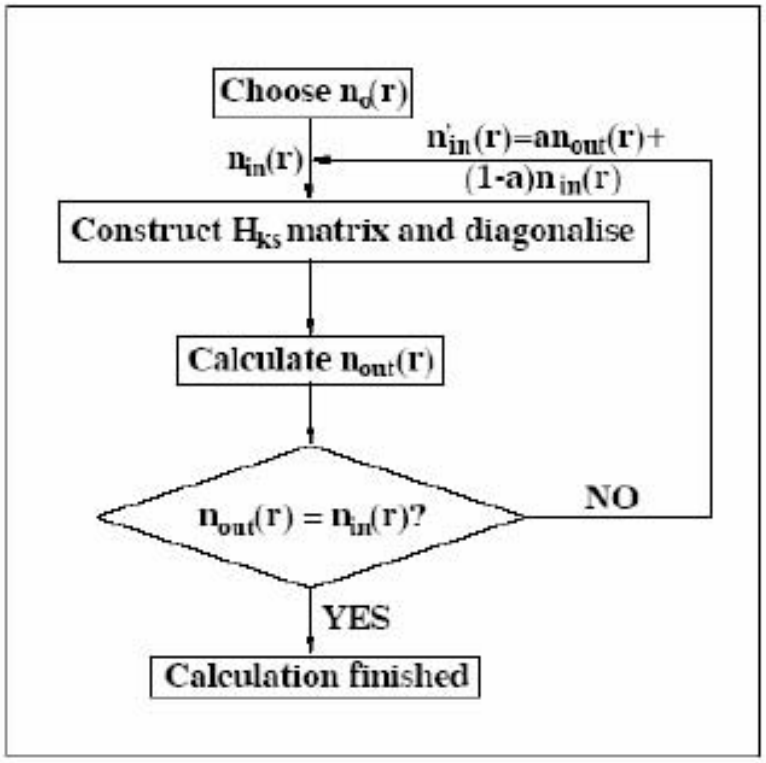
$$\rho_{in} \rightarrow V_{eff}(r) \rightarrow \varepsilon_i;\psi_i \rightarrow \rho_{out}$$

$$\rho_{in}^{n+1} = (1-\alpha)\rho_{in}^n + \alpha\rho_{out}^n$$

$(\rho(r) = n(r))$

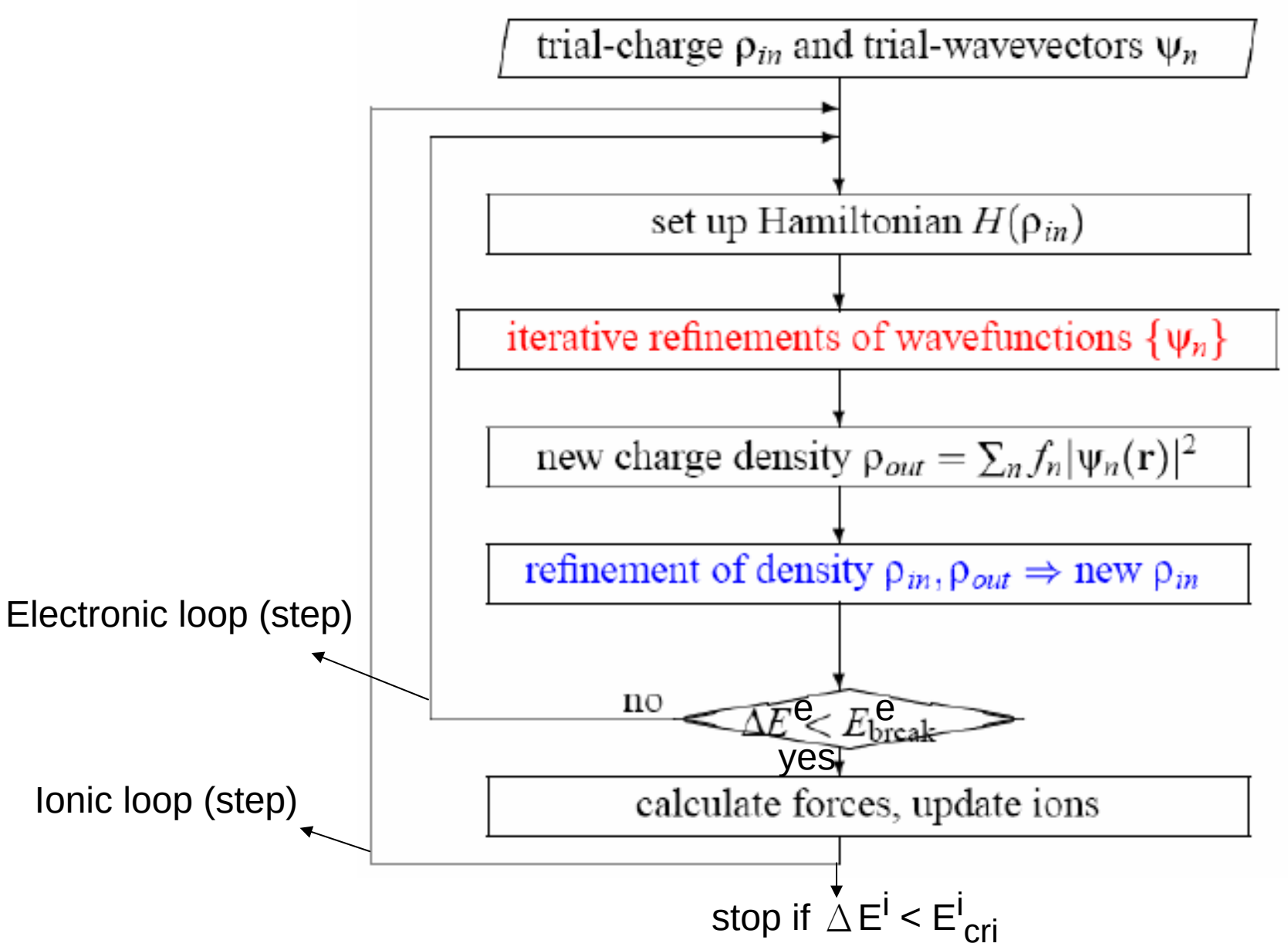
self-consistent scheme

Self-consistent field (SCF) calculations of total energy



- $V_H(\mathbf{r})$ and $V_{XC}(\mathbf{r})$ depend on $n(\mathbf{r})$
- $n(\mathbf{r})$ depends on $\{\psi_i(\mathbf{r})\}$
- But we are trying to find $\{\psi_i(\mathbf{r})\}$ and the corresponding energy levels — we need *self-consistency*

SCF on structure optimization



Stress and strain

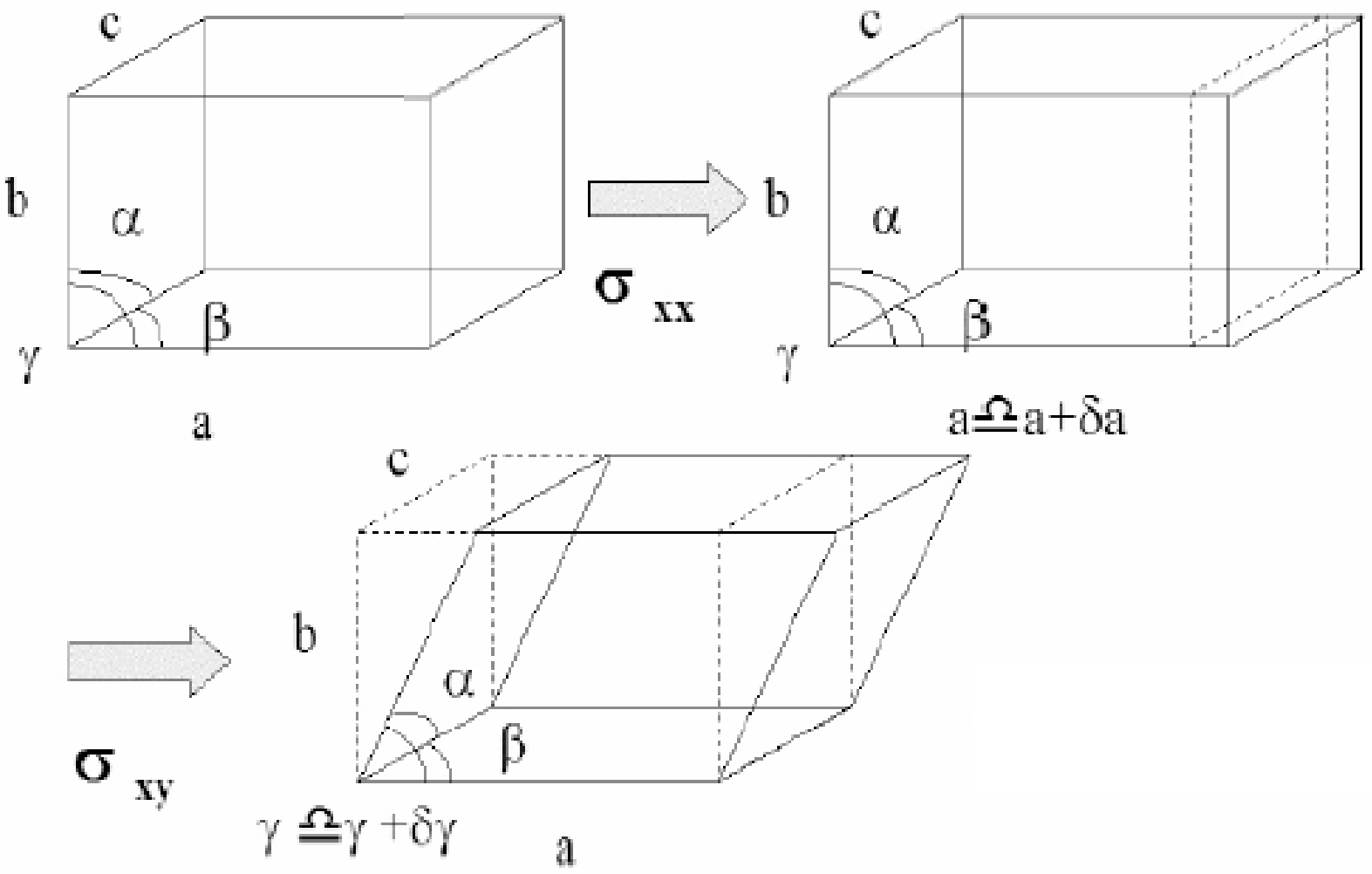
- The concept of forces is straightforward, but you can also take derivatives with respect to the crystal unit cell
- The application of a *strain* changes the shape of the unit cell
- If we write the three unit cell vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ as columns of a matrix $\mathbf{h}$ the shape change is described by:

$$\mathbf{h}' = (\mathbf{I} + \epsilon)\mathbf{h}$$

- The *stress* tensor σ is related to the strain tensor ϵ:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega}\frac{\partial E}{\partial \epsilon_{\alpha\beta}}$$

where $\Omega = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the volume of the unit cell


c
b
α
β
γ
a
σ xx
c
b
α
β
γ
a≙a+δa
σ xy
c
b
α
β
γ ≙γ +δγ
a

Hellman Feynman theorem

- Classically, the force $\mathbf{F}$ acting on a particle at $\mathbf{R}$ is given by the derivative of the potential energy:

$$\mathbf{F} = -\nabla_{\mathbf{R}} U(\mathbf{R})$$

- We might expect the quantum mechanical equivalent to be:

$$\mathbf{F} = -\nabla_{\mathbf{R}} \langle E \rangle \text{ where}$$

$$\langle E \rangle = \langle \Psi | H | \Psi \rangle, \text{ if } |\Psi\rangle \text{ are normalised}$$

- The Hellman-Feynman Theorem:

$$\frac{\partial E}{\partial \lambda} = \langle \frac{\partial \Psi}{\partial \lambda} | H | \Psi \rangle + \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle + \langle \Psi | H | \frac{\partial \Psi}{\partial \lambda} \rangle = F_{\lambda}$$

λ : coordination of a chosen atom

$$H|\Psi\rangle = E|\Psi\rangle \text{ and so}$$

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle + E \frac{\partial}{\partial \lambda} \langle \Psi | \Psi \rangle$$

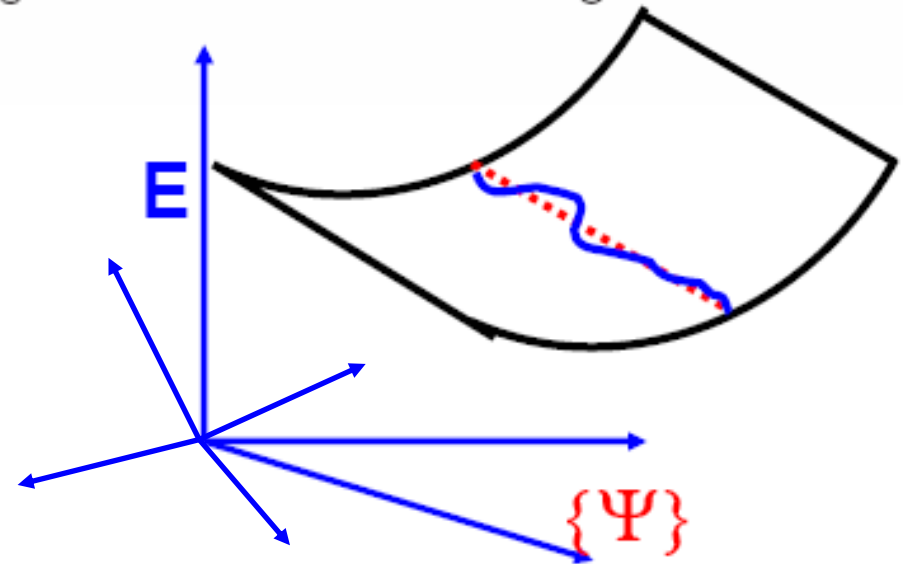
$$\boxed{\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle}$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$$

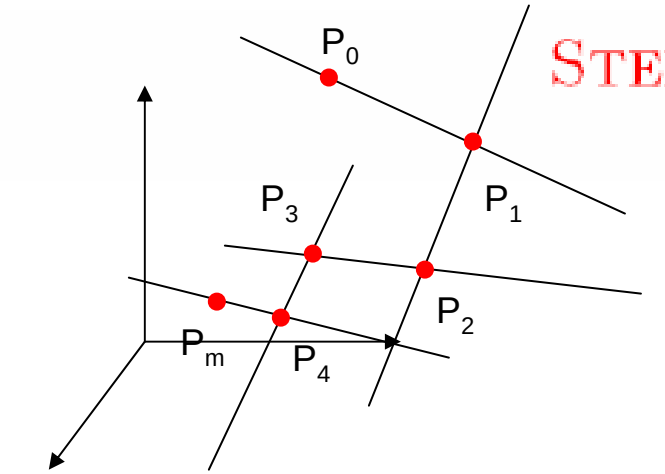
Structure optimization

- Assume that electrons adapt instantaneously to the ionic configuration
  - this is the Born-Oppenheimer approximation
- The ionic positions can be considered to be parameters, the total energy is a function of the ionic coordinates
- Finding the ground-state structures is a classic optimisation problem
- The *phase space* grows with the system size
- There are many local minima (corresponding to meta-stable structures)
- In general, we must start with a good guess for the structure (from exp.)

and go forwards to the optimized structure according to HF forces



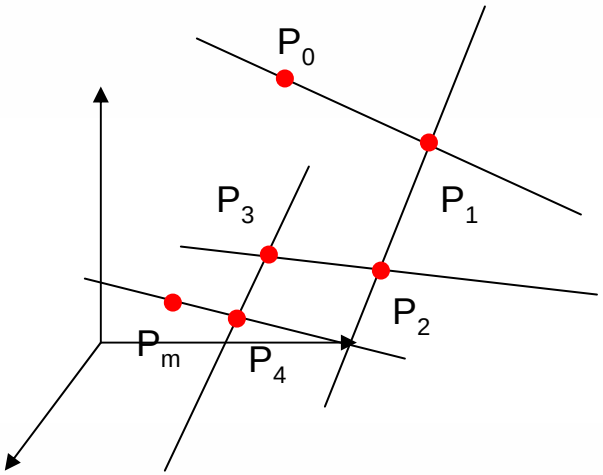
Concluding remarks



Steepest Descents

- This is the simplest approach:
  - take a downhill step along the local steepest gradient, and a trial step length
  - use line minimisation to find the optimal step length
- Advantages:
  - simple to implement, and robust
  - reliable – will find the minima eventually
- Disadvantages:
  - very slow to converge
  - can get stuck in a local minima

Conjugate Gradients



- This improves on steepest descents:
  - the gradient is constructed to be conjugate to all previous directions
  - a quick line minimization using gradient Is performed

- Advantages:
  - rapid convergence – in a quadratic energy landscape,
  - low storage requirements
- Disadvantages:
  - more complex to implement than SD
  - can get stuck in a local minima

Low temperature Magnetite Fe3O4

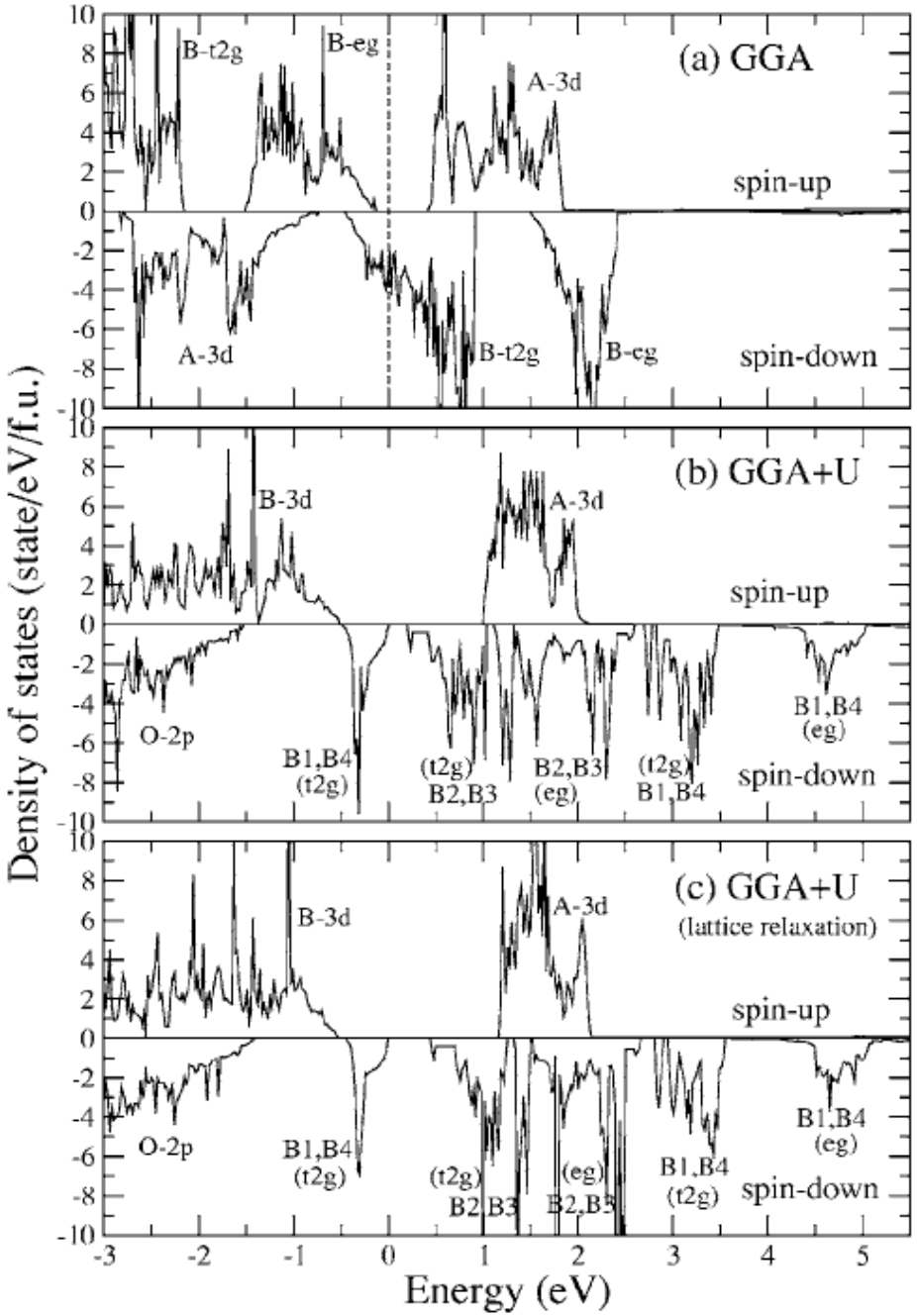


FIG. 2. Spin-resolved density of states of Fe_3O_4 in low-T mono-

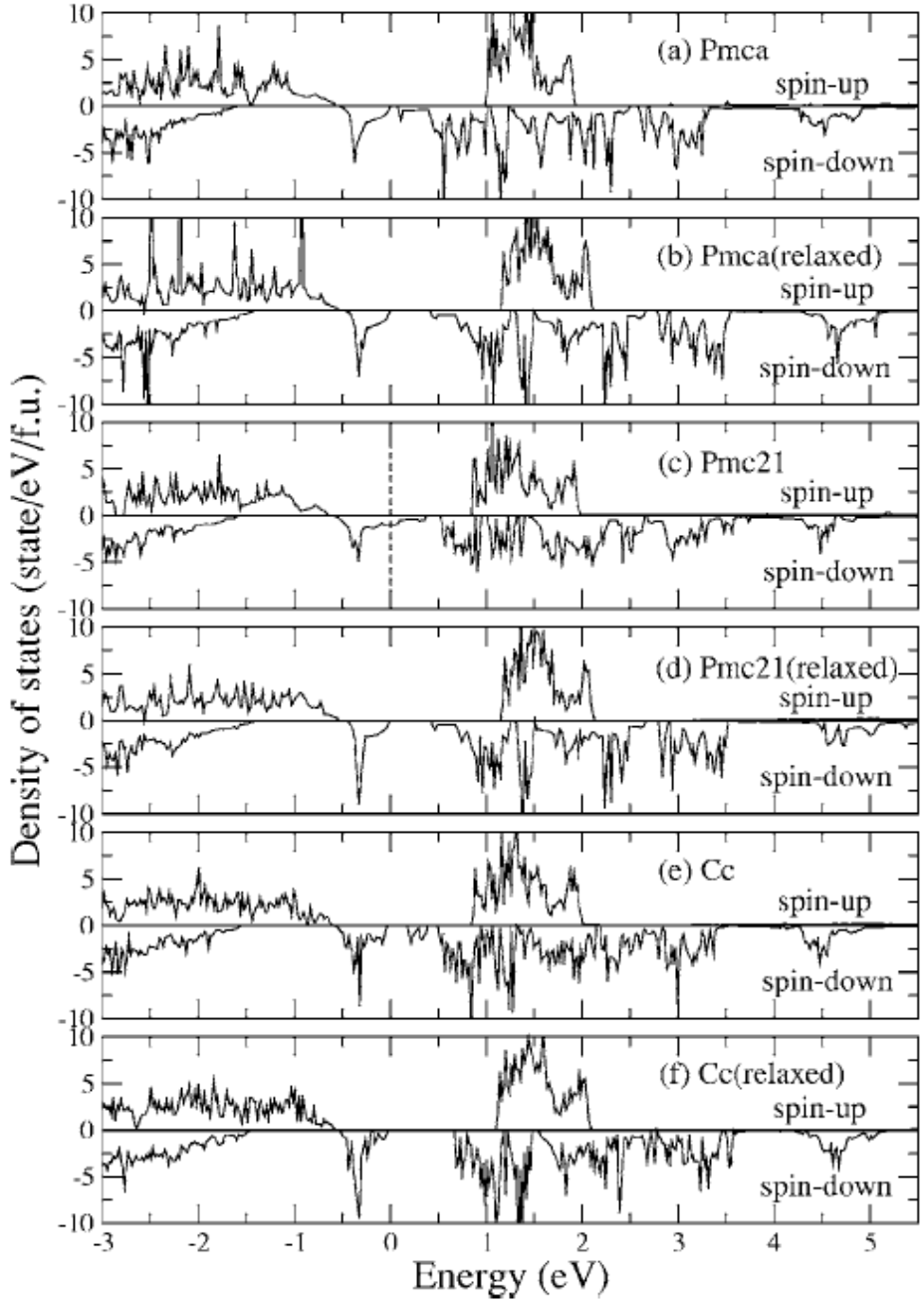
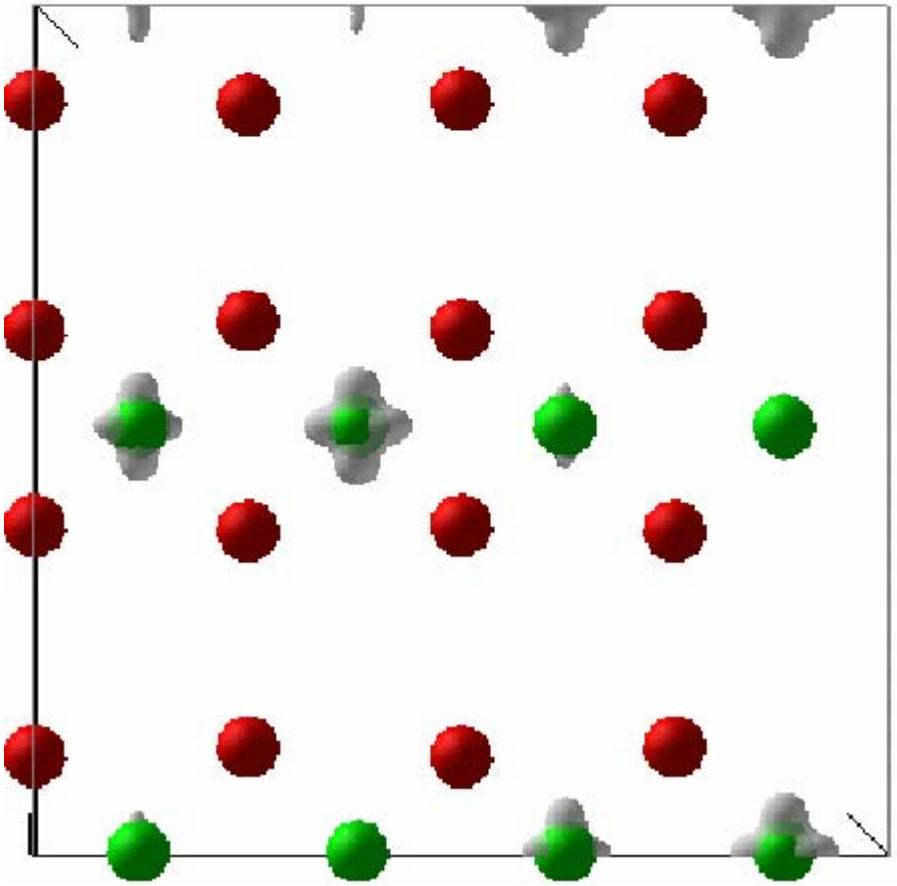
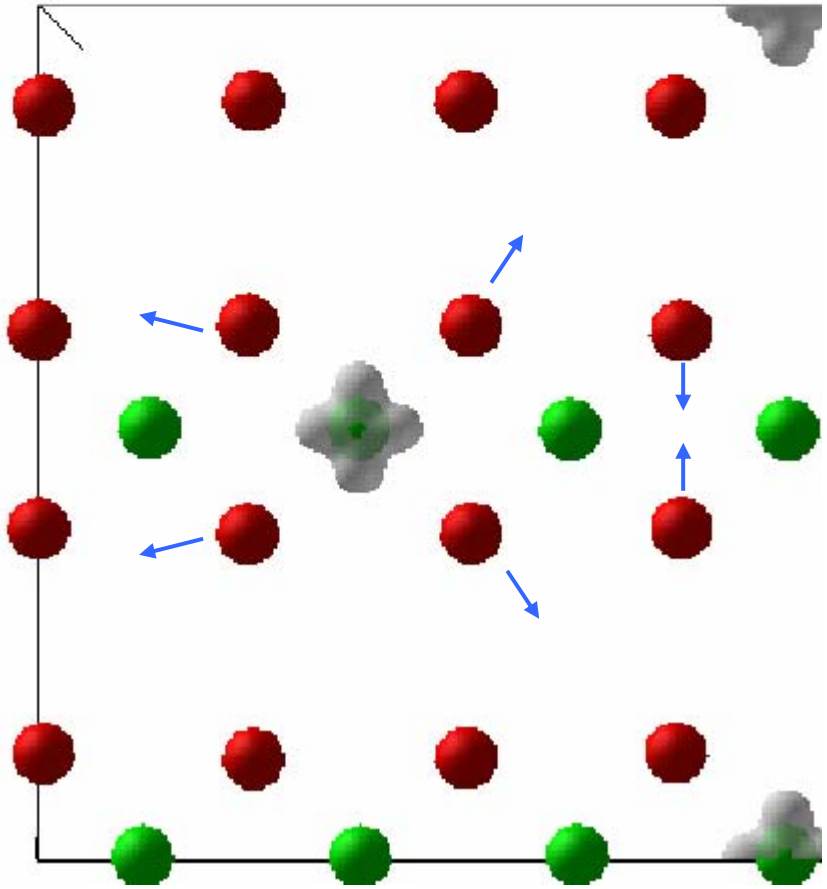


FIG. 4. Spin-resolved density of states of Fe_3O_4 in low-T *Pmca* (a, b), $Pmc2_1$ (c, d), and *Cc* (e, f) lattices from GGA+U and

Lattice relaxation and charge redistribution in Cc Fe_3O_4 at z=2/8

unrelaxed dE=0.15eV/fu relaxed





CMS II-7 Hands-on: lattice relaxation calculation

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Working list

- Calculate optimized lattice structure of nonmagnetic semiconductor Si(Dia)
- Calculate optimized lattice structure of magnetic metal Fe(BCC)

Lattice optimization of Si(Dia)

INCAR(SCF):

SYSTEM = Si Diamond

DOS related values
ISMEAR = -5
RWIGS = 1.3
NSW = 50
ISIF = 3
IBRION = 2
POTIM = 0.1

CONTCAR: The relaxed lattice

1. To be compared with POSCAR
2. mv CONTCAR POSCAR and rerun VASP if the ionic step is not converged

Maximum number of ionic step
Fully relaxation
Ionic relaxation method (conjugate gradient)
Step size

Spin polarized lattice optimization of Fe(BCC)

INCAR:

SYSTEM = Fe BCC

DOS related values
ISMEAR = -5
ISPIN = 2
MAGMOM = 5
GGA = 91
RWIGS = 1.3
NSW = 50
ISIF = 3
IBRION = 2
POTIM = 0.1

figure out the format of DOSCAR

OSZICAR contains the total energy of each ionic step

Maximum number of ionic step
Fully relaxation
Ionic relaxation method (conjugate gradient)
Step size

ISIF: controls whether the stress tensor is calculated

ISIF	calculate force	calculate stress tensor	relax ions	change cell shape	change cell volume
0	yes	no	yes	no	no
1	yes	trace only *	yes	no	no
2	yes	yes	yes	no	no
3	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	no
5	yes	yes	no	yes	no
6	yes	yes	no	yes	yes
7	yes	yes	no	no	yes

IBRION :determines how the ions are updated and moved

$$\text{IBRION} = \begin{cases} -1 & \text{ions are not move} \\ 0 & \text{ab-initio MD} \\ 1 & \text{quasi-Newton} \\ 2 & \text{CG} \end{cases}$$

NSW :defines the number of ionic steps (max.)

EDIFFG: defines the break condition for the ionic relaxation loop

EDIFF: defines the break condition for the electronic loop

Default: EDIFF=10^-4, EDIFFG=10^-3

Output of relaxation calculation

OSZICAR:

```
 N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.118903853891E+02   -0.11890E+02   -0.51514E-08   544   0.157E-03    0.679E-05
DAV:   2    -0.118903853899E+02   -0.84432E-09   -0.67687E-09   520   0.587E-04

   1 F= -.11890385E+02 E0= -.11890385E+02  d E =-.118904E+02
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.118916612818E+02   -0.11892E+02   -0.44662E-03  1216   0.374E-01    0.432E-02
DAV:   2    -0.118915710975E+02    0.90184E-04   -0.86588E-05  1048   0.587E-02

   2 F= -.11891571E+02 E0= -.11891571E+02  d E =-.118571E-02
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.118932471685E+02   -0.11893E+02   -0.36655E-02  1240   0.108E+00    0.130E-01
DAV:   2    -0.118924300860E+02    0.81708E-03   -0.75583E-04  1264   0.170E-01    0.720E-02
DAV:   3    -0.118920526488E+02    0.37744E-03   -0.87419E-04  1176   0.148E-01    0.103E-02
DAV:   4    -0.118920490217E+02    0.36270E-05   -0.76967E-06   528   0.252E-02

   3 F= -.11892049E+02 E0= -.11892049E+02  d E =-.166363E-02
```

Electronic step

Ionic step

%grep E0 OSZICAR

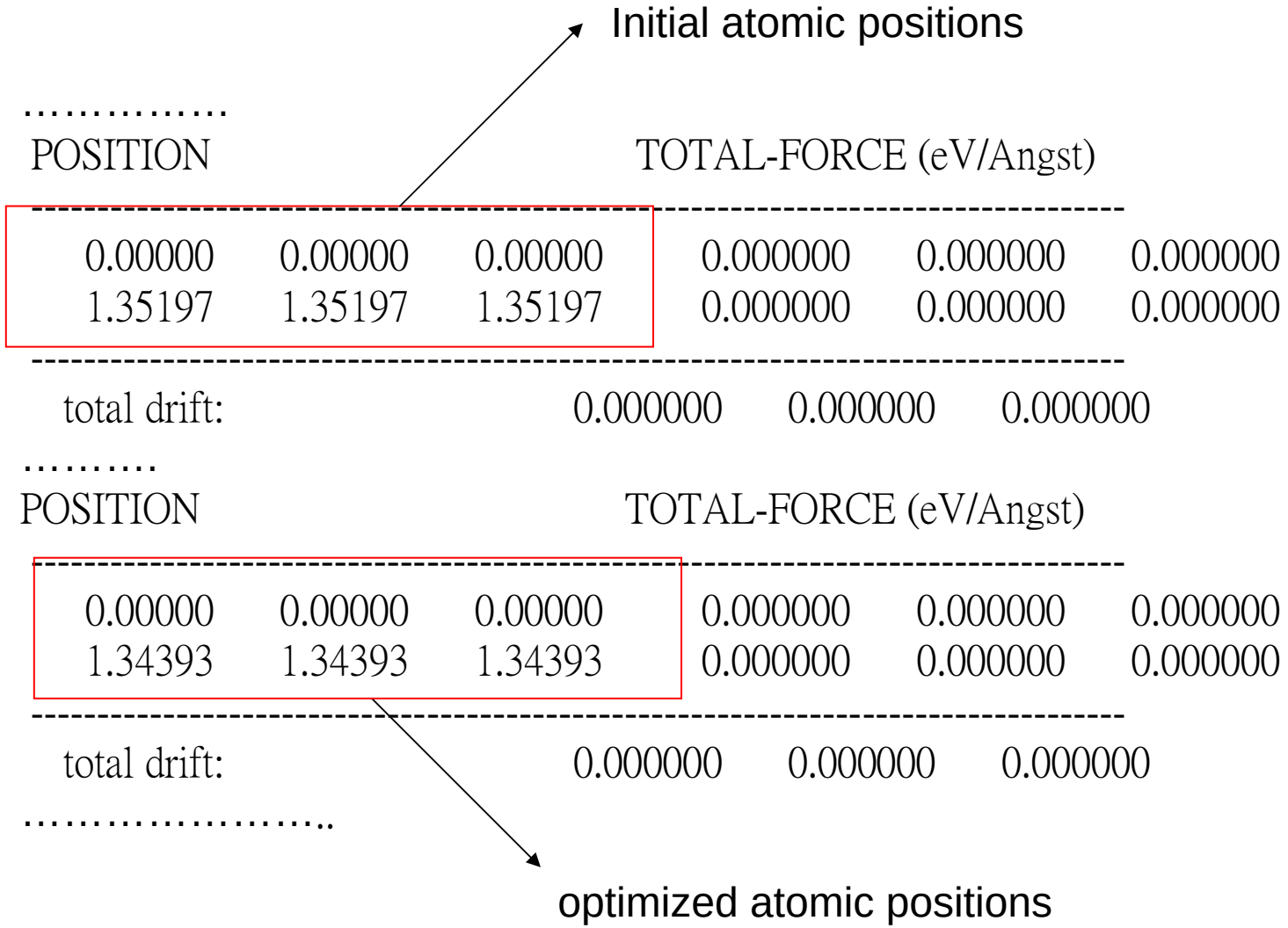
```
1 F= -.11890385E+02 E0= -.11890385E+02  d E =-.118904E+02
2 F= -.11891571E+02 E0= -.11891571E+02  d E =-.118571E-02
3 F= -.11892049E+02 E0= -.11892049E+02  d E =-.166363E-02
```

CONTCAR: optimized lattice structure

```
Si Diamond
   5.375700000000000
    0.0000000000000000    0.5029912498056555    0.5029912498056555
    0.5029912498056555    0.0000000000000000    0.5029912498056555
    0.5029912498056555    0.5029912498056555    0.0000000000000000
  2
Direct
 0.0000000000000000  0.0000000000000000  0.0000000000000000
 0.2500000000000000  0.2500000000000000  0.2500000000000000

 0.00000000E+00  0.00000000E+00  0.00000000E+00
 0.00000000E+00  0.00000000E+00  0.00000000E+00
```

OUTCAR:


Initial atomic positions
.....
POSITION TOTAL-FORCE (eV/Angst)
0.00000 0.00000 0.00000 0.000000 0.000000 0.000000
1.35197 1.35197 1.35197 0.000000 0.000000 0.000000
total drift: 0.000000 0.000000 0.000000
.....
POSITION TOTAL-FORCE (eV/Angst)
0.00000 0.00000 0.00000 0.000000 0.000000 0.000000
1.34393 1.34393 1.34393 0.000000 0.000000 0.000000
total drift: 0.000000 0.000000 0.000000
.....
optimized atomic positions

Homework

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

- Compare the previously obtained LDA DOS and BS with the optimized DOS and BS of Si(Dia) and C(Dia)
- Compare the previously obtained GGA DOS and BS with the optimized DOS and BS of Fe(BCC), Co(HCP), and Ni(FCC)
- Compare the optimized lattice constant with exp. Lattice constant of the above 5 cases
- Compare the magnetic moment of exp. lattice and optimized lattice of the last 3 cases