The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1855-14

School and Workshop on Highly Frustrated Magnets and Strongly Correlated Systems: From Non-Perturbative Approaches to Experiments

30 July - 17 August, 2007

Ab initio calculations

Roser Valenti

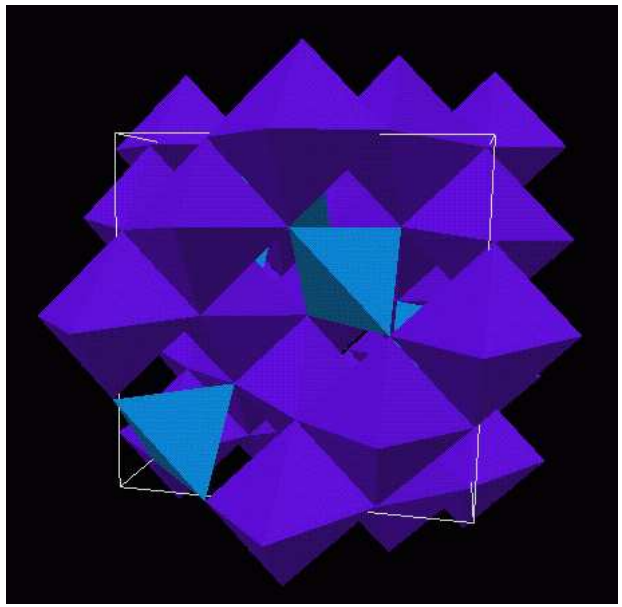
Institut fur Theoretische Physik,
J.W.Goethe-Universitat Frankfurt, Germany

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

Ab initio calculations

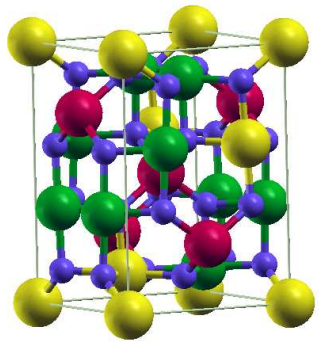
Roser Valentí

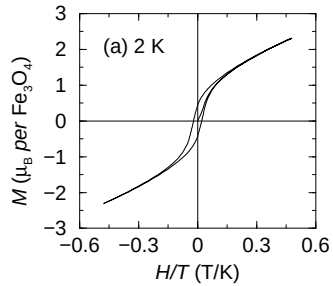
Institut für Theoretische Physik,
J.W.Goethe-Universität Frankfurt

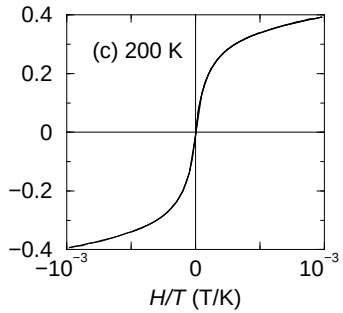


Introduction

- **Electronic structure calculations**
  - **tools to understand properties of matter**
  - **allow predictions for real materials**







spinel $GaZnFe_2O_4$

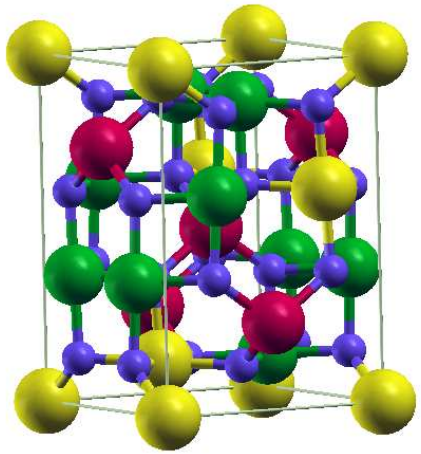
- **Microscopic description**

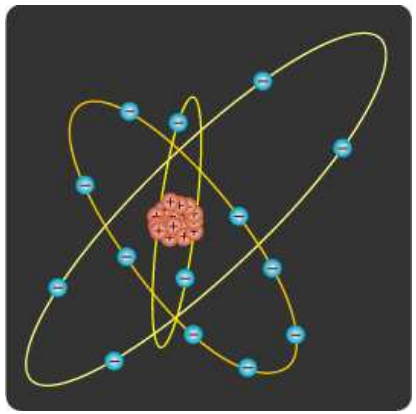
***ab initio* Density Functional Theory**

first principles theory derived from the fundamental equations for the electrons and nuclei

Microscopic description

- **solid with N Electrons, M Ions:**





write fundamental equations for electrons and nuclei

Interaccions in the solid

- **N Electrons, M Ions:**

$$T_s = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m_e}, \qquad V_{e-e} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{k,k',k\neq k'}^{N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

$$T_i = \sum_{l=1}^{M} \frac{\mathbf{P}_l^2}{2M_l}, \qquad V_{i-i} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{l,l',l\neq l'}^{M} \frac{e^2}{|\mathbf{R}_l - \mathbf{R}_{l'}|}$$

$$V_{e-i} = \sum_{l=1}^{M}\sum_{k=1}^{N} v^i(|\,\mathbf{R}_l - \mathbf{r}_k\,|)$$

- **many-body Schrödinger equation:**

$$\boxed{(T_s + T_i + V_{e-e} + V_{e-i} + V_{i-i})\Psi = E\Psi} \qquad \Psi = \Psi(\{\mathbf{r}_k, \sigma_k\}, \{\mathbf{R}_l\})$$

- **adiabatic approximation:**

$$\boxed{(T_s + V_{e-e} + V_{ext})\Phi = E_e\Phi} \qquad \Phi = \Phi(\{\mathbf{r}_k, \sigma_k\}) \sim 10^{23} \text{ degrees of freedom!}$$

Approaches

Microscopic description

ab initio calculations

Density Functional Theory

Effective models

many−body methods

ab initio DFT + **many−body methods**

Density Functional Theory (DFT)

- **Hohenberg-Kohn theorem:** (1964) **W. Kohn: Nobel Prize 1998**

(i) The total energy, of a system of interacting electrons in an external potential is given exactly as a functional of the ground state electronic density, n:

$$E = E[n]$$

(ii) The true ground state density is the density that minimizes $E[n]$.

Density Functional Theory (DFT)

- **Hohenberg-Kohn theorem:** (1964) **W. Kohn: Nobel Prize 1998**

(i) The total energy, of a system of interacting electrons in an external potential is given exactly as a functional of the ground state electronic density, n:

$$E = E[n]$$

(ii) The true ground state density is the density that minimizes $E[n]$.

- **Kohn-Sham ansatz:** (1965)

replace the original many-body problem by an auxiliary independent-particle problem.

$$n_{interacting} = n_{independent}$$

$$\boxed{E[n] = T_S[n] + E_{ext}[n] + E_{Hartree}[n] + E_{xc}[n]}$$

$E_{Hartree}$: Hartree component of the electron-electron energy

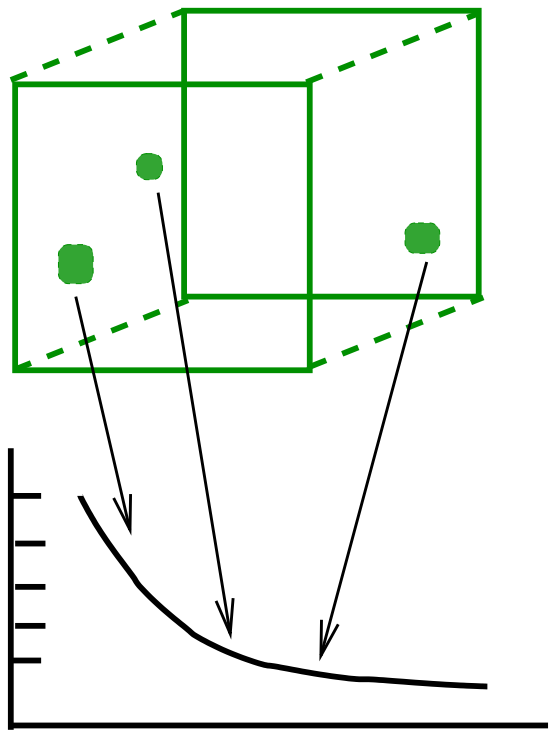
$$E_{Hartree}[n] = \frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$E_{xc}[n]$: exchange-correlation energy

Local Density Approximation (LDA)

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \hat{E}_{xc}(n(\mathbf{r}))$$

$\hat{E}_{xc}(n(\mathbf{r}))$ is approximated by a local function of the density.



$-\hat{E}_{xc}$ Ceperley-Adler homogeneous electron gas (QMC)

n

Local Density Approximation (LDA)

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \hat{E}_{xc}(n(\mathbf{r}))$$

$\hat{E}_{xc}(n(\mathbf{r}))$ is approximated by a local function of the density.

- **Kohn-Sham equations:**

$$(T + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r}))\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where

$n(\mathbf{r}) = \sum_{occ} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$ $\psi_i(\mathbf{r})$ are *single* particle orbitals.

$$V_{Hartree}(\mathbf{r}) = \frac{\delta E_{Hartree}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Solve self-consistently.

Basis Set:

- **Plane wave methods :**

  use of plane waves to solve the Kohn-Sham equations

- **Localized atomic(-like) orbitals (LCAO):**

  basis that captures the atomic-like features of solids and molecules

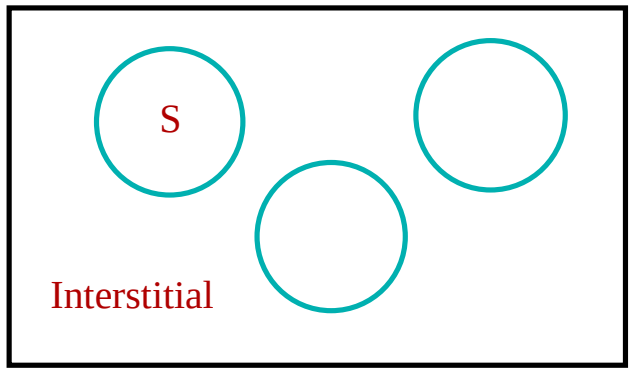
- **Atomic sphere methods:**

  efficient representation of atomic-like features that are rapidly varying near each nucleus and smoothly varying functions between the atoms

Basis Set:

→ **APW**.- Augmented Planewave

$$\psi_k(\mathbf{r},E) = \begin{cases} \frac{1}{\Omega^{1/2}} \sum_G c_G e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} & r \varepsilon I \\ \sum_{lm} A_{lm}^{\mathbf{k}} u_l(r,E) Y_{lm}(\mathbf{r}) & r \varepsilon S \end{cases}$$



$$\{-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l\} r u_l(r) = 0$$

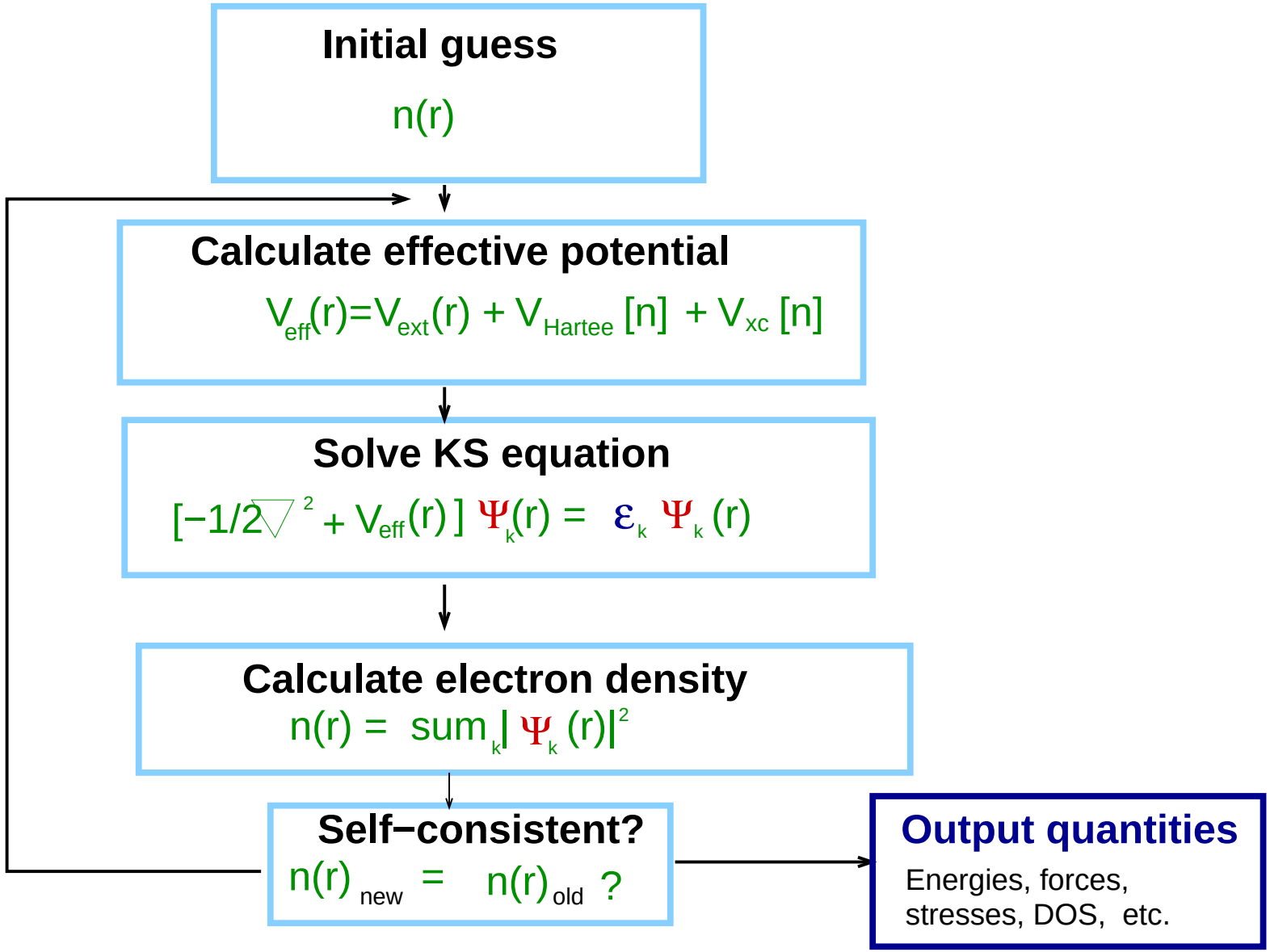
→ **MTO**.- Muffin Tin Orbitals

$$\psi_L(\mathbf{r},E) = \begin{cases} K_l(r) Y_L(\mathbf{r}) & r \varepsilon I \\ N_L(E) u_l(r,E) Y_L(\mathbf{r}) + P_L(E) J_l(r) Y_L(\mathbf{r}) & r \varepsilon S \end{cases}$$

$J_l(\mathbf{r}), K_l(\mathbf{r})$ Bessel Functions $L = lm$

- calculation of the Energy bands through the KKR - equation *(Tail-cancellation theorem).*

Self-consistent Kohn-Sham equations



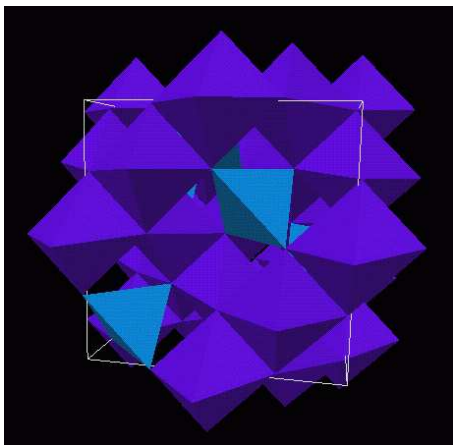
DFT - LDA what do we calculate?

- **chemical bonding**
- **electronic structure and electronic densities**
- **densities of states**

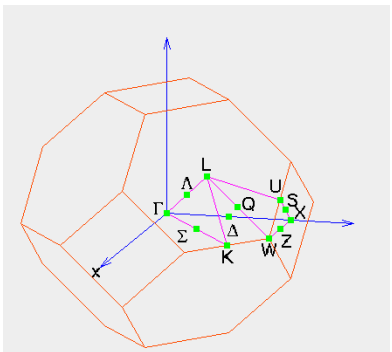
Example

non-magnetic spinel $ZnGa_2O_4$

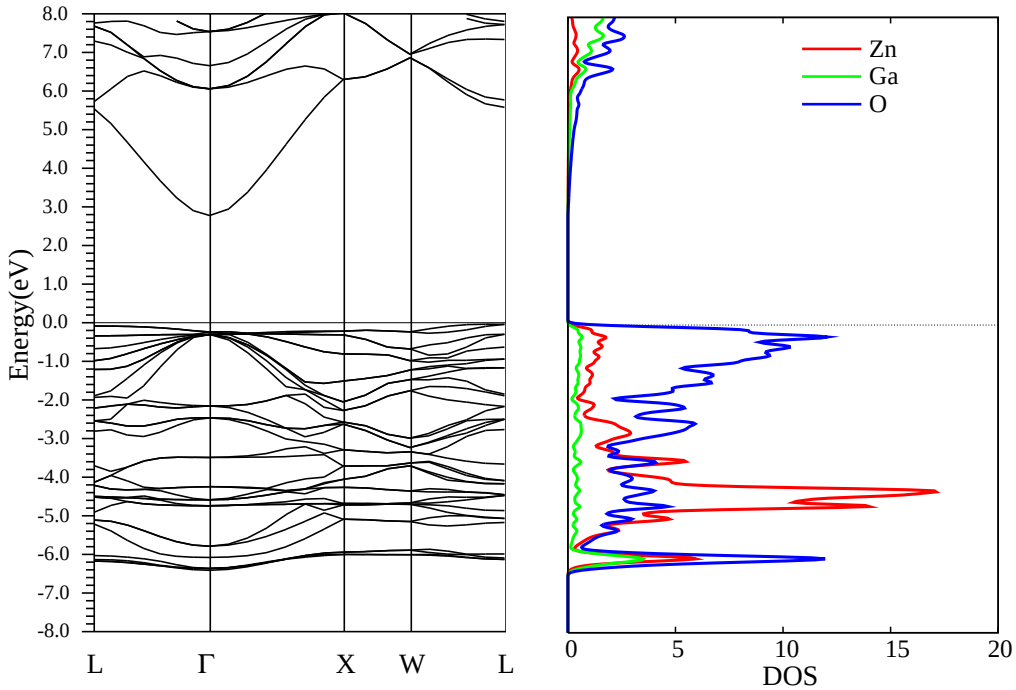
Zn^{2+} - Ga^{3+} filled-shell semiconductor



direct space

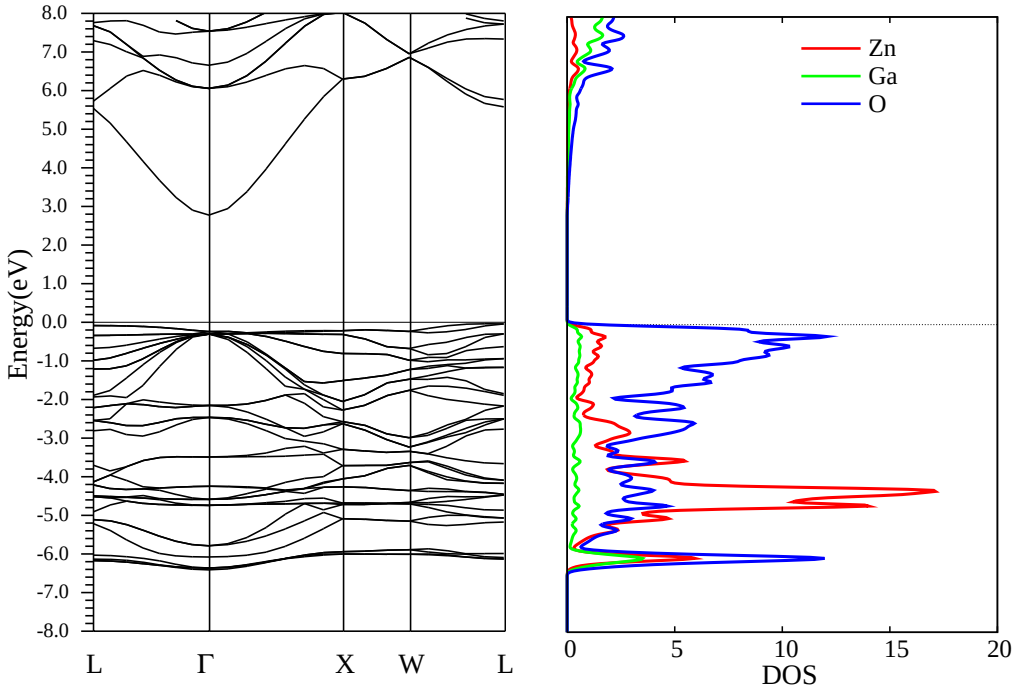


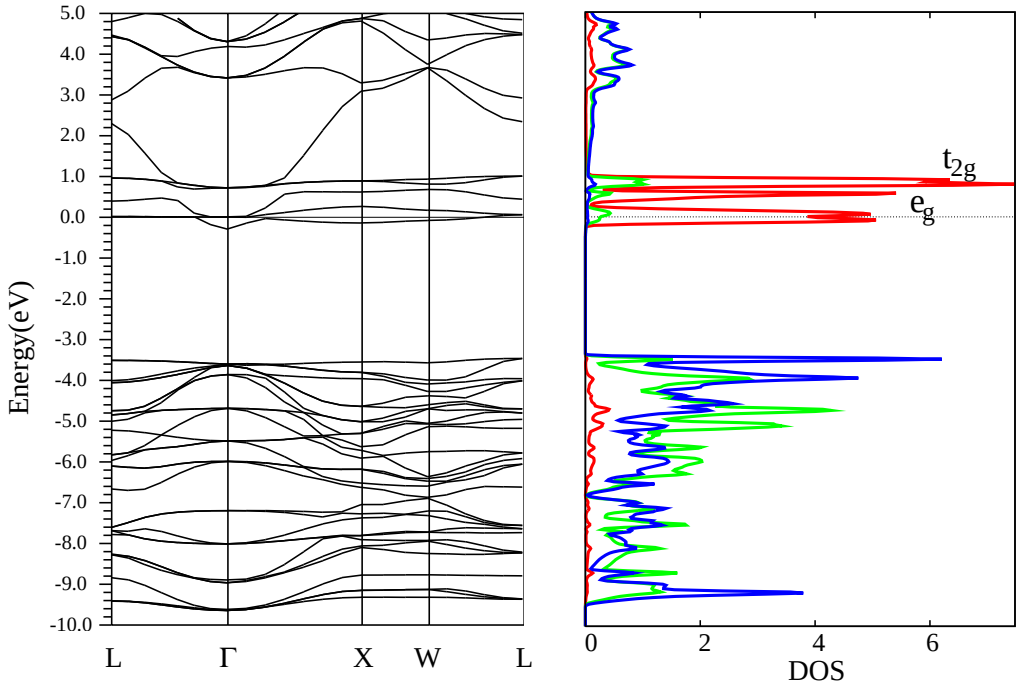
reciprocal space



DFT - LDA

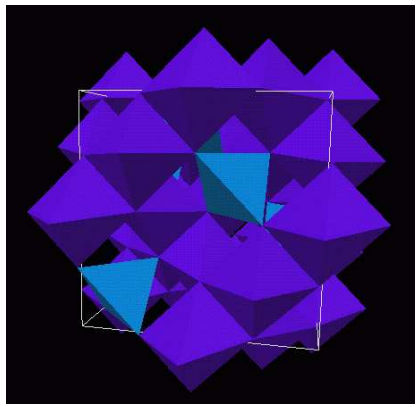
Example





non-magnetic spinel $ZnGa_2O_4$

Zn^{2+} - Ga^{3+} filled-shell semiconductor



magnetic spinel $Fe_xZn_{1-x}Ga_2O_2O_2$

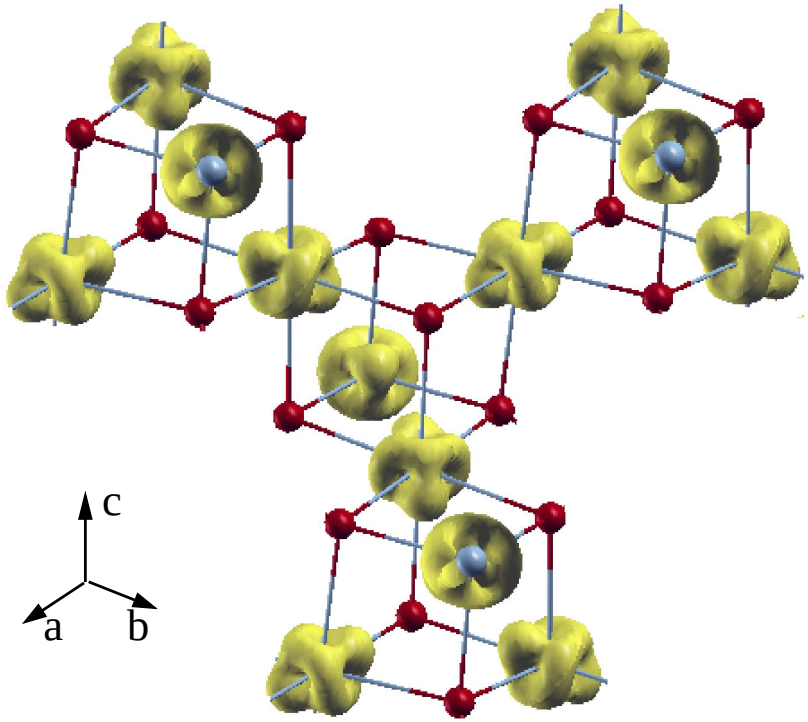
(spin down channel) metallic behaviour

Fe: $3d^{5\uparrow}d^{1\downarrow}$

DFT - LDA

- **electronic density at the Fermi level** **n(r)**

ZnV_2O_4



DFT - LDA drawbacks

but ...

→ **non-local exchange and**

electron-correlations are not correctly described

f.i. FeO, CoO, NiO are predicted to be metals while they are insulators

(Mott insulators)

Implementations

- **LDA+U**
- **LDA+DMFT (Dynamical Mean Field Theory)**
- **DFT + effective models**

LDA+U

Anisimov, Zaanen, Andersen, Phys. Rev. B **44**,943 (1991)

- **Based on the Hubbard model:**

$$H_{Hu} = -\sum_{<i,j>,\sigma} t_{ij} [\hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + \hat{c}^{\dagger}_{j,\sigma} \hat{c}_{i,\sigma}] + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$

- approach not anymore rigorously *ab initio* $\rightarrow U$

- **Functional:**

$$E = E^{LDA} - \frac{U}{2} N(N-1) + \frac{U}{2} \sum_{j,k,\sigma} n_{j,\sigma} n_{k,-\sigma}$$

  - 2nd term substracts the average Coulomb interaction of the N(N-1)/2 pairs
  - 3rd term Coulomb interaction betwen orbital pairs $\rightarrow$ orbital polarization

- **Janak's theorem:**

$$\frac{\partial E}{\partial n_k} = \varepsilon_k, \quad \varepsilon_k = \varepsilon_k^{LDA} + U(\frac{1}{2} - n_k)$$

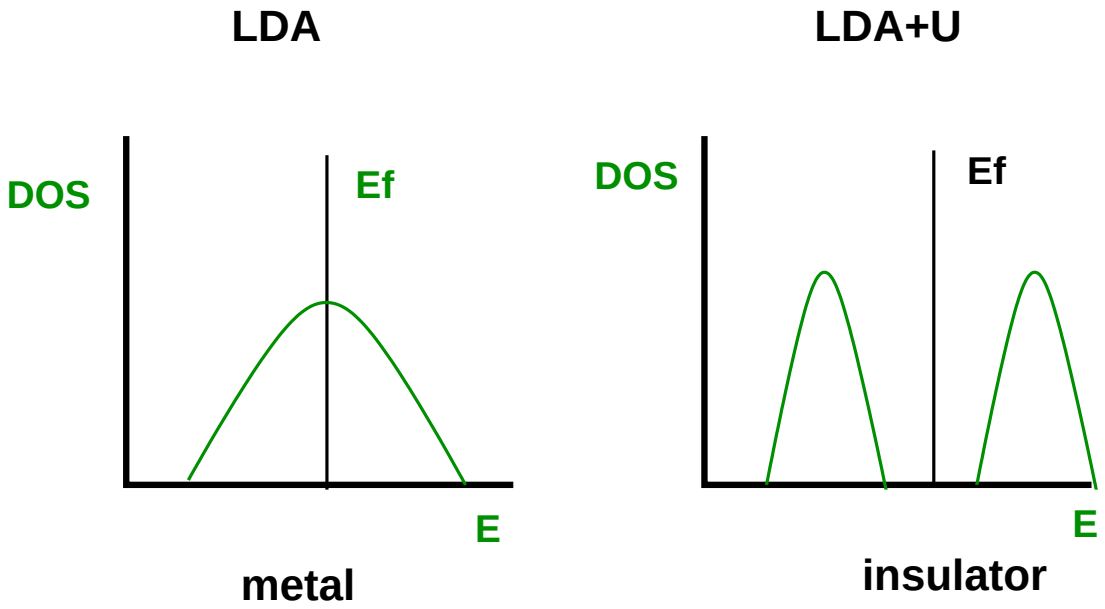
LDA+U

Anisimov, Zaanen, Andersen, Phys. Rev. B **44**,943 (1991)

- **Inclusion of exchange correlation J (Hund's exchange):**

$$E = E^{LDA} - \frac{U}{2}N(N-1) + \frac{J}{2}[N^{\uparrow}(N^{\uparrow}-1) + N^{\downarrow}(N^{\downarrow}-1)] + \frac{U}{2}\sum_{j,k,\sigma} n_{j,\sigma} n_{k,-\sigma} + \frac{1}{2}(U-J)\sum_{i\neq j,\sigma} n_{i,\sigma} n_{j,\sigma}$$

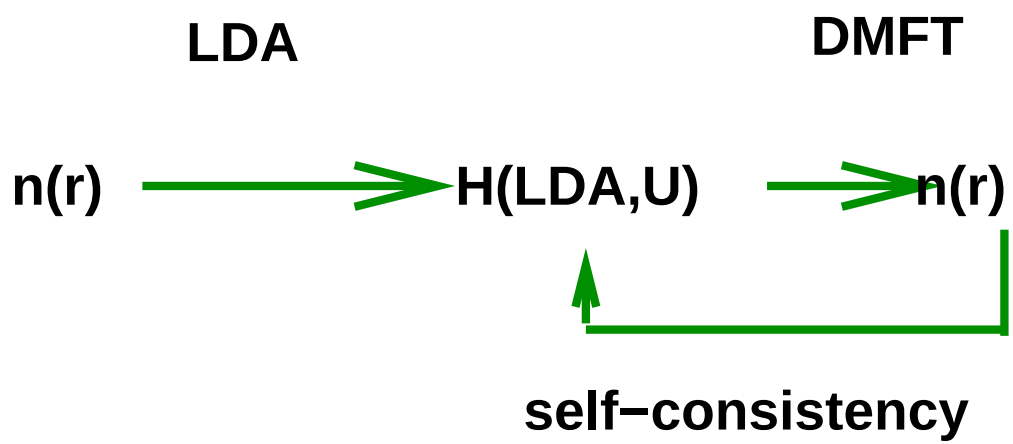
  - electrons with the same spin feel interaction $U - J$
  - electrons with different spin feel interaction U



LDA+DMFT

G. Kotliar, A. Georges, D. Vollhardt, A. Lichtenstein,. . .

- **Missing in LDA and LDA+U is the quasiparticle physics**
- **first attempt to combine a one-electron method (LDA) with a many-body method (DMFT)**
- **Dynamical Mean Field Theory (DMFT):**
  - **idea: replace a lattice model by a single-site quantum impurity**
  - **the impurity model offers an intuitive picture of the local dynamics of a quantum many-body system**
  - **full account of local quantum fluctuations**



ab initio + effective models

- **Density Functional Theory.- Electronic structure**

↓ ***downfolding* of the bandstructure + electron correlation**

(LDA+U, LDA+DMFT)

Effective Model **Hubbard, Heisenberg, t-J,..**

↓

- **Many-body methods**.- Bond-Operator Theory, variational Ansätze, DMRG, QMC, ...

↓

Physical Picture

Tutorial

- **Discuss various Basis sets**
- **Discuss various E_{xc}**
- **Discuss a DFT code (f.i. WIEN2k) step by step**
- **Discuss properties to be calculated with DFT (f.i. phonon calculations, relaxed structures, ...)**