Electronic structure of strongly correlated materials
Part I

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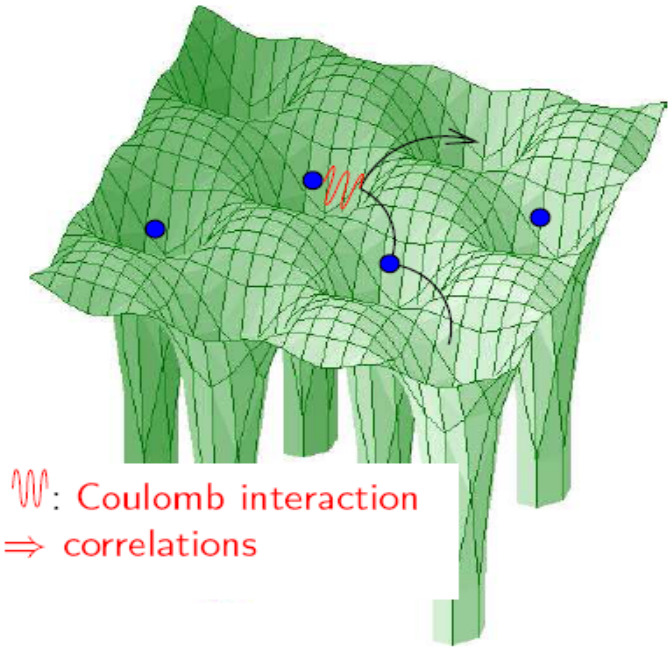
Outline

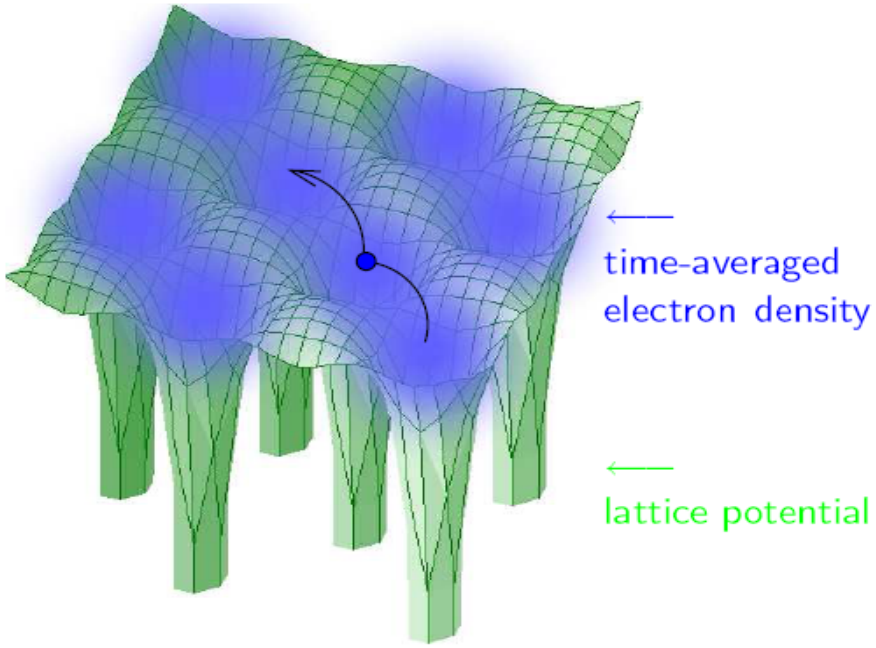
- **Density Functional Theory**
- **Wannier functions and Hamiltonian construction**
- **Static mean-field approximation: LDA+U method**
- **LDA+U method applications to real materials with orbital, charge and spin order**
- **Dynamical mean-filed theory (DMFT), impurity solvers**
- **LDA+DMFT method and its applications to strongly correlated metals and paramagnetic insulators**
- **Electronic structure and correlation effects**

Problem

Correlated electrons
motion with full
Coulomb interaction

Independent electrons
motion with static mean-field
Coulomb interaction potential
from Density Functional Theory



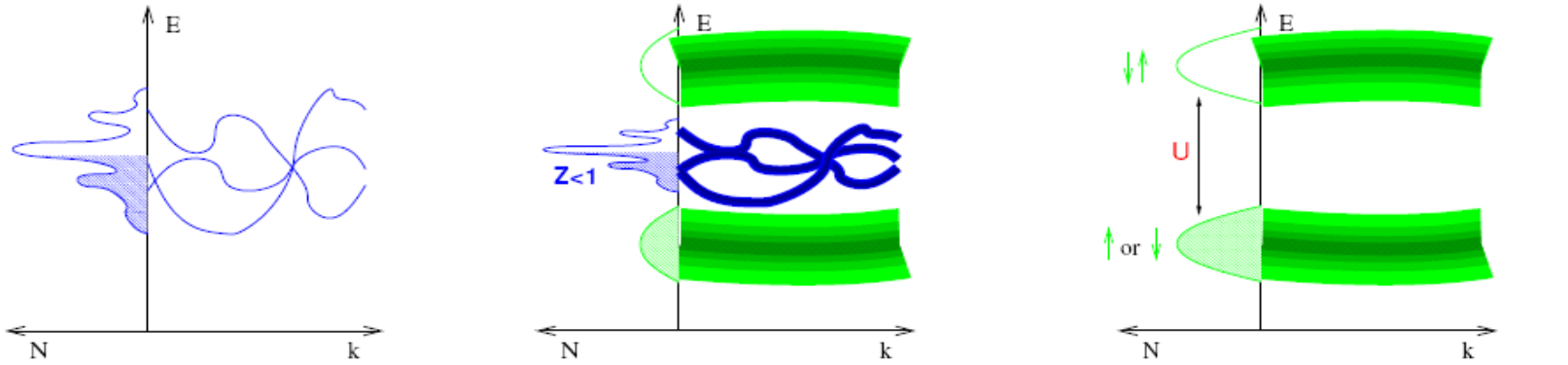


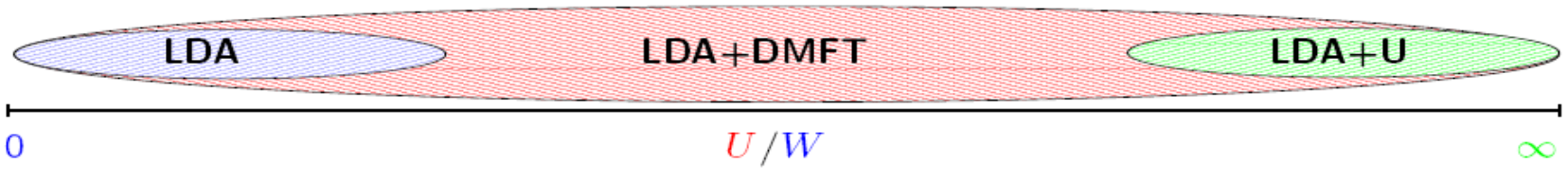
Problem

Weakly correlated systems

Strongly correlated metals

Localized electrons in Mott insulators



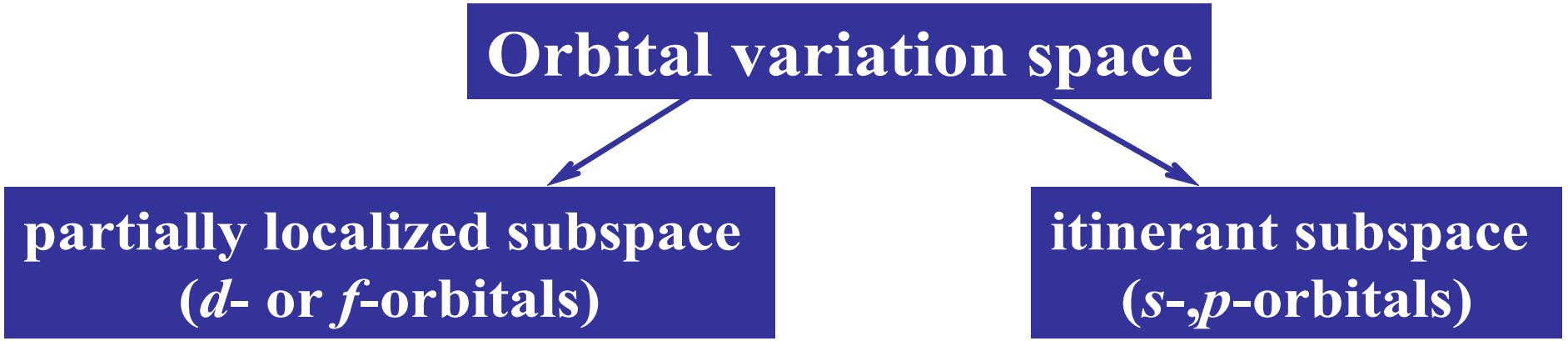


Problem

Coulomb correlations problem

Model Hamiltonians	**Density Functional Theory**
Hubbard and Anderson models	**LDA**
unknown parameters	***ab-initio***
many-body	**one-electron**
explicit Coulomb correlations	**averaged Coulomb interaction**

combined LDA+U and LDA+DMFT approaches
(GW, Time Dependent DFT are also a promising way)



L(S)DA calculations produces:

- **one-particle Hamiltonian for itinerant states**
- **one-particle non-interacting Hamiltonian for localized states**
- **hybridization term between localized and itinerant states**
- **Coulomb interaction parameters (direct *U* and exchange *J*) for localized states**

Many-electrons equations

$$H\Psi = E\Psi$$

where $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ is many electron wave function depending on

$\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$ coordinates of all N electrons

Hamiltonian is a sum of one-electron and many-electron (Coulomb interaction) parts

$$H = \sum_{\mu=1}^{N} H_\mu + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\substack{\nu=1 \\ \nu \neq \mu}}^{N} \frac{e^2}{|\mathbf{x}_\mu - \mathbf{x}_\nu|}$$

Many-electrons equations

$$H_\mu = -\frac{\hbar^2}{2m}\nabla_\mu{}^2 + V_Z(\mathbf{x}_\mu)$$

$$V_Z = -\frac{Ze^2}{|\mathbf{x}_\mu|}$$

Kinetic energy
and nuclear charge
potential energy contributions
to one-electron Hamiltonians

Electrons variables separation leads to one-electron approximation:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = u_1(\mathbf{x}_1)u_2(\mathbf{x}_2)\ldots u_N(\mathbf{x}_N)$$

u_μ is one-electron wave function

Hartree-Fock approximation

$$\Psi = \frac{1}{\sqrt{N}} \begin{vmatrix} u_1(\mathbf{x}_1) & u_1(\mathbf{x}_2) & \dots & u_1(\mathbf{x}_N) \\ u_2(\mathbf{x}_1) & u_2(\mathbf{x}_2) & \dots & u_2(\mathbf{x}_N) \\ . & . & . & . \\ . & . & . & . \\ u_N(\mathbf{x}_1) & u_N(\mathbf{x}_2) & \dots & u_N(\mathbf{x}_N) \end{vmatrix}$$

Slater determinant satisfies antisymmetric properties of fermionic wave function

Hartree-Fock equations

$$H_\mu u_\mu(\mathbf{x}_\mu) + \sum_{\nu=1}^{N} \int u^*_\nu(\mathbf{x}_\nu) \frac{2}{|\mathbf{x}_\mu - \mathbf{x}_\nu|} \{u_\nu(\mathbf{x}_\nu) u_\mu(\mathbf{x}_\mu) -$$

$$\delta_{\sigma(\mu),\sigma(\nu)} u^*_\nu(\mathbf{x}_\mu) u_\mu(\mathbf{x}_\nu)\} \mathbf{dx}_\nu = \varepsilon_\mu u_\mu(\mathbf{x}_\mu), \quad 1 \le \mu \le N$$

Mean-field potential with direct and exchange parts.
Terms with $\mu = \nu$ explicitly cancel self-interaction.

Hartree-Fock equations

$$H_\mu u_\mu(\mathbf{x}_\mu) + \left(\sum_{\nu=1}^{N} \int u^*_\nu(\mathbf{x}_\nu) \frac{2}{|\mathbf{x}_\mu - \mathbf{x}_\nu|} u_\nu(\mathbf{x}_\nu) \mathbf{dx}_\nu \right) u_\mu(\mathbf{x}_\mu) -$$

$$\delta_{\sigma(\mu),\sigma(\nu)} \sum_{\nu=1}^{N} \left(\int u^*_\nu(\mathbf{x}_\nu) \frac{2}{|\mathbf{x}_\mu - \mathbf{x}_\nu|} u_\mu(\mathbf{x}_\nu) \mathbf{dx}_\nu \right) u_\nu(\mathbf{x}_\mu) = \varepsilon_\mu u_\mu(\mathbf{x}_\mu), 1 \le \mu \le N$$

Direct terms can be expressed via electron density:

$$V_H(\mathbf{x}) = \sum_\nu \int u^*_\nu(\mathbf{s}) \frac{2}{|\mathbf{x}-\mathbf{s}|} u_\nu(\mathbf{s}) \mathbf{ds} = \int \rho(\mathbf{s}) \frac{2}{|\mathbf{x}-\mathbf{s}|} \mathbf{ds}$$

$$\rho(\mathbf{s}) = \sum_\nu u^*_\nu(\mathbf{s}) u_\nu(\mathbf{s})$$

$$\nabla^2 V_H = 8\pi\rho$$

Hartree-Fock equations

Exchange terms can be written as a sum of pair potentials:

$$V_{\mu\nu}(\mathbf{x}) = \int u_\nu^*(\mathbf{s}) \frac{2}{|\mathbf{x}-\mathbf{s}|} u_\mu(\mathbf{s}) d\mathbf{s}$$

Hartree-Fock equations have a form:

$$\{-\nabla^2 + V_Z + V_H\} u_\mu - \sum_\nu \delta_{\sigma(\mu),\sigma(\nu)} V_{\mu\nu} u_\nu = \varepsilon_\mu u_\mu$$

Orbital dependent potential that couples equations in the system with each other

Slater approximation for exchange

Exchange potential for homogeneous electron gas:

$$V_{ex}(\mathbf{x}) = -6\left(\frac{3\rho(\mathbf{x})}{8\pi}\right)^{1/3}$$

Local density approximation:

$$\{-\nabla^2 + V_Z + V_H + V_{exc}\}u_\mu = \varepsilon_\mu u_\mu$$

Decoupled one-electron equations

Density Functional

According to Hohenberg-Kohn theorem that is a basis of DFT, all ground state properties of inhomogeneous interacting electron gas can be described by minimization of the total energy as a functional of electron density $\rho(\mathbf{r})$:

$$E[\rho] = T[\rho] + \int d\mathbf{r}\rho(\mathbf{r})V_{ext}(\mathbf{r}) + \int d\mathbf{r}\rho(\mathbf{r}) \int \frac{\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r}' + E_{xc}[\rho]$$

where $T[\rho]$ is kinetic energy, $V_{ext}(\mathbf{r})$ - external potential acting on electrons (usually that is attractive nuclear potential), third term describes Coulomb interaction energy (Hartree energy) corresponding to charge distribution $\rho(\mathbf{r})$ and E_{xc} is so called exchange-correlation energy.

Electron density variation

For practical applications $\rho(\mathbf{r})$
can be expressed via one-electron wave functions $\varphi_i(\mathbf{r})$:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} | \phi_i(\mathbf{r}) |^2$$

where N is total number of electrons.
To minimize the functional one need to vary it over new variables $\varphi_i(\mathbf{r})$ with additional condition that wave functions are normalized. That leads to the system of Kohn-Sham differential equations:

Kohn-Sham equations

$$\left[-\nabla^2 - \sum_I \frac{2Z_I}{|\,\mathbf{r}-\mathbf{R}_I\,|} + 2\int \frac{\rho(\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|}d\mathbf{r}' + V_{xc}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Here $\mathbf{R}_I$ is position vector for nucleus with charge Z_I ; ε_i are Lagrange multipliers having the meaning of one-electron eigenenergies and exchange-correlation potential V_{xc} is a functional derivative of exchange-correlation energy E_{xc}:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}$$

Eigenvalue ε_i is derivative of the total energy in respect to the occupancy of the corresponding one-electron state n_i:

$$\varepsilon_i = \frac{\partial E_{tot}}{\partial n_i}$$

In Hartree-Fock $\varepsilon_i = E[n_i = 1] - E[n_i = 0]$

Local Density Approximation (LDA)

DFT applications are based predominantly on so called Local Density Approximation (LDA) where exchange-correlation energy is defined as an integral over space variables ***r*** with an expression under integral depending only on local value of electron density $\rho(\mathbf{r})$:

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))d\mathbf{r}$$

Here $\varepsilon_{xc}(\rho)$ is contribution of exchange and correlation effects in total energy (per one electron) of homogeneous interacting electron gas with density ρ.

For spin-polarized systems one can use Local Spin Density Approximation (LSDA)

$$E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho^{\uparrow}(\mathbf{r}), \rho^{\downarrow}(\mathbf{r}))d\mathbf{r}$$

Local Density Approximation (LDA)

In Local Density Approximation (LDA) exchange-correlation potential in some space point ***r*** depends only on local value of electron density $\rho(\mathbf{r})$:

$$V_{xc}(\mathbf{r}) = \frac{d}{d\rho}(\rho\varepsilon_{xc}(\rho))$$

An explicit form of exchange-correlation potential as a function of local value of electron density $\rho(\mathbf{r})$ is:

$$V_{xc}(\mathbf{r}) = -(1+0.0316 r_s \ln(1+24.3/r_s))4\left(\frac{3\rho(\mathbf{r})}{8\pi}\right)^{1/3}$$

where $r_s = \left[\frac{3}{4\pi\rho}\right]^{1/3}$

Pure exchange potential:

$$V_{ex}(\mathbf{r}) = -4\left(\frac{3\rho(\mathbf{r})}{8\pi}\right)^{1/3}$$

Bloch functions in crystal

Kohn-Sham equations for periodic crystal (translational invariant potential *V(**r**+**l**)= V(**r**)*, ***l*** is lattice translation vector):

$$H\psi(\mathbf{r}) = \{-\nabla^2 + V(\mathbf{r})\}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Solution satisfying periodicity condition is Bloch function for wave vector ***k*** having a form of a plane wave modulated by periodic function:

$$\psi(\mathbf{r}) \equiv \psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad u_{\mathbf{k}}(\mathbf{r}+\mathbf{l}) = u_{\mathbf{k}}(\mathbf{r})$$

Bloch function satisfies to relation:

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{l}) = \exp(i\mathbf{k}\cdot\mathbf{l})\psi_{\mathbf{k}}(\mathbf{r})$$

Electronic structure calculations methods

Calculations schemes for Kohn-Sham equations are based on variational approach. Wave functions are expressed as series in complete set of basis functions:

$$|\phi_i\rangle = \sum_n a_n^i |\varphi_n\rangle$$

$$\hat{H}|\phi_i\rangle = \varepsilon_i |\phi_i\rangle$$

Equivalent set of linear equations for coefficients a_n^i

$$\sum_n H_{n'n} a_n^i = \varepsilon_i \sum_n O_{n'n} a_n^i$$

Hamiltonian and overlap matrices

$$H_{n'n} = \langle \varphi_{n'} | \hat{H} | \varphi_n \rangle$$

$$O_{n'n} = \langle \varphi_{n'} | \varphi_n \rangle$$

Linearized Muffin-Tin Orbitals (LMTO) method

Existing DFT methods could be divided in two major groups. One of them uses as a basis set atomic-like orbitals centered at atoms and decaying with increasing a distance from the center, for example Muffin-tin orbital (MTO) in Linearized Muffin-Tin Orbitals (LMTO) method :

$$\varphi_{lm}(\mathbf{r}) = \phi_l(|\mathbf{r}|)Y_{lm}(\hat{\mathbf{r}})$$

$$\phi_l(|\mathbf{r}|) = \begin{cases} R_l(|\mathbf{r}|, E) & |\mathbf{r}| < S, \\ C|\mathbf{r}|^{-l-1} & |\mathbf{r}| > S \end{cases}$$

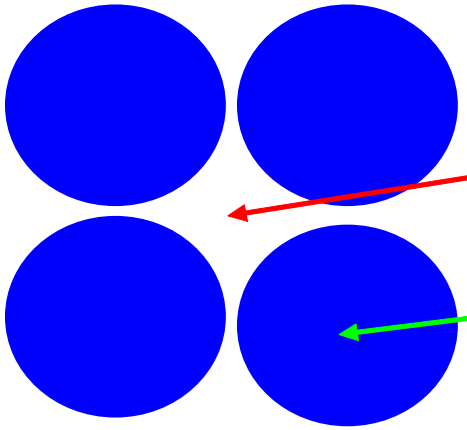
$R_l(|\boldsymbol{r}|,E)$ is radial variable dependent part of Kohn-Sham equation solution for spherically symmetric potential inside atomic sphere with radius S.

Plane wave basis

Another group of DFT methods uses delocalized plane waves as a basis set:

$$|\mathbf{k}-\mathbf{g}\rangle = e^{(\mathbf{k}-\mathbf{g})\mathbf{r}}$$

where ***k*** is wave vector and ***g*** - reciprocal lattice vector.



Plane waves are good basis for
inter-atomic regions
where potential varies slowly
while atomic like orbitals describe better
intra-atomic areas with strong potential
and wave functions variations

Linearized Augmented Plane Waves (LAPW) method

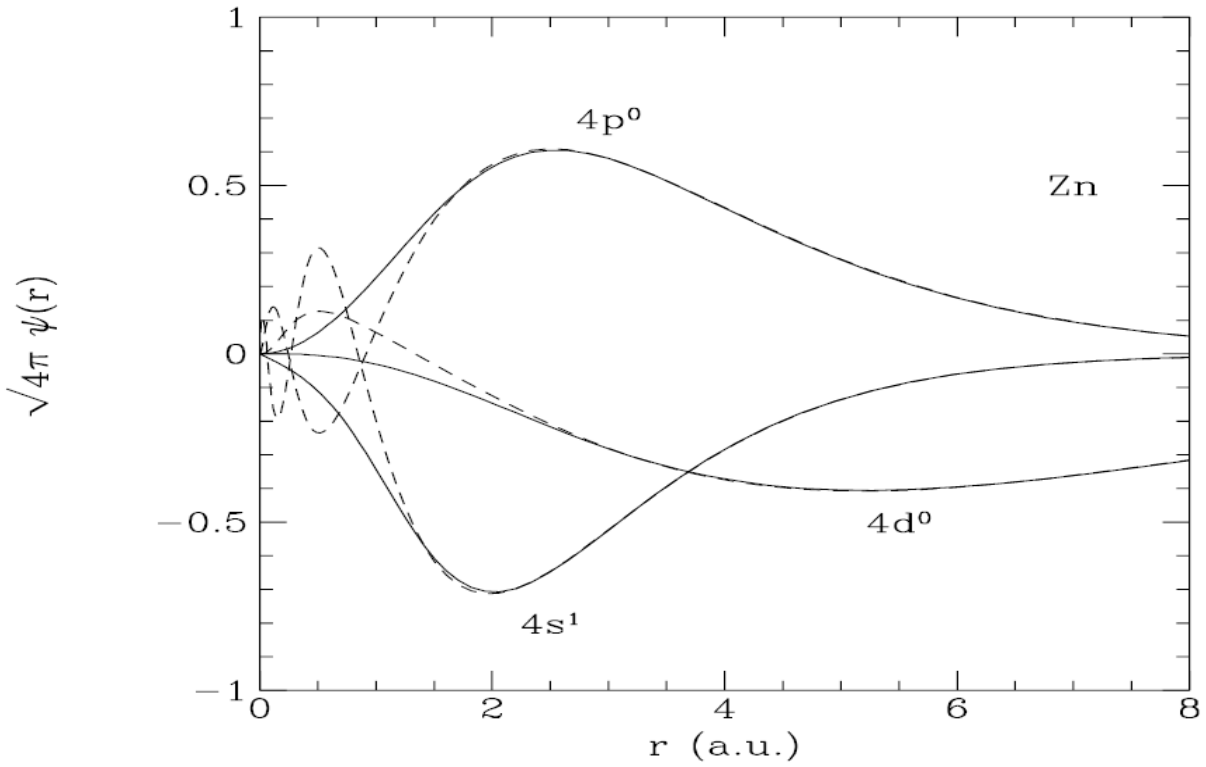
Augmented Plane Wave is defined as

$$|\mathbf{k}-\mathbf{g}\rangle_{LAPW} = \begin{cases} \sum_{lm} b_{lm} R_l(|\mathbf{r}|, E) Y_{lm}(\hat{\mathbf{r}}) & \text{if } |\mathbf{r}| < S \\ C e^{(\mathbf{k}-\mathbf{g})\mathbf{r}} & \text{if } |\mathbf{r}| > S \end{cases}$$

Combined nature of LAPW basis functions allows
good description of Bloch functions in all space regions
(inter-atomic as well as intra-atomic)

Pseudopotential approach

Real potential and wave function are replaced by some pseudopotential and corresponding pseudofunction that coincide with real functions and real potential outside atomic core area



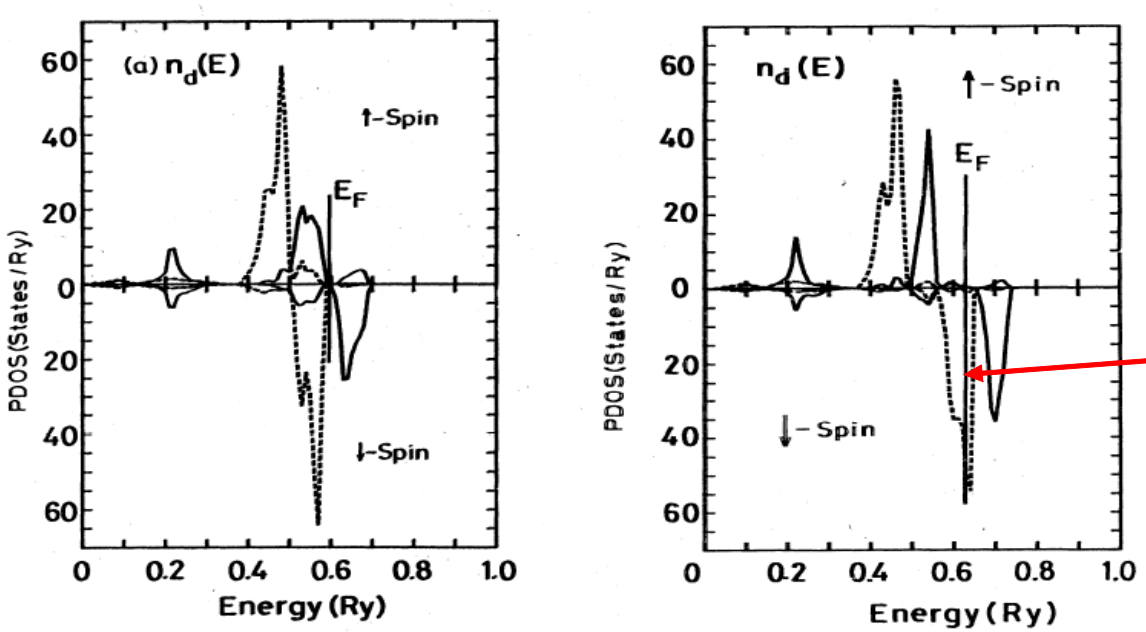
Smooth behavior of pseudofunction inside atomic core area allows to use plane wave basis for whole crystal

Breakdown of LDA for strongly correlated systems

LDA potentials are the same for all orbitals with the possible difference due to exchange interaction:

$$V_\uparrow - V_\downarrow = \frac{\delta E^{LSDA}}{\delta \rho_\uparrow(\mathbf{r})} - \frac{\delta E^{LSDA}}{\delta \rho_\downarrow(\mathbf{r})}$$

NiO CoO



NiO and CoO are experimentally wide gap insulators (Mott insulators) but LSDA gave small gap insulator for NiO and metal for CoO with partially filled t_{2g} spin-down electronic subshell

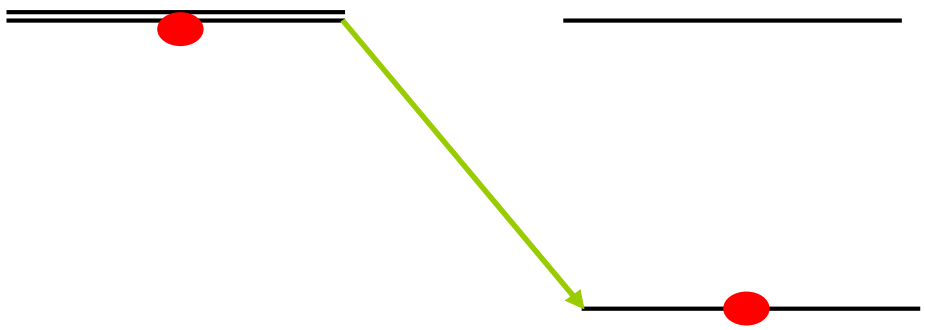
Self-Interaction Correction (SIC) method

Orbital dependent potential with “residual self-interaction” present in LDA explicitly canceled for all occupied states *i*:

$$V_i(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r}) - V_H[\rho_i](\mathbf{r}) - V_{xc}[\rho_i](\mathbf{r})$$

$\rho_i = |\psi_i(\mathbf{r})|^2$ is charge density for state *i*

SIC correction is absent for empty states and so energy separation between occupied and empty states results in energy gap appearance



Corrections to Density Functional Theory

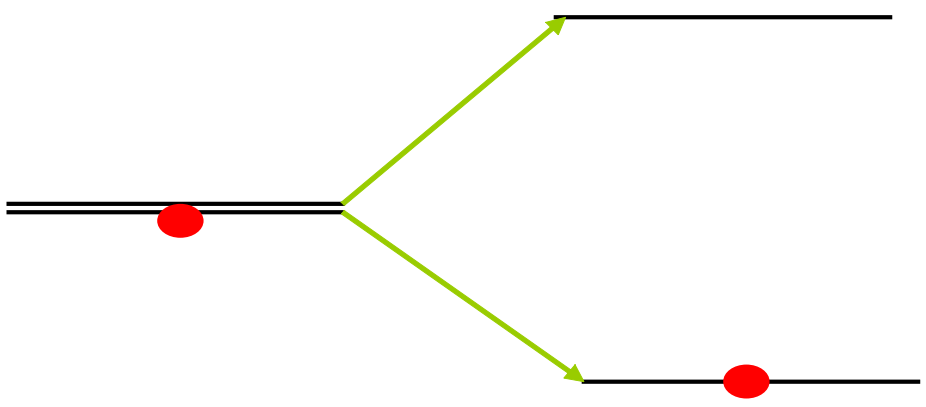
Generalized Transition State (GTS) method

Excitation energy for electron removal from state *i* is
equal to total energy difference between final and initial configurations:

$$\Delta_i = E[n_i = 1] - E[n_i = 0] \approx \epsilon_i(n_i = 1/2) \quad =$$

$$= \tilde{\epsilon}_i^{LDA} + (1/2 - \tilde{n}_i)\frac{\partial \tilde{\epsilon}_i}{\partial \tilde{n}_i}\Big|_{\tilde{n}_i = 1/2} \qquad \text{using:} \qquad \varepsilon_i = \frac{\partial E_{tot}}{\partial n_i}$$

GTS correction is positive for empty states and negative for occupied states
and energy separation between occupied and empty states appears



Many other corrections
were developed to imitate
Mott energy gap:
GW, Optimized Effective potential,
Hybrid Functional *et ct*

Basic models in strongly correlated systems theory

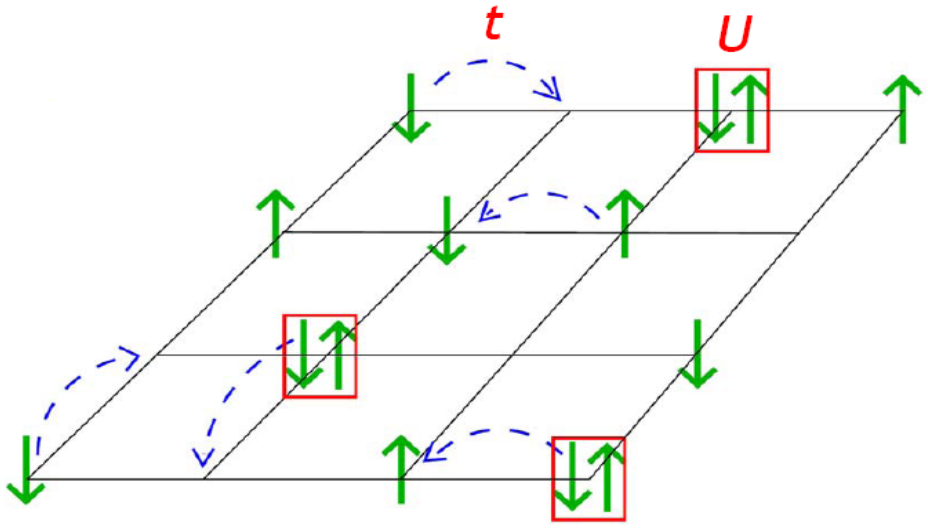
Hubbard model

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} \hat{c}^{+}_{i\sigma} \hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Local Coulomb interaction between electrons with Coulomb parameter *U* defined as an energy needed to put two electrons on the same atomic site:

$$U \equiv E(2) + E(0) - 2E(1)$$

t_{ij} is hopping matrix element describing kinetic energy terms .



Basic models in strongly correlated systems theory

tJ-model

$$\mathcal{H} = t\sum_{ij\sigma}\tilde{c}^{+}_{i\sigma}\tilde{c}_{j\sigma} + J\sum_{ij}(\mathbf{S}^{\mathrm{e}}_{i}\mathbf{S}^{\mathrm{e}}_{j})$$

$\tilde{c}^{+}_{i\sigma} = \hat{c}^{+}_{i\sigma}(1-\hat{n}_{i-\sigma})$ creation operator for correlated electrons,

$J = 4t^2/U$ Anderson kinetic exchange.

tJ-model can be derived from Hubbard model in the limit *U*>>*t*

Basic models in strongly correlated systems theory

Kondo lattice model

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}\sigma} + J \sum_{i} \mathbf{S}_i \mathbf{s}_i$$

S is spin operator for localized electrons,

$$\mathbf{s}_i = \sum_{\mu\nu} \hat{c}^{\dagger}_{i\mu} \boldsymbol{\sigma}_{\mu\nu} \hat{c}_{i\nu}$$

Itinerant electrons spin operator.

Usually is applied to rare-earth elements compounds where 4f-electrons are considered to be completely localized with exchange-only interaction with itinerant metallic electrons

Basic models in strongly correlated systems theory

Periodic Anderson model (PAM)

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} \hat{c}^{+}_{i\sigma} \hat{c}_{j\sigma} + \varepsilon_d \sum_{i\sigma} \hat{n}^{d}_{i\sigma} + U \sum_{i} \hat{n}^{d}_{i\uparrow} \hat{n}^{d}_{i\downarrow} + \sum_{ij\sigma} (V_{ij} \hat{c}^{+}_{i\sigma} \hat{d}_{j\sigma} + V^{*}_{ij} \hat{d}^{+}_{j\sigma} \hat{c}_{i\sigma})$$

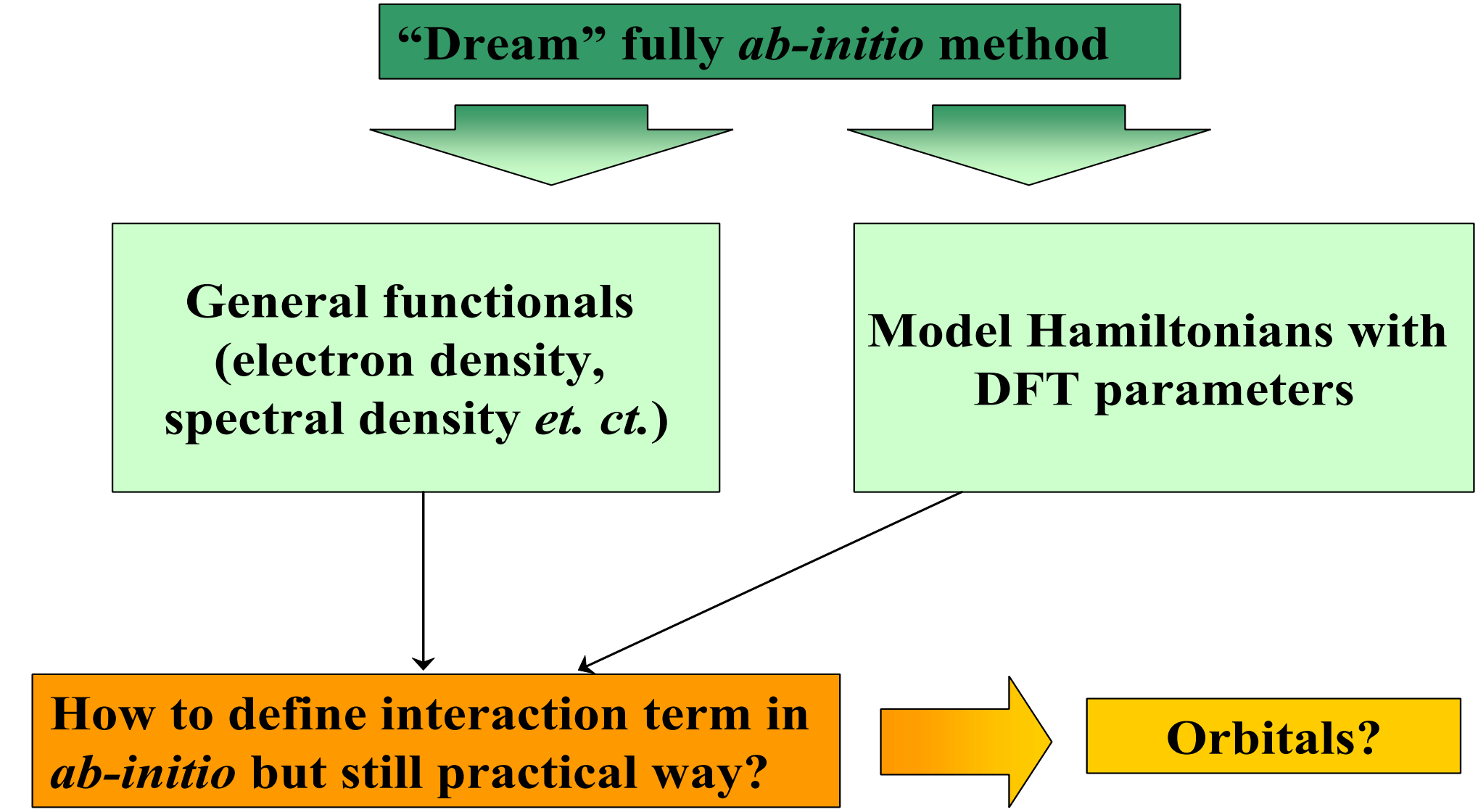
$\hat{c}_{i\sigma}(\hat{c}^{+}_{i\sigma})$ and $\hat{d}_{i\sigma}(\hat{d}^{+}_{i\sigma})$

Fermi operators for itinerant *s*- and localized *d*-electrons respectively

V_{ij} *s-d* hybridization parameter.

If hopping between d-electrons term is added to PAM then the most general model Hamiltonian is defined that gives complete description of any material.

Problem


"Dream" fully *ab-initio* method
General functionals (electron density, spectral density *et. ct.*)
Model Hamiltonians with DFT parameters
How to define interaction term in *ab-initio* but still practical way?
Orbitals?

DFT-input: non-interacting Hamiltonian and Coulomb interaction parameters (H^0, U)

Standard approximation: Green functions are calculated using DOS (N^0) from DFT

(-) *Reliable results only for high-symmetry (cubic) systems*

Self-energy operator for cubic systems:

$$\Sigma(\omega) = \begin{pmatrix} \sigma(\omega) & 0 & \dots & 0 \\ 0 & \sigma(\omega) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \sigma(\omega) \end{pmatrix} \Rightarrow$$

Green function:

$$G(\omega) = \int_{IBZ} (\omega - \Sigma(\omega) - H^0_{LDA}(\mathbf{k}))^{-1} d\mathbf{k} =$$

$$= G^0(\omega - \sigma(\omega)) = \int \frac{N^0(\epsilon)}{\omega - \sigma(\omega) - \epsilon} d\epsilon$$

DFT + correlations: general case

Low-symmetry systems?

General formula using non-interacting Hamiltonian obtained by projection of the correlated states into full-orbital DFT Hamiltonian space

Open questions:

1) Choice of basis for projected Hamiltonian
2) Procedure of projecting

Problem of orbitals definition

What are Hubbard model basis orbitals?

Some kind of atomic-like site-centered localized orbitals without explicit definition. Matrix elements are considered as a fitting parameters.

Why not to use LMTO basis?

Pure atomic orbitals neglect strong covalency effects. For example unoccupied Cu-3d x^2-y^2 symmetry states in cuprates have predominantly oxygen 2p-character.

One need new “physically justified” orbital basis set for Hamiltonian defined on the correlated states subspace

Why Wannier Functions?

Wannier functions in real space [1]:

$$W_i(\mathbf{r}-\mathbf{T}) = \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{T}} \langle \mathbf{r}|\psi_{i\mathbf{k}}\rangle$$ ← Bloch functions

Advantages of Wannier function basis set:

<Explicit form of the orbitals
forming complete basis set

Localized orbitals
Orbitals are centered on atoms } like in Hubbard model

Uncertainty of WF definition for a many-band case:

$$|\psi_{i\mathbf{k}}\rangle = \sum_j U_{ji}^{(\mathbf{k})} |\psi_{j\mathbf{k}}\rangle$$

Unitary matrix

[1] G.H. Wannier, Phys. Rev. **52**, 192 (1937)

Wannier functions and projection

WF in k-space – projection of the set of trial functions [2] (atomic orbitals) into Bloch functions subspace :

$$|\widetilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle\langle\psi_{i\mathbf{k}}|\phi_n\rangle$$

Bloch functions in DFT basis (LMTO or plane waves):

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_j c_{ji}(\mathbf{k})\phi_j^{\mathbf{k}}(\mathbf{r})$$

Eigenvector element

Bloch sums of LMTO orbitals

$$|\widetilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2}\sum_j c_{ji}(\mathbf{k})c_{ni}^{\star}(\mathbf{k})|\phi_j^{\mathbf{k}}\rangle = \sum_j \tilde{b}_{jn}^{\mathbf{k}}|\phi_j^{\mathbf{k}}\rangle$$

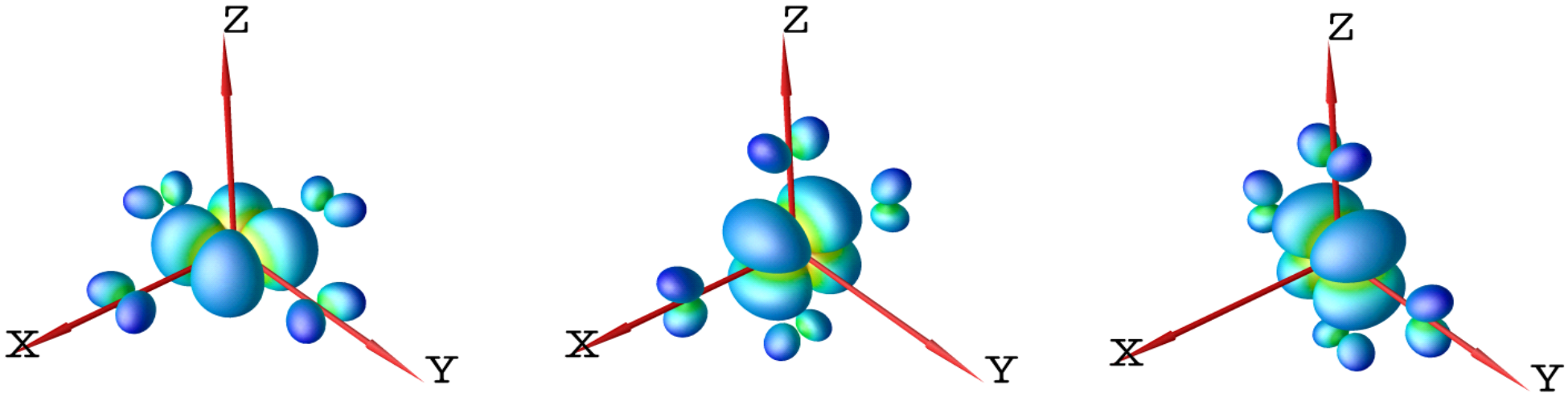
coefficients of WF expansion in LMTO-orbitals:

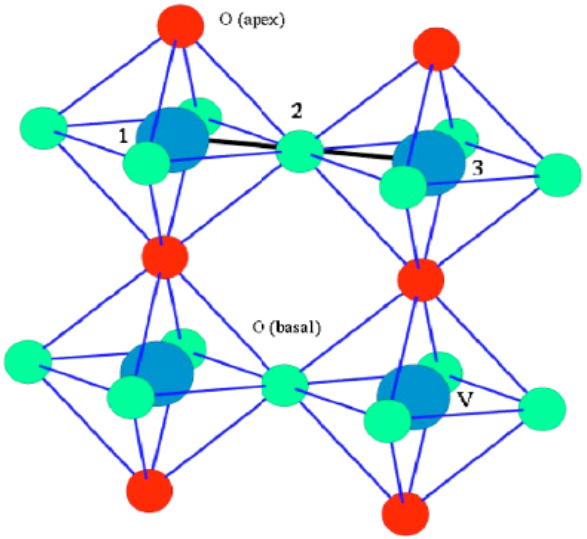
$$\tilde{b}_{jn}^{\mathbf{k}} = \sum_{i=N_1}^{N_2} c_{ji}(\mathbf{k})c_{ni}^{\star}(\mathbf{k})$$

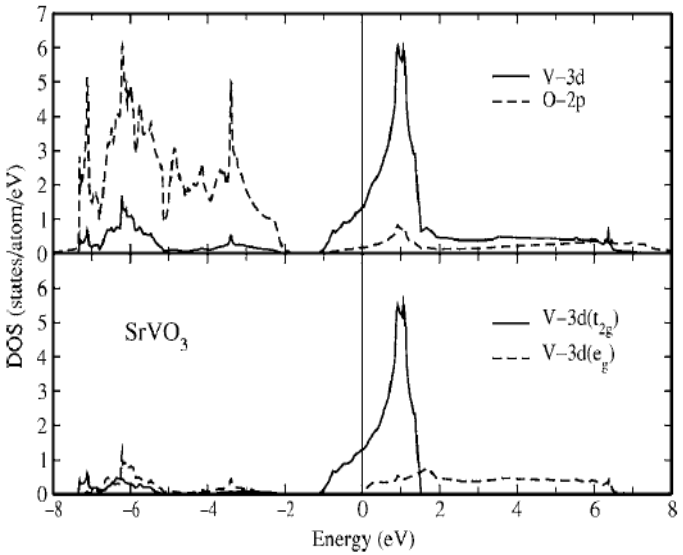
[2] D.Vanderbildt et al, Phys. Rev.B **56**, 12847 (1997)

Example of WF in real space

WF basis set for V-3d (t_{2g}) subband of $SrVO_3$: *XY, XZ, YZ* - orbitals



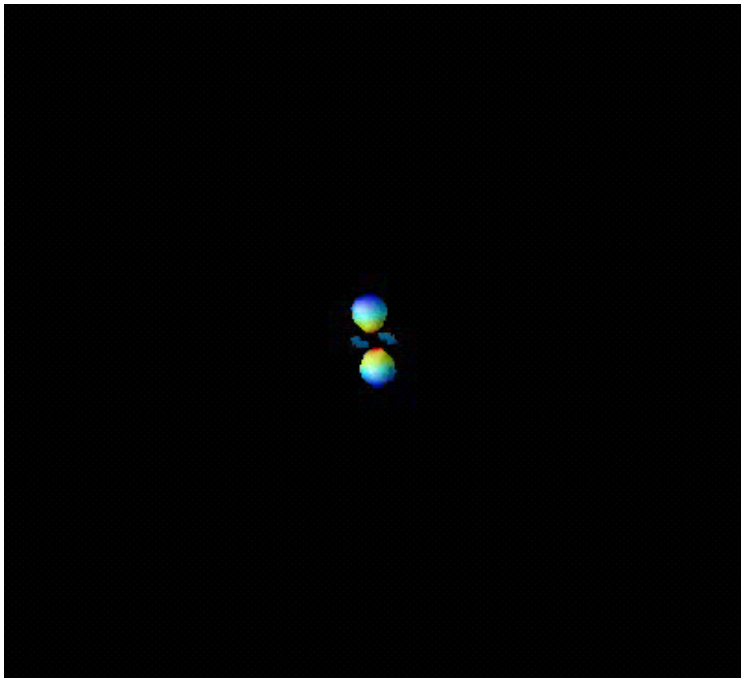




Example of WF in real space

V-3d ($3z^2$-r^2) WF orbital for $SrVO_3$

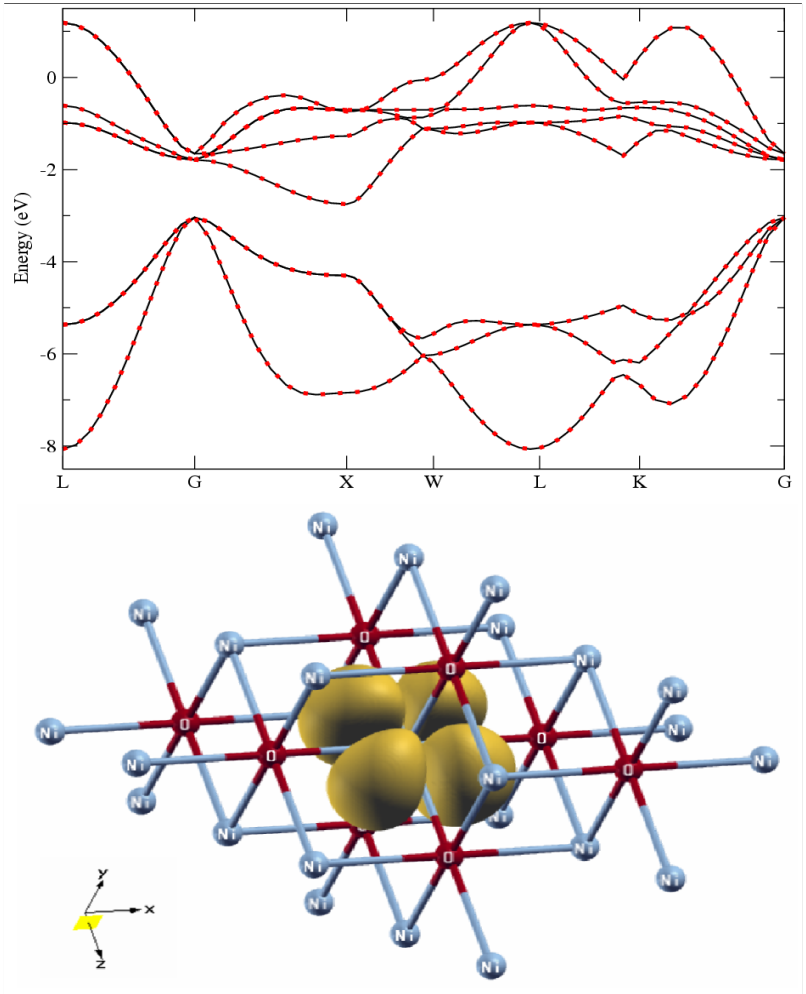
Max{|WF|} = 1



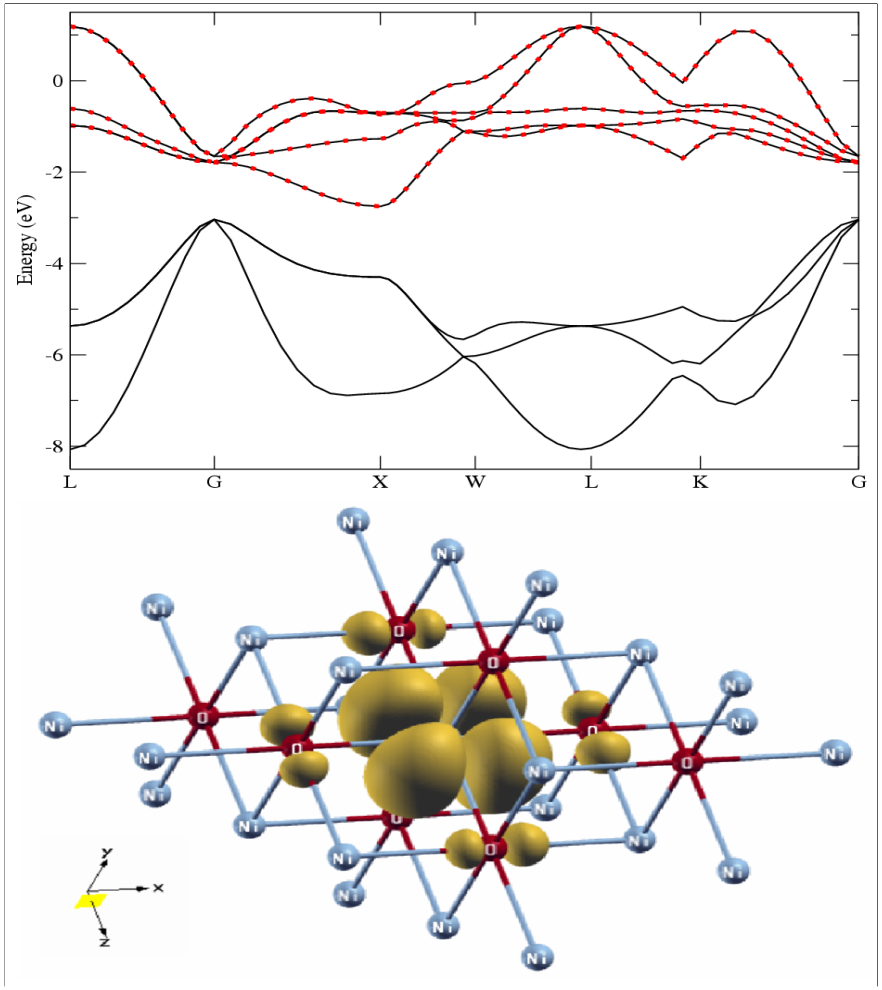
3D plot of WF isosurface:

1. decrease from |WF| = 0.5 to 0.02
2. rotation around *z*-axis
3. rotation around *x*,*z* axes and increase to |WF| = 0.5

d-xy WF for NiO



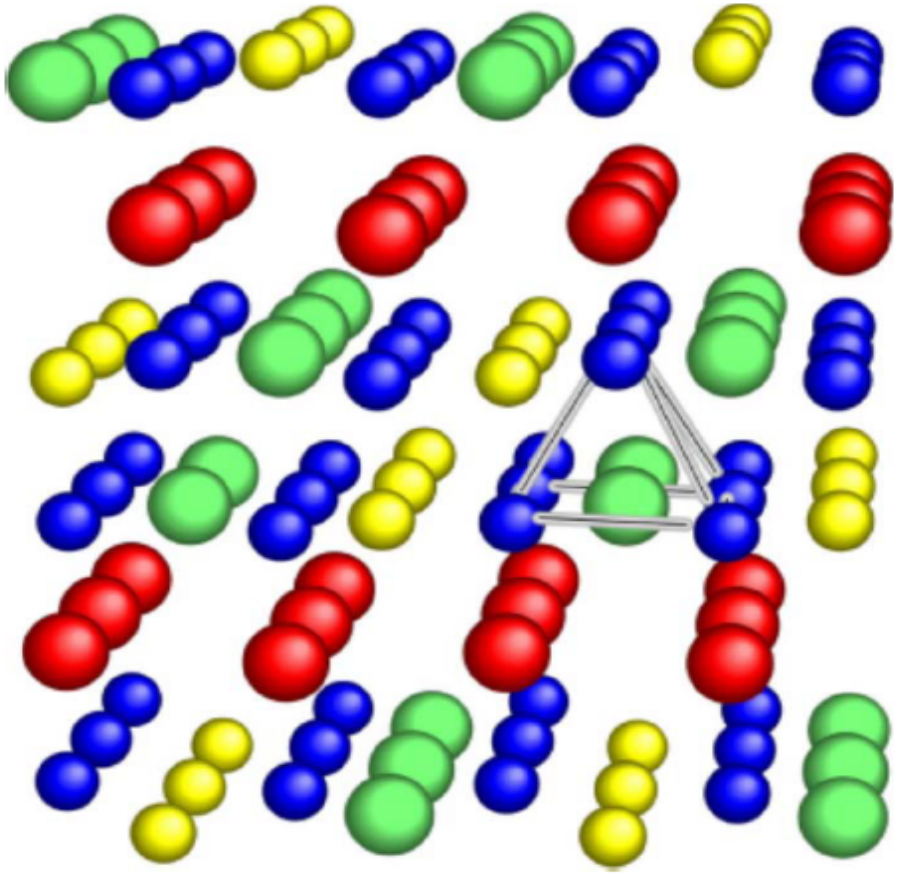
Full bands projection



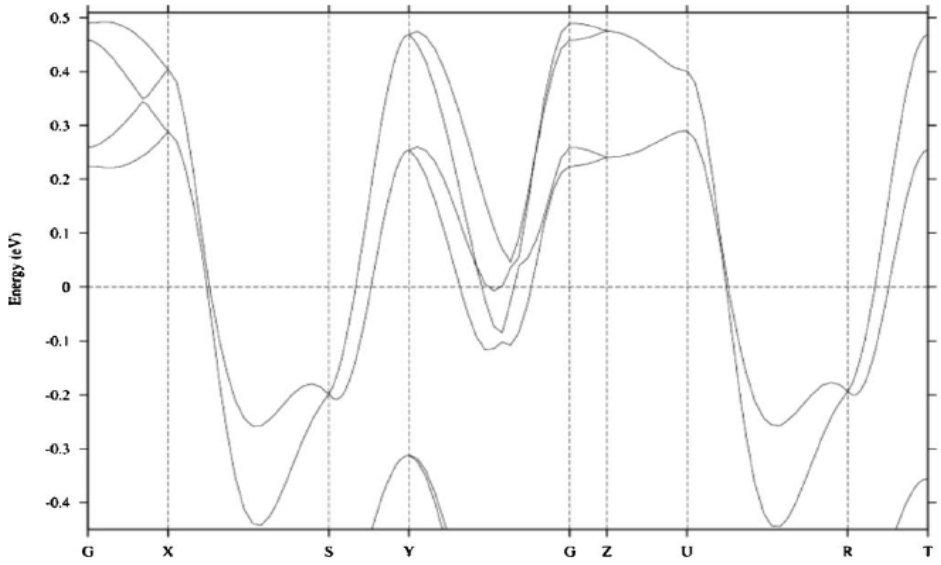
d-bands only projection

Dm.Korotin et al, Europ. Phys. J. B 65, 91 (2008).

WF in cuprates

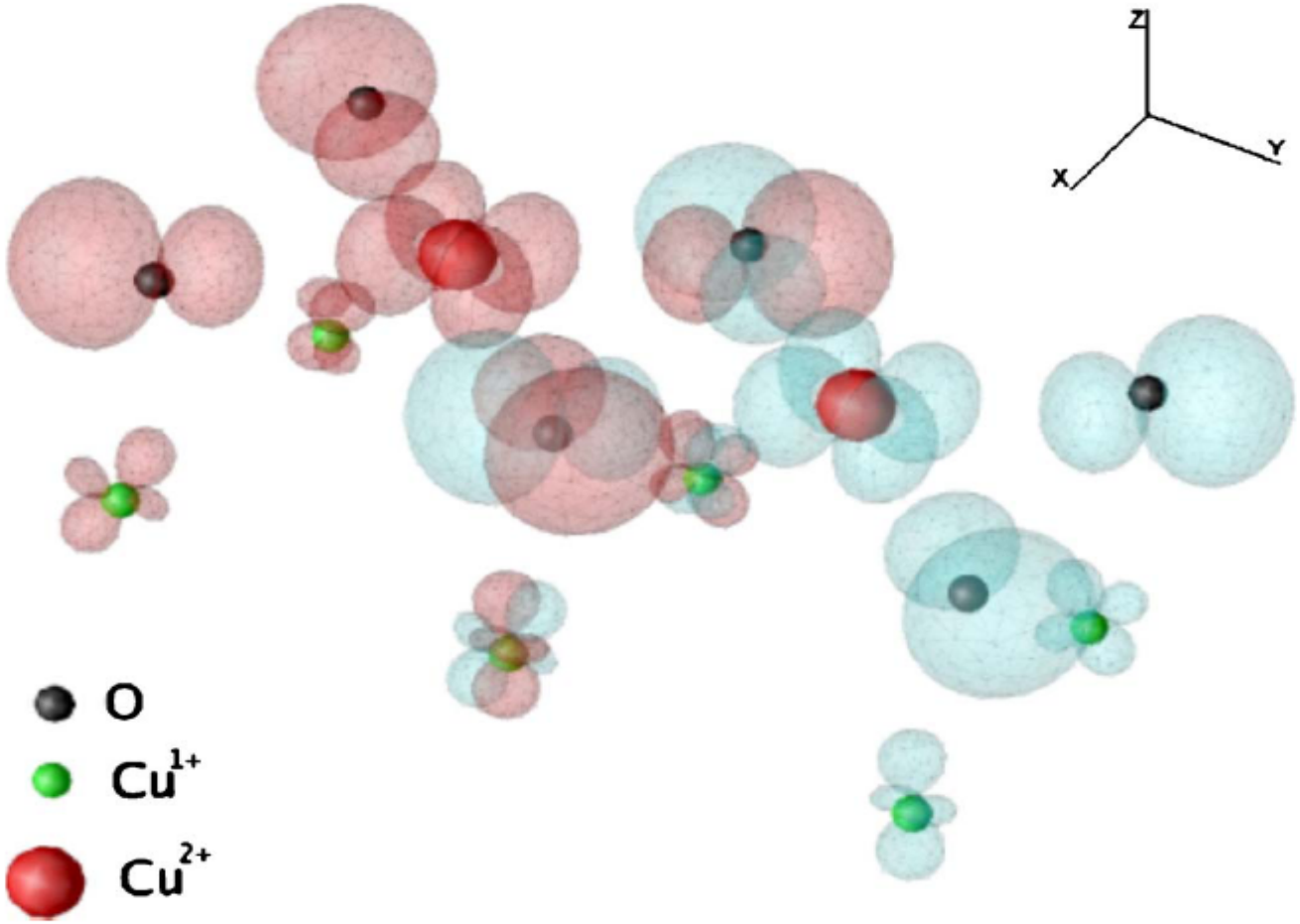


Crystal structure of $LiCu_2O_2$
Green, red, blue, black, and yellow spheres are Cu^{2+} Cu^{+},O, and Li ions, respectively.



V. V. Mazurenko, et al, Phys. Rev. B 75, 224408 (2007)

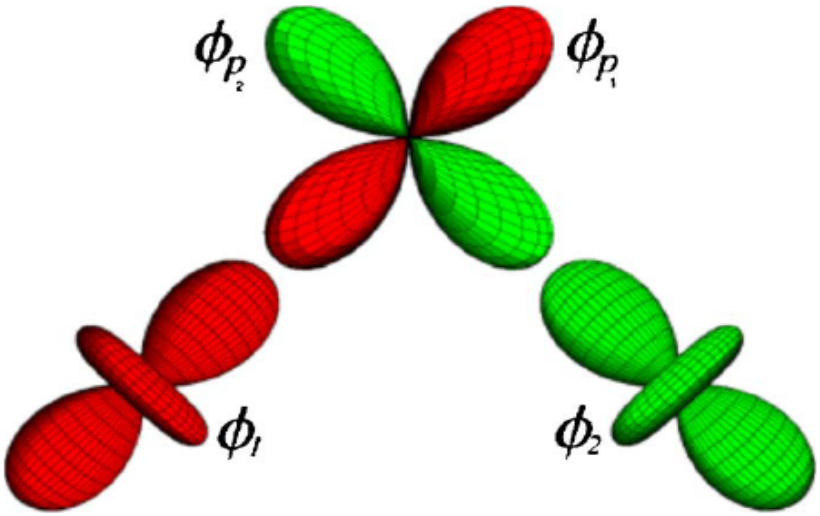
WF in cuprates

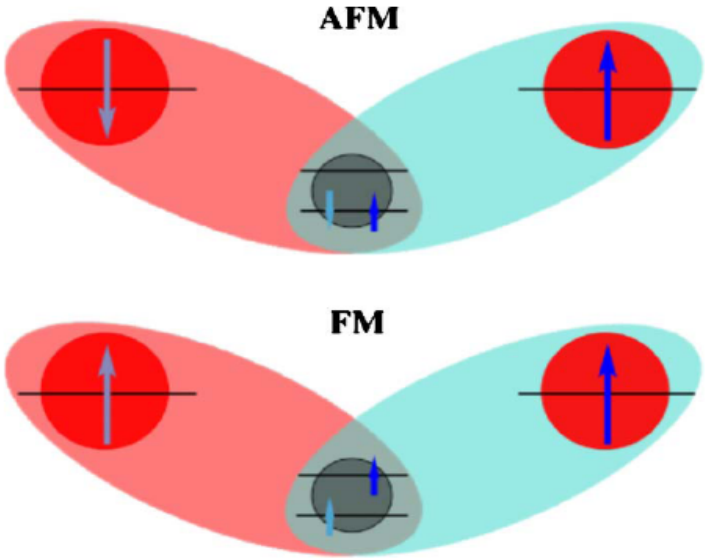


Wannier orbitals centered on neighboring copper atoms along the *y* axis.

V. V. Mazurenko, et al, Phys. Rev. B 75, 224408 (2007)

WF in cuprates

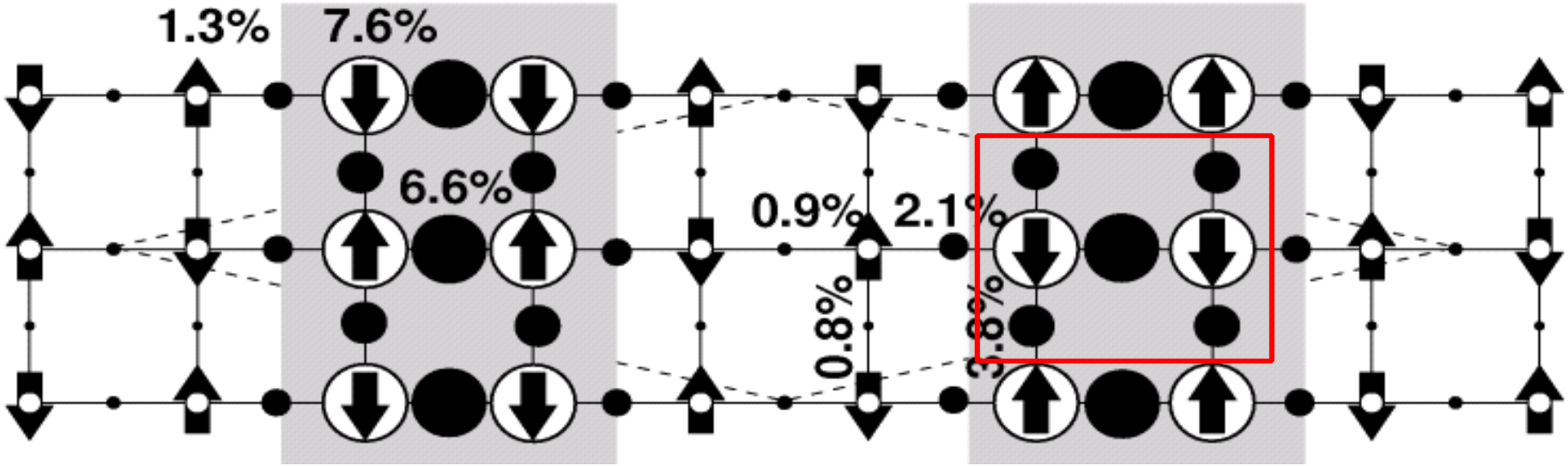


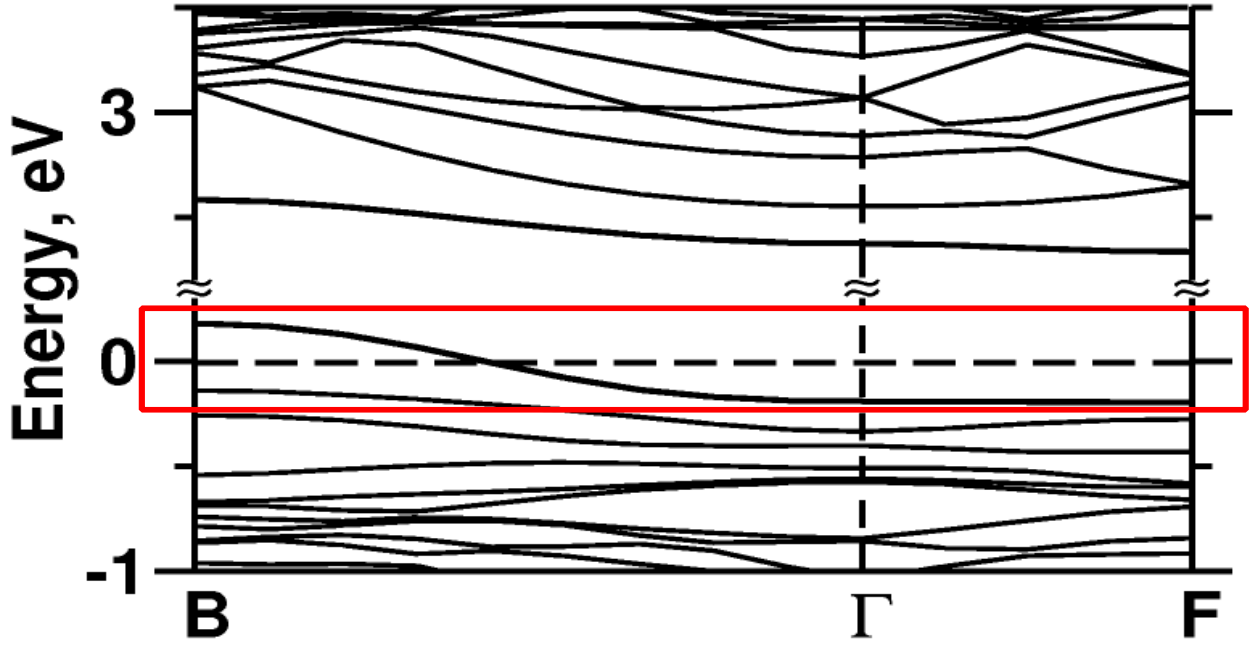


90^0 bond between Cu Wannier functions cancels antiferromagnetic kinetic energy exchange. Overlap on oxygen atoms gives ferromagnetic exchange due to Hund interaction on oxygen 2p-orbitals

V. V. Mazurenko, et al, Phys. Rev. B 75, 224408 (2007)

WF for stripe phase in cuprates



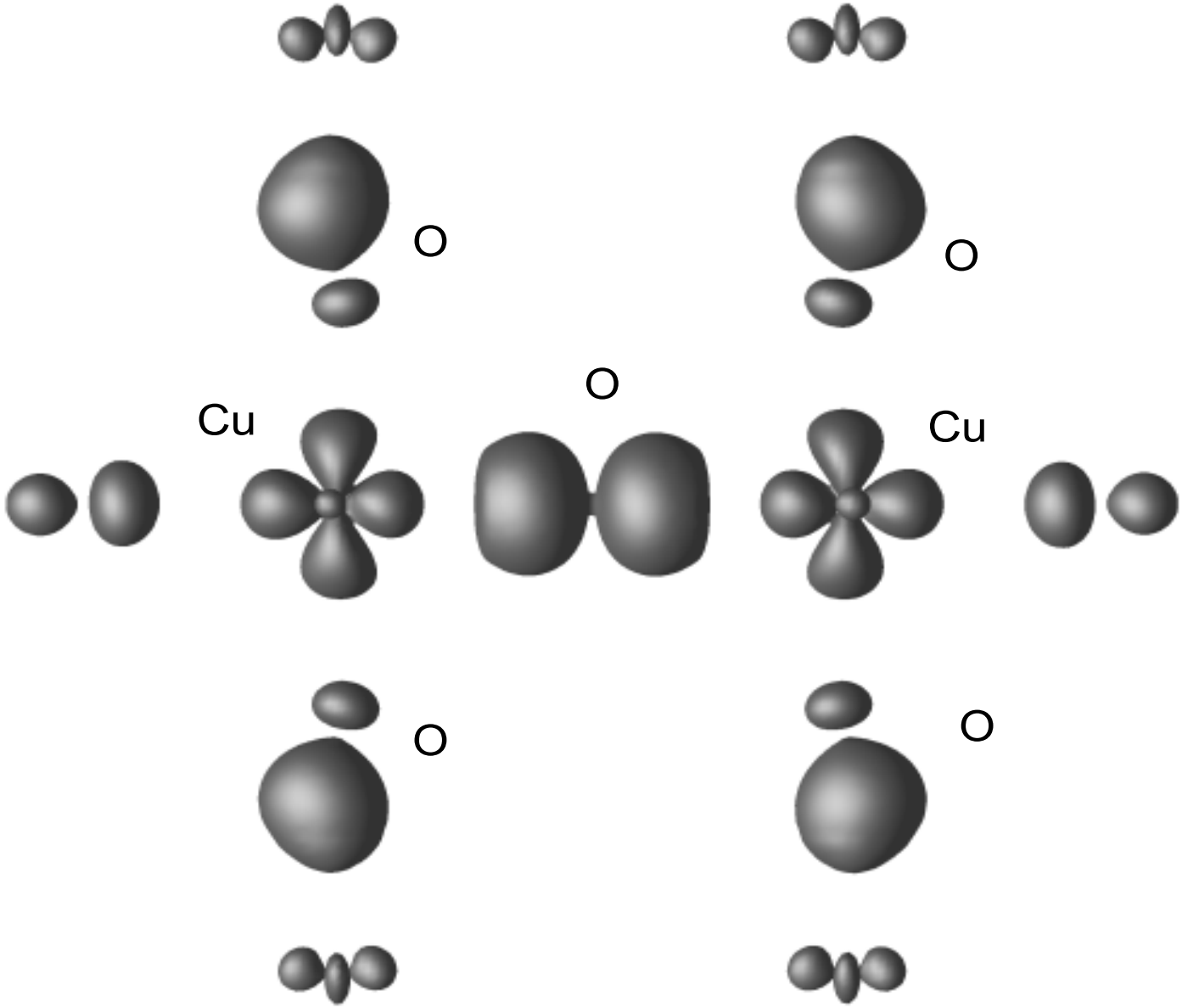


$La_{7/8}Sr_{1/8}CuO_4$

Half-filled band

V.Anisimov et al, Phys. Rev. B 70, 172501 (2004)

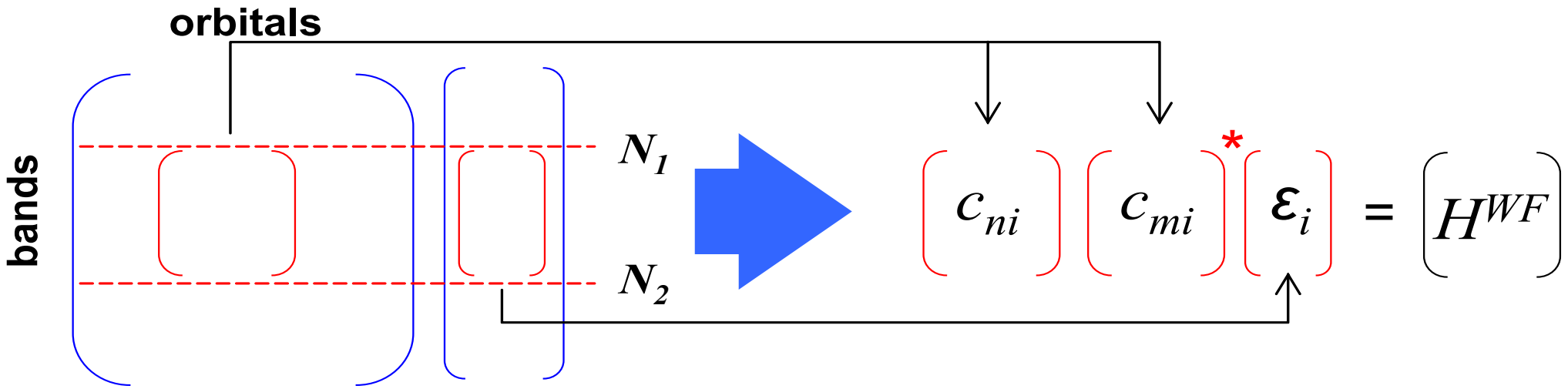
WF for stripe phase in cuprates



Projection procedure for Hamiltonian

Matrix elements of projected Hamiltonian:

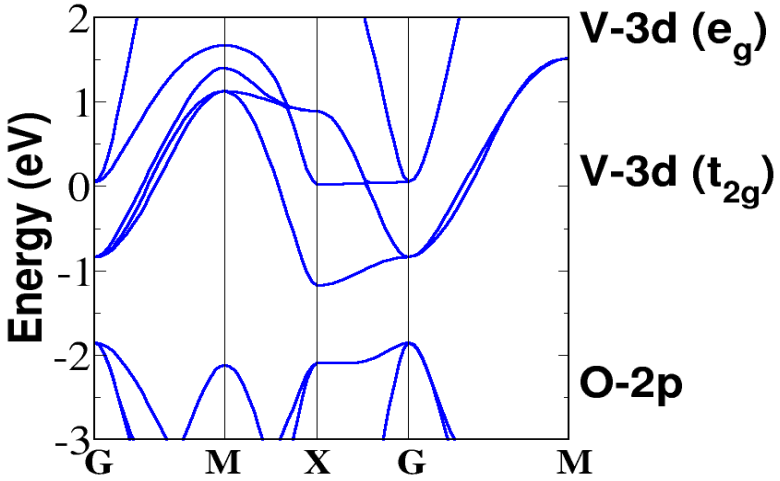
$$\widetilde{H}^{WF}_{nm}(\mathbf{k}) = \langle \widetilde{W}_{n\mathbf{k}} | \Big(\sum_{i\mathbf{k}'} |\psi_{i\mathbf{k}'}\rangle \epsilon_i(\mathbf{k}') \langle \psi_{i\mathbf{k}'}| \Big) | \widetilde{W}_{m\mathbf{k}} \rangle = \sum_{i=N_1}^{N_2} c_{ni}(\mathbf{k}) c^{\star}_{mi}(\mathbf{k}) \epsilon_i(\mathbf{k})$$



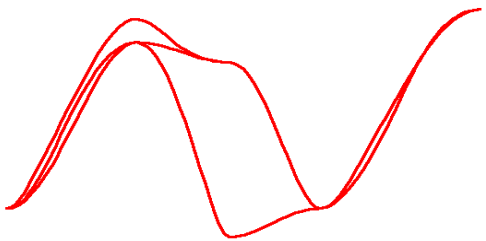
LMTO Eigenvectors, Eigenvalues

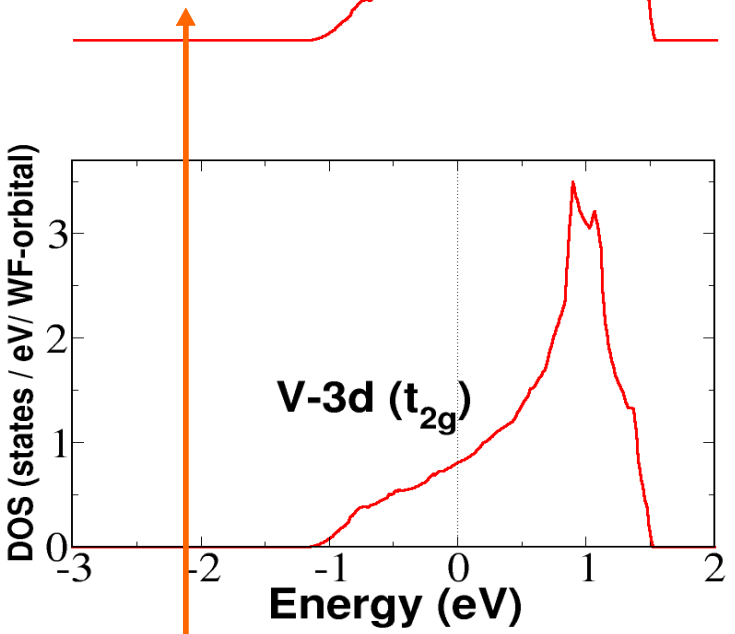
Projection results for $SrVO_3$

Full-orbital Hamiltonian



Projected Hamiltonian





Eigenvalues of full-orbital and projected Hamiltonians are the same

Projected Hamiltonian DOS corresponds to the total DOS of full-orbital Hamiltonian

Constrain DFT Calculation of U

Matrix of projected Hamiltonian in real space:

$$H_{nm}^{WF} = \langle W_n^{\mathbf{0}} | \Big(\sum_{\mathbf{k}} \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle \epsilon_i(\mathbf{k}) \langle \psi_{i\mathbf{k}}| \Big) |W_m^{\mathbf{0}}\rangle = \sum_{\mathbf{k}} \sum_{i=N_1}^{N_2} \bar{c}_{ni}(\mathbf{k}) \bar{c}_{mi}^{\star}(\mathbf{k}) \epsilon_i(\mathbf{k})$$

Density matrix operator:

$$Q_{nm}^{WF} = \langle W_n^{\mathbf{0}} | \Big(\sum_{\mathbf{k}} \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle \theta(\epsilon_i(\mathbf{k}) - E_f) \langle \psi_{i\mathbf{k}}| \Big) |W_m^{\mathbf{0}}\rangle = \sum_{\mathbf{k}} \sum_{i=N_1}^{N_2} \bar{c}_{ni}(\mathbf{k}) \bar{c}_{mi}^{\star}(\mathbf{k}) \theta(\epsilon_i(\mathbf{k}) - E_f)$$

Energy of *n*-th WF: $E_n = H_{nn}^{WF}$

Occupation of *n*-th WF: $Q_n = Q_{nn}^{WF}$

Coulomb interaction

$$U \equiv \frac{\partial E_n}{\partial Q_n}$$

Definition of WF using Green-functions

WF definition:

$$\widetilde{W}_{n\mathbf{k}}(\mathbf{r}) = -\frac{1}{\pi} Im \int_{E_1}^{E_2} d\varepsilon \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}',\varepsilon)\phi_n^{\mathbf{k}}(\mathbf{r}') = \sum_{\mu} \tilde{b}_{\mu n}^{\mathbf{k}} \phi_{\mu}^{\mathbf{k}}(\mathbf{r})$$

where $\tilde{b}_{\mu n}^{\mathbf{k}} \equiv -\frac{1}{\pi} Im \int_{E_1}^{E_2} d\varepsilon G_{\mu n}^{k}(\varepsilon)$

In the absence of Self-energy:

$$G_{\mu\nu}^{\mathbf{k}}(\varepsilon) = (\varepsilon - H(\mathbf{k}) + i\eta)_{\mu\nu}^{-1} = \sum_i \frac{c_{\mu i}(\mathbf{k}) c_{\nu i}^{\star}(\mathbf{k})}{\varepsilon - \epsilon_i(\mathbf{k}) + i\eta}$$

$$\widetilde{W}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mu} \phi_{\mu}^{\mathbf{k}}(\mathbf{r}) \left(-\frac{1}{\pi} Im \int_{E_1}^{E_2} d\varepsilon G_{\mu n}^{\mathbf{k}}(\varepsilon)\right) = \sum_{\mu} \sum_{i=N_1}^{N_2} c_{\mu i}(\mathbf{k}) c_{ni}^{\star}(\mathbf{k}) \phi_{\mu}^{\mathbf{k}}(\mathbf{r})$$

Coincides with definition of WF using Bloch functions

Calculation scheme

Coulomb interaction Hamiltonian:

$$\hat{H}_{Coulomb} = \frac{1}{2} \sum_{i=i_d, l=l_d} \sum_{m,m',m'',m''',\sigma,\sigma'} \langle m, m' | V_{ee} | m'', m''' \rangle \times$$
$$\times \hat{c}^{+}_{ilm\sigma} \hat{c}^{+}_{ilm'\sigma'} \hat{c}_{ilm''\sigma} \hat{c}_{ilm'''\sigma'} \ ,$$

where V_{ee} is screened Coulomb interaction between electrons in $i_d n_d l_d$ shell with matrix elements expressed via complex spherical harmonics and effective Slater integral parameters F^k

$$\langle m, m' | V_{ee} | m'', m''' \rangle = \sum_k a_k(m, m'', m', m''') F^k$$

where $k = 0, 2, \ldots, 2l$

Coulomb interaction Hamiltonian:

$$a_k(m,m'',m',m''') = \frac{4\pi}{2k+1}\sum_{q=-k}^{k}\langle lm|Y_{kq}|lm''\rangle\langle lm'|Y_{kq}^{*}|lm'''\rangle$$

where Y_{kq} are complex spherical harmonics.

Gaunt coefficients, *L=(l,m):*

$$C_{LL'L''} = \int Y_L(\hat{\mathbf{r}})Y^*{}_{L'}(\hat{\mathbf{r}})Y_{L''}(\hat{\mathbf{r}})d\Omega$$

$$C_{LL'L''} = (-1)^{m''}\frac{(2l''-1)!(2l'-1)!}{(2l-1)!}\left[\frac{(2l'+1)(2l''+1)}{4\pi(2l+1)}\right]^{\frac{1}{2}}\times$$

$$\times\left[\frac{(l+m)!(l-m)!}{(l''+m'')!(l''-m'')!(l'+m')!(l'-m')!}\right]^{\frac{1}{2}}$$

Calculation scheme

Coulomb interaction Hamiltonian:

$$F^k = e^2 \int_0^\infty r^2 dr [\varphi_d(r)]^2 \int_0^\infty (r')^2 dr' [\varphi_d(r')]^2 \frac{r_<^k}{r_>^{k+1}}$$

$$U = F^0,$$

$$J = \frac{1}{14}(F^2 + F^4)$$

For d electrons one needs to know F^0, F^2 and F^4 and these can be linked to the Coulomb and Stoner parameters *U* and *J* obtained from the constrain DFT procedures, while the ratio F^2/F^4 is ~ 0.625 for the 3d elements. For f electrons the corresponding expressions are $J = (286F^2 + 195F^4 + 250F^6)/6435$ and ratios F^4/F^2 and F^6/F^2 equal to 451/675 and 1001/2025.

Calculation scheme

Coulomb parameter U calculations:

$$U = \int d\mathbf{r}d\mathbf{r}' |W_n(\mathbf{r})|^2 U(\mathbf{r},\mathbf{r}') |W_n(\mathbf{r}')|^2$$

Screened Coulomb potential: $U = [1 - vP]^{-1} v$

Unscreened Coulomb potential: $v(\mathbf{r},\mathbf{r}') = 1/(\mathbf{r} - \mathbf{r}')$

Polarization operator:

$$P(\mathbf{r},\mathbf{r}') = \sum_i^{occ} \sum_j^{unocc} \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}') \left\{ \frac{1}{\epsilon_i - \epsilon_j + i0^+} - \frac{1}{\epsilon_j - \epsilon_i - i0^+} \right\}$$

Strong dependence on the number of occupied and empty states included in the summation for polarization operator

Calculation scheme

Coulomb parameter U calculations: Constrain DFT method

Definition: $$U \equiv E(2) + E(0) - 2E(1)$$

DFT analogue: $$U = \frac{\partial^2 E_{DFT}}{\partial^2 n_d}$$

Connection of one-electron eigenvalues and total energy in DFT: $$\epsilon_d = \frac{\partial E_{DFT}}{\partial n_d} \Rightarrow U = \frac{\partial \epsilon_d}{\partial n_d}$$

DFT calculations with constrain potential: $$\hat{H}_{constr} = \sum_n |W_n\rangle \delta V_n \langle W_n|$$

Energy of *n*-th WF: $E_n = H_{nn}^{WF}$

Occupation of *n*-th WF: $Q_n = Q_{nn}^{WF}$

$$U \equiv \frac{\partial E_n}{\partial Q_n}$$

Calculation scheme

Coulomb interaction Hamiltonian:

The general Hamiltonian assumes possibility of mixing for orbitals with different *m* values (or in other words possibility for electrons occupy arbitrary linear combinations of |*inlmσ*> orbitals). However in many cases it is possible to choose "natural" orbital basis where mixing is forbidden by crystal symmetry. In this case terms $c^{+}_{ilm\sigma}c_{ilm'\sigma}$ with *m* non equal to *m'* are absent and Coulomb interaction Hamiltonian can be written as

$$\hat{H}_{Coulomb} = \frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m,m',\sigma}\{U_{mm'}\hat{n}_{ilm\sigma}\hat{n}_{ilm'\bar{\sigma}} + (U_{mm'} - J_{mm'})\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma}\} -$$

$$-\frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\neq m',\sigma} J_{mm'}\{\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm\bar{\sigma}}\hat{c}^{+}_{ilm'\bar{\sigma}}\hat{c}_{ilm'\sigma} + \hat{c}^{+}_{ilm\sigma}\hat{c}^{+}_{ilm\bar{\sigma}}\hat{c}_{ilm'\sigma}\hat{c}_{ilm'\bar{\sigma}}\}\ .$$

Third terms corresponds to spin flip for electron on *m* orbital with simultaneous reverse spin flip on orbital *m'* that allows to describe *x* and *y* spin components while the fourth term describes pair transition of two electrons with opposite spin values from one orbital to another.

Calculation scheme

Coulomb interaction Hamiltonian:

$$\hat{n}_{ilm\sigma} = \hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm\sigma}$$

is particle number operator for electrons on orbital |*inlmσ*>
Here we have introduced matrices of direct
$U_{mm'}$ and exchange $J_{mm'}$ Coulomb interaction:

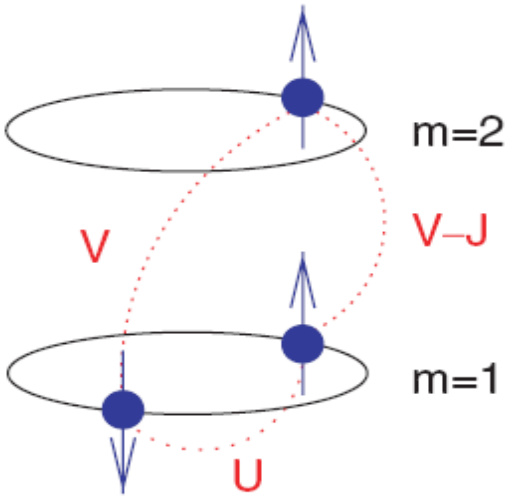
$$U_{mm'} \equiv \langle m, m'|V_{ee}|m, m'\rangle, \;\; J_{mm'} \equiv \langle m, m'|V_{ee}|m', m\rangle$$

Neglecting spin-flip effects and leaving only density-density terms we have:

$$\hat{H}_{Coulomb} = \frac{1}{2} \sum_{i=i_d, l=l_d} \sum_{m,m',\sigma} \{U_{mm'}\hat{n}_{ilm\sigma}\hat{n}_{ilm'\bar{\sigma}} + (U_{mm'} - J_{mm'})\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma}\}$$

Coulomb interaction Hamiltonian:

Kanamori parameterization is usually used where for the same orbitals ($m = m'$) direct Coulomb interaction $U_{mm} \equiv U$, for different orbitals (m non equal m') $U_{mm'} \equiv U'$ with $U' \equiv U - 2J$ and exchange interaction parameter does not depend on orbital index $J_{mm'} \equiv J$. In this approximation Hamiltonian is:



$$\hat{H}_{Coulomb} = \frac{1}{2} \sum_{i=i_d, l=l_d} \sum_{m,m',\sigma} \{[U\delta_{mm'} + U'(1-\delta_{mm'})]\hat{n}_{ilm\sigma}\hat{n}_{ilm'\bar{\sigma}} + (U' - J)\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma}\} \ .$$

Double-counting problem for Coulomb interaction

Full Hamiltonian is defined as:

$$\hat{H} = \hat{H}_{\mathrm{LDA}} - \hat{H}_{DC} + H_{Coulomb}$$

In DFT Coulomb interaction energy is a functional of electron density that is defined by the total number of interacting electrons n_d. Hence it is reasonable to assume that Coulomb interaction energy in DFT is simply a function of n_d :

$$E_{DFT} = \frac{1}{2}\bar{U} n_d (n_d - 1)$$

Double-counting problem for Coulomb interaction

To obtain correction to atomic orbital energies ε_d in this approximation one needs to recall that in DFT one-electron eigenvalues are derivatives of the total energy over corresponding state occupancy n_d

$$\epsilon_d = \frac{\partial E_{DFT}}{\partial n_d}$$

and hence correction to atomic orbital energy ε_{DC} can be determined as:

$$\epsilon_{DC} = \bar{U}(n_d - \frac{1}{2})$$

and the term in Hamiltonian responsible for “double counting” correction H_{DC} is

$$\hat{H}_{DC} = \sum_{inlm\sigma} \epsilon_{DC} \hat{n}_{inlm\sigma}$$

Calculation scheme

LDA+correlations Hamiltonian: $\hat{H}_{LDA+correl} = \hat{H}^0 + \hat{H}_{Coulomb}$

$$\hat{H}_{Coulomb} = \sum_{i=i_d, l=l_d, m\sigma, m'\sigma'} U^{\sigma\sigma'}_{mm'} \hat{n}^{\sigma}_{ilm} \hat{n}^{\sigma'}_{ilm'}$$

Coulomb interaction term

$$\hat{H}^0 = \hat{H}_{LDA} - \hat{H}_{DC} = \sum_{\alpha\alpha'\sigma} \delta_{\alpha\alpha'} \varepsilon^0_{\alpha} \hat{n}^{\sigma}_{\alpha} + t_{\alpha\alpha'} \hat{c}^{\sigma *}_{\alpha} \hat{c}^{\sigma}_{\alpha'}$$

Non-interacting Hamiltonian

Double-counting correction:

$$\varepsilon^0_{\alpha} = \frac{\partial}{\partial n_{\alpha}} \left(E_{LDA} - \frac{1}{2} U n_d (n_d - 1) \right) = \varepsilon_{\alpha} - U \left(n_d - \frac{1}{2} \right)$$

LDA+U method: static mean-filed approx.

Static mean-field decoupling of four Fermi operators product:

$$\hat{c}^{+}_{ilm\sigma}\hat{c}^{+}_{ilm'\sigma'}\hat{c}_{ilm''\sigma}\hat{c}_{ilm'''\sigma'} \Rightarrow$$
$$-\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm''\sigma}\langle\hat{c}^{+}_{ilm'\sigma'}\hat{c}_{ilm'''\sigma'}\rangle - \langle\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm''\sigma}\rangle\hat{c}^{+}_{ilm'\sigma'}\hat{c}_{ilm'''\sigma'} +$$
$$+\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm'''\sigma'}\langle\hat{c}^{+}_{ilm'\sigma'}\hat{c}_{ilm''\sigma}\rangle + \langle\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm'''\sigma'}\rangle\hat{c}^{+}_{ilm'\sigma'}\hat{c}_{ilm''\sigma} \ .$$

results in one-electron Hamiltonian:

$$\widehat{H}_{LDA+U} = \widehat{H}_{LDA} + V^{\sigma}_{mm'}\hat{c}^{+}_{ilm\sigma}\hat{c}_{ilm'\sigma} = \widehat{H}_{LDA} + \sum_{mm'}|ilm\sigma\rangle V^{\sigma}_{mm'}\langle ilm'\sigma|$$

$$V^{\sigma}_{mm'} = \sum_{\{m\}}\{\langle m,m''|V_{ee}|m',m'''\rangle n^{-\sigma}_{m''m'''} + (\langle m,m''|V_{ee}|m',m'''\rangle -$$
$$-\langle m,m''|V_{ee}|m''',m'\rangle)n^{\sigma}_{m''m'''}\} - \bar{U}(n_d - \frac{1}{2})$$

LDA+U method: static mean-filed approx.

LDA+U functional: $$E = E_{LDA} - \frac{1}{2} U n_d (n_d - 1) + \frac{1}{2} U \sum_{i \neq j} n_i n_j$$

One-electron energies: $$\varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon_{LDA} + U\left(\frac{1}{2} - n_i\right)$$

Occupied states: $$n_i = 1 \quad \Rightarrow \quad \varepsilon_i = \varepsilon_{LDA} - \frac{U}{2}$$

Empty states: $$n_i = 0 \quad \Rightarrow \quad \varepsilon_i = \varepsilon_{LDA} + \frac{U}{2}$$

Mott-Hubbard gap

$$U \equiv \frac{\partial \varepsilon_{LDA}}{\partial n_d}$$

Coulomb interaction parameter

LDA+U method: general formalism

LDA+U functional:

$$E_{LDA+U}[\rho^{\sigma}(\mathbf{r}),\{n^{\sigma}\}] = E_{LSDA}[\rho^{\sigma}(\mathbf{r})] + E_{U}[\{n^{\sigma}\}] - E_{DC}[\{n^{\sigma}\}]$$

Interaction term:

$$E_{U}[\{n^{\sigma}\}] = \frac{1}{2}\sum_{\{m\}\sigma}\{U_{mm'm''m'''}n^{\sigma}_{mm'}n^{-\sigma}_{m''m'''} + (U_{mm'm''m'''} - J_{mm'm''m'''})n^{\sigma}_{mm'}n^{\sigma}_{m''m'''}\}$$

Double-counting term:

$$E_{DC}[\{n^{\sigma}\}] = \frac{1}{2}Un_{d}(n_{d} - 1) - \frac{1}{2}J[n^{\uparrow}_{d}(n^{\uparrow}_{d} - 1) + n^{\downarrow}_{d}(n^{\downarrow}_{d} - 1)]$$

V.Anisimov et al, Phys. Rev.B **44,** 943 (1991); J.Phys.: Condens. Matter **9,**767 (1997)

LDA+U potential correction

Non-local LDA+U potential operator:

$$\hat{H}_{LDA+U} = \hat{H}_{LSDA} + \sum_{mm'\sigma} | inlm\,\sigma > V^{\sigma}_{mm'} < inl\,m'\sigma |$$

Potential correction matrix:

$$\mathbf{V}^{\sigma}_{\mathbf{mm'}} = \sum_{\mathbf{m''m'''}} \{\mathbf{U}_{\mathbf{mm'm''m'''}}\mathbf{n}^{-\sigma}_{\mathbf{m''m}} + (\mathbf{U}_{\mathbf{mm'm''m'''}} - \mathbf{J}_{\mathbf{mm'm''m'''}})\mathbf{n}^{\sigma}_{\mathbf{m''m}}\} -$$

$$- \mathbf{U}(\mathbf{n}_{\mathbf{d}} - \frac{\mathbf{1}}{\mathbf{2}}) + \mathbf{J}(\mathbf{n}^{\sigma}_{\mathbf{d}} - \frac{\mathbf{1}}{\mathbf{2}})$$

Occupation matrix:

$$n_{mm'} \equiv -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} d\varepsilon [\varepsilon - \hat{H}_{LDA+U}]^{-1}_{mm'}$$

Exchange interaction couplings

Heisenberg Hamiltonian parameters:

$$E = \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j \qquad J_{ij} = \frac{\partial^2 E}{\partial \theta_i \partial \theta_j}$$

Calculation of J from LDA+U results:

$$J_{ij} = \sum_{\{m\}} I^i_{mm'} \chi^{ij}_{mm'm''m'''} I^j_{m''m'''} \qquad I^i_{mm'} \equiv V^{i\uparrow}_{mm'} - V^{i\downarrow}_{mm'}$$

$$\chi^{ij}_{mm'm''m'''} = \sum_{knn'} \frac{f_{nk\downarrow} - f_{n'k\uparrow}}{\varepsilon_{nk\uparrow} - \varepsilon_{n'k\downarrow}} c^{ilm*}_{nk\uparrow} c^{jlm''*}_{nk\uparrow} c^{ilm'}_{n'k\downarrow} c^{jlm'''}_{n'k\downarrow}$$

LDA+U eigenvalues and eigenfunctions:

$$\varepsilon_{nk\sigma}; \qquad \Psi_{nk\sigma} = \sum_{ilm} c^{ilm}_{nk\sigma} \mid ilm >$$

A.Lichtenstein et al, Phys. Rev.B **52,** R5467 (1995)