

Electronic structure calculations

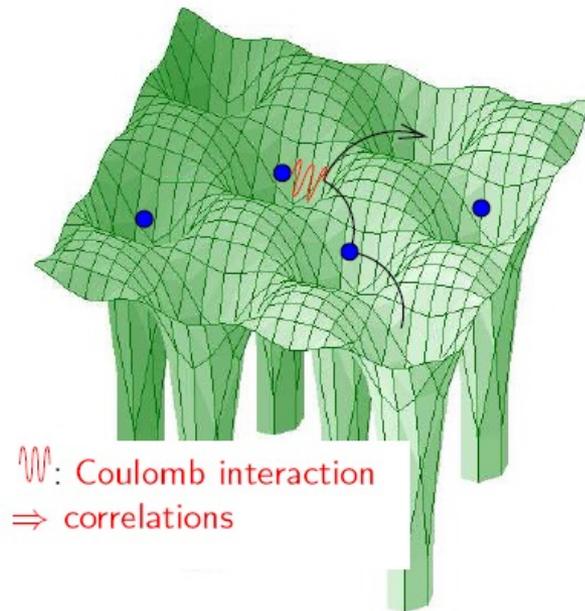
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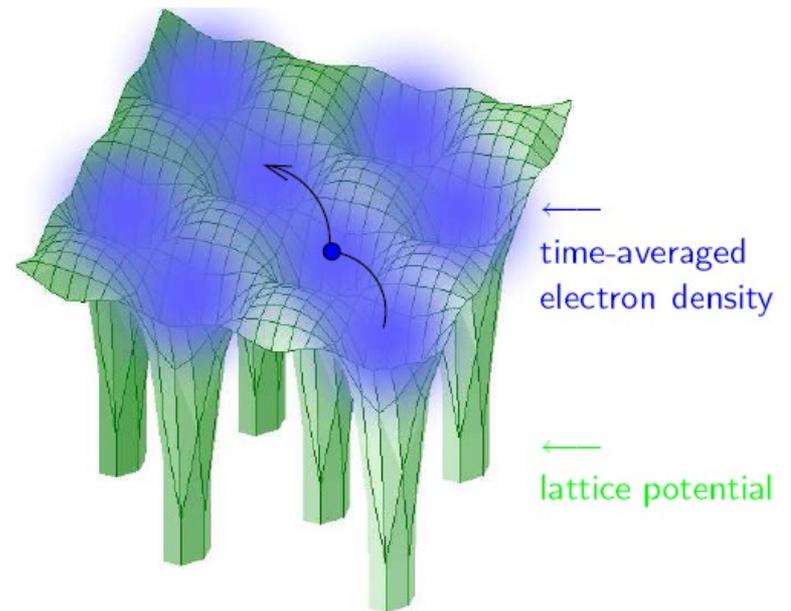


- **Many electron problem and Hartree-Fock approximation**
- **Density Functional Theory (DFT), Local Density Approximation (LDA) and its extensions (GGA)**
- **Corrections to DFT: GW approximation, Self Interactions Correction (SIC), Hybrid functional**
- **Model Hamiltonian combined with DFT approach: Wannier functions and Hamiltonian construction**
- **Static mean-field approximation: LDA+U method**
- **LDA+U method applications to real strongly correlated materials with orbital, charge and spin order**

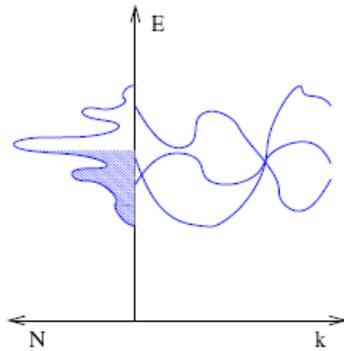
Correlated electrons
motion with full
Coulomb interaction



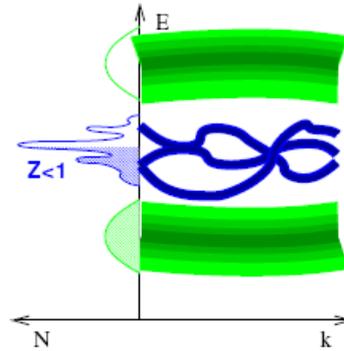
Independent electrons
motion with static mean-field
Coulomb interaction potential
from Density Functional Theory



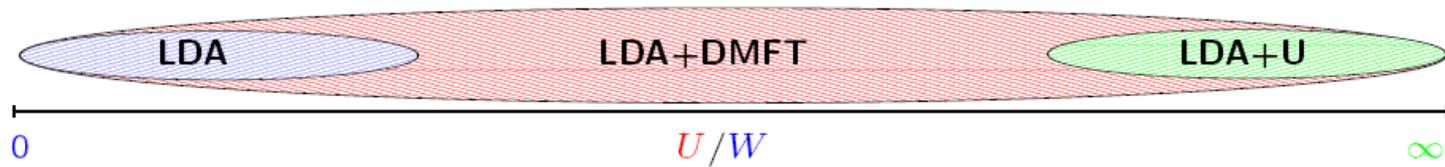
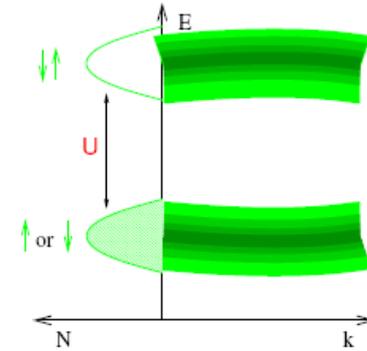
Weakly correlated systems



Strongly correlated metals



Localized electrons in Mott insulators



Coulomb correlations problem



Model Hamiltonians

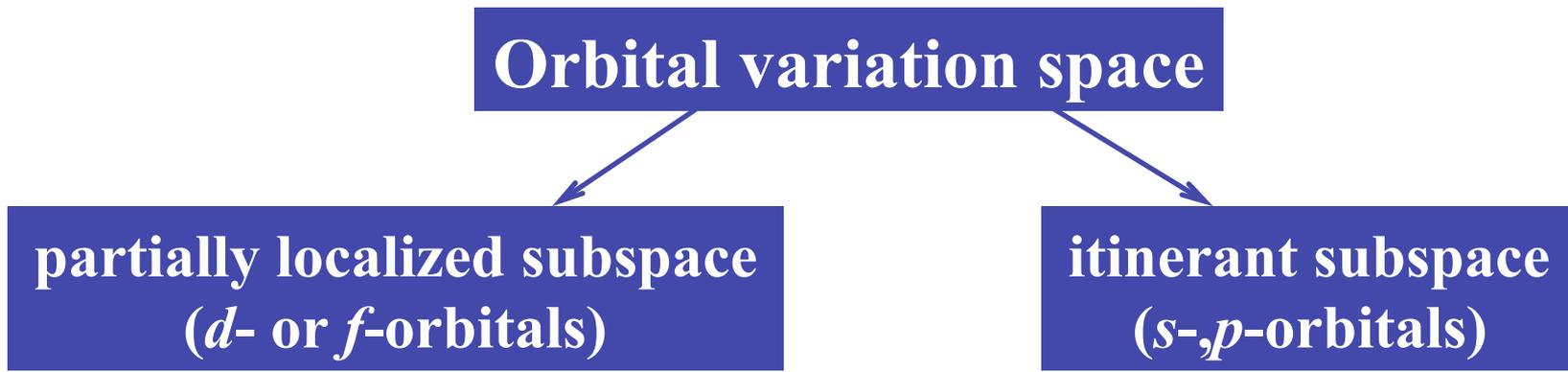
**Hubbard and Anderson models
unknown parameters
many-body
explicit Coulomb correlations**

Density Functional Theory

**LDA
ab-initio
one-electron
averaged Coulomb interaction**



combined LDA+U and LDA+DMFT approaches



LDA 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

$$\hat{H} \Psi = E \Psi$$

where $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is many electron wave function depending on $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ coordinates of all N electrons

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

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


Many-electrons equations

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

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

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

Electrons variables separation leads to one-electron approximation:

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

$u_\mu(\mathbf{x})$ is a one-electron wave function

Hartree-Fock approximation

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

Slater determinant satisfies antisymmetric properties of fermionic wave function in respect to electrons transposition

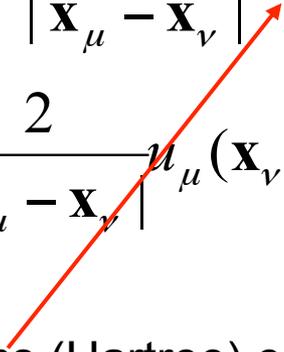
Hartree-Fock equations

$$H_{\mu}u_{\mu}(\mathbf{x}_{\mu}) + \sum_{\nu=1}^N \int u_{\nu}^*(\mathbf{x}_{\nu}) \frac{2}{|\mathbf{x}_{\mu} - \mathbf{x}_{\nu}|} \{u_{\nu}(\mathbf{x}_{\nu})u_{\mu}(\mathbf{x}_{\mu}) - \delta_{\sigma(\mu),\sigma(\nu)} u_{\nu}^*(\mathbf{x}_{\mu})u_{\mu}(\mathbf{x}_{\nu})\} d\mathbf{x}_{\nu} = \epsilon_{\mu} u_{\mu}(\mathbf{x}_{\mu}), \quad 1 \leq \mu \leq N$$

Mean-field potential with direct and exchange parts.
Exchange terms with $\mu = \nu$ explicitly cancel self-interaction while others significantly reduce repulsion energy for electrons with the same spin state.

A system of integral-differential equations with all N one-electron wave functions coupled with each other.

Hartree-Fock equations

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


Direct Coulomb potential terms (Hartree) can be expressed via electron density:

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

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

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

Hartree-Fock equations

Exchange terms can be written as a sum of pair potentials that can not be expressed via density :

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

Hartree-Fock equations have a form:

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

One-electron part with local Hartree potential defined by Electron density only

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

Slater approximation for exchange potential

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 allows to replace orbital dependent exchange interaction operator by local potential defined as a functional of electron density:

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


Decoupled one-electron equation with the same potential for all wave functions instead of the integral-differential equations system

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 $\rho(\mathbf{r})$:

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

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 functional.

Exact form of E_{xc} is unknown!

Electron density variation

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

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

where N is total number of electrons.

To minimize the functional one need to vary it over new variables $\phi_i(\mathbf{r})$ with additional condition that wave functions are normalized. That leads to the system of Kohn-Sham differential equations for one-electron wave functions:

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 $\varepsilon_i = E[n_i = 1] - E[n_i = 0]$

Kohn-Sham eigenvalues can not be directly used to calculate excitation spectra!

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 \mathbf{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 \mathbf{r} depends only on local value of electron density $\rho(\mathbf{r})$:

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

One of the explicit forms of exchange-correlation potential calculated for homogeneous electron gas as a function of local value of electron density $\rho(\mathbf{r})$ is:

$$V_{xc}(\mathbf{r}) = -(1 + 0.0545 r_s \ln(1 + 11.4/r_s)) 4 \left(\frac{3\rho(\mathbf{r})}{8\pi} \right)^{1/3}$$

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

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

Local Spin Density Approximation (LSDA)

In Local Spin Density Approximation (LSDA) exchange-correlation energy depends on two spin densities: $\epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})$

Correspondingly exchange-correlation potential will be different for electrons with spin-up and spin-down projections:

$$V_{\sigma}(\mathbf{r}) = \frac{d}{d\rho_{\sigma}} (\rho \epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow}))$$

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

can result in spin-polarized solution for Kohn-Sham equations with ferromagnetic or antiferromagnetic ground state

Generalized Gradient Approximation (GGA)

Exchange-correlation energy can depend not only on local value of density as in LSDA

$$E_{XC}^{LSD} [n_{\uparrow}, n_{\downarrow}] = \int d^3 r n \epsilon_{XC}^{unif} (n_{\uparrow}, n_{\downarrow})$$

but also on electron density gradient ∇n_{σ}

$$E_{XC}^{GGA} [n_{\uparrow}, n_{\downarrow}] = \int d^3 r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

Explicit form (Perdew et al) is defined by enhancement factor $F_{XC} = (1 + \dots)$

$$E_{XC}^{GGA} [n_{\uparrow}, n_{\downarrow}] = \int d^3 r n \epsilon_X^{unif} (n) F_{XC} (r_s, \zeta, s)$$

GGA sometimes corrects and sometimes overcorrects the LSDA predictions

DFT self-consistent calculation scheme

Initial electron density defines starting potential $\rho_{in}(\mathbf{r}) \Rightarrow V_{in}(\mathbf{r})$

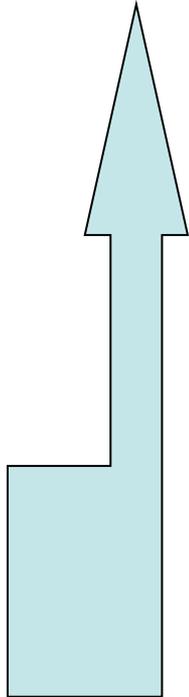
Kohn-Sham equations solution $[-\nabla^2 + V(\mathbf{r})]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

results in a set of eigenvalues and eigenfunctions $E_i, \Psi_i(\mathbf{r})$

That gives a new value of electron density $\rho_{out}(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2$

which is used as an input density on the next iteration $\rho_{out}(\mathbf{r}) \Rightarrow \rho_{in}(\mathbf{r})$

Self-consistency condition: $\int d\mathbf{r}(\rho_{out}(\mathbf{r}) - \rho_{in}(\mathbf{r}))^2 < \varepsilon$



Bloch functions in crystal

Kohn-Sham equations for periodic crystal (translational invariant potential $V(\mathbf{r}+\mathbf{l})=V(\mathbf{r})$, \mathbf{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 \mathbf{k} having a form of a plane wave modulated by periodic function:

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

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 to a 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 :

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

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

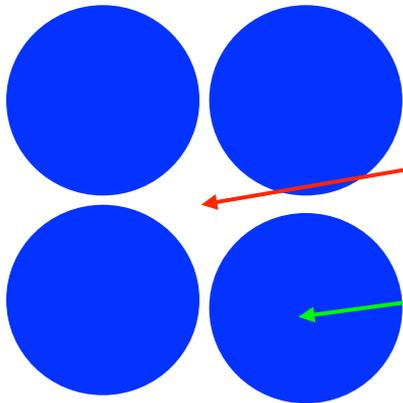
$R_l(|r|, E)$ is radial variable dependent part of Kohn-Sham equation solution for spherically symmetric potential inside atomic sphere with radius S .

Plane waves 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 \mathbf{k} is wave vector and \mathbf{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

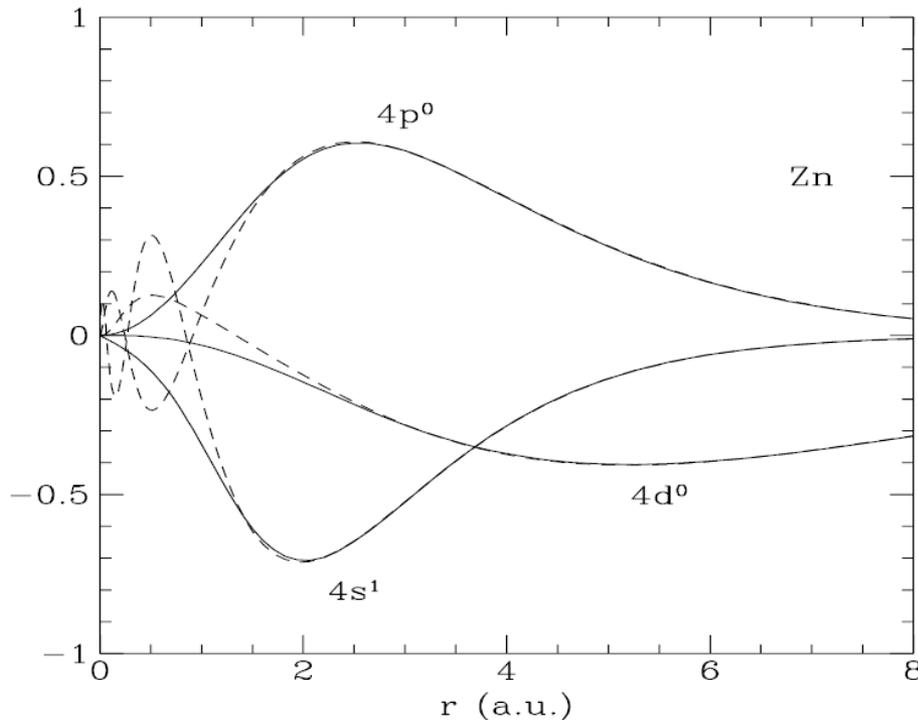
Augmented Plane Wave is defined as

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

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 giving the same eigenvalues



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

DFT problems for real materials

Systematic underestimations for energy gap value of band insulator materials.

TABLE I. Comparison of calculated and experimental energy gap values (eV).

	LDA	GTS	Expt.
MgO	5.04	7.73	7.83 ^a
Si	0.44	1.04	1.17 ^b
NiO	0.11	3.76	4.0–4.3 ^c
BaBiO ₃	0.15	0.51	0.48 ^d

DFT problems for real materials

Systematic overestimation for cohesive energy.

Example of silicon:

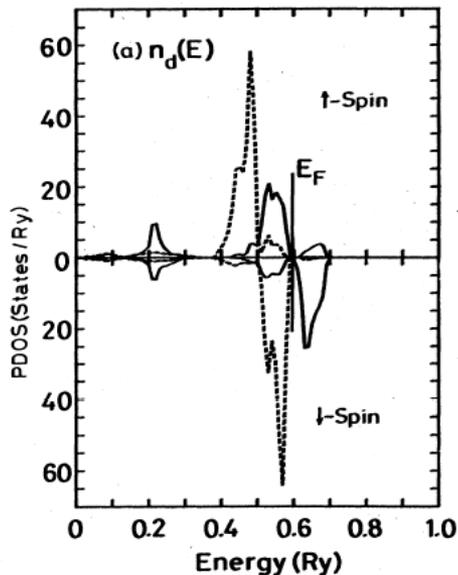
	LDA	GGA	expt.
a (Å)	5.378	5.463	5.429
B (Mbar)	0.965	0.882	0.978
E_c (eV/atom)	6.00	5.42	4.63

Breakdown of LDA for strongly correlated systems

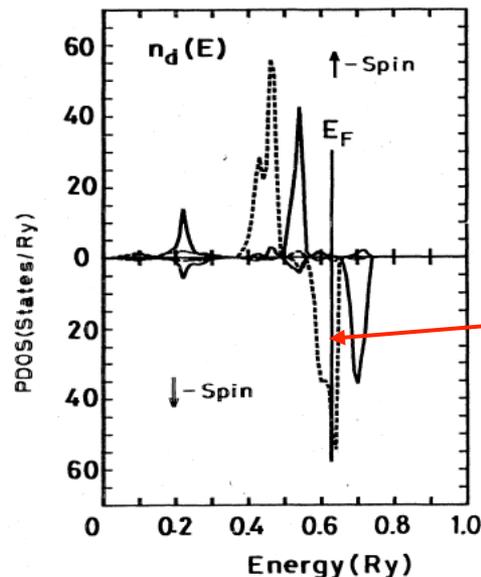
LDA potentials are the same for all orbitals with the possible difference due to exchange interaction:

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

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

Corrections to Density Functional Theory

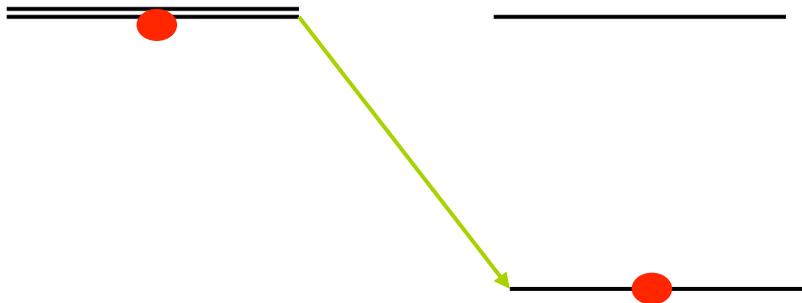
Self-Interaction Correction (SIC) method

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

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

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

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



SIC results usually overestimate energy separation between occupied and empty states similar to Hartree-Fock method due to the absence of screening effects

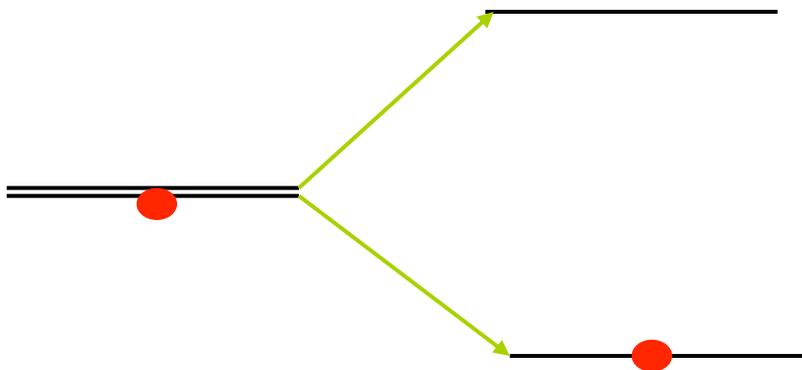
Corrections to Density Functional Theory

Slater Transition State method

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

$$\Delta_i = E[n_i = 1] - E[n_i = 0] \approx \epsilon_i(n_i = 1/2) = \\ = \tilde{\epsilon}_i^{LDA} + (1/2 - \tilde{n}_i) \left. \frac{\partial \tilde{\epsilon}_i}{\partial \tilde{n}_i} \right|_{\tilde{n}_i=1/2} \quad \text{using:} \quad \epsilon_i = \frac{\partial E_{tot}}{\partial n_i}$$

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



Good results for excitation energies values in atoms, molecules and solids calculated as a difference of one-electron eigenvalues with half-filled occupancy for initial and final states

Corrections to Density Functional Theory

GW method

Ideologically GW method is not related to DFT but is based on diagrammatic technique for inter-electron Coulomb interaction where static and local potential

$V(\mathbf{r})$ is replaced by an energy dependent non-local self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega')$$

Here $G(\mathbf{r}, \mathbf{r}', \omega)$ is a Green function and

$W(\mathbf{r}, \mathbf{r}', \omega)$ is screened Coulomb inter-electron interaction

Corrections to Density Functional Theory

GW method

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \int d^3 r'' \epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega) v(\mathbf{r}'' - \mathbf{r}')$$

$\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ is inverse dielectric matrix

$v(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$ is bare Coulomb interaction

dielectric matrix is expressed via polarization operator

$$P(\mathbf{r}, \mathbf{r}', \omega)$$

that can be calculated in Random Phase Approximation (RPA) using eigenvalues and eigenfunctions obtained in DFT calculations.

GWA systematically improves calculated energy gap values for semiconductors and band insulators but has serious problems for strongly correlated materials like transition metal oxides.

Hybrid functionals

DFT systematically underestimate energy gap values while Hartree-Fock (HF) strongly overestimate them due to the neglect of screening effects.

Hybrid functionals solve this problem by mixing both approximations in expression for exchange-correlation energy:

$$E_{xc}^{hyb} = (1 - a)E_{xc}^{DFT} + aE_x^{HF}$$

$a=1/4$ is a mixing parameter chosen to give good agreement with experimental data

This *ad hoc* formulae works surprisingly well for a wide range of materials and is very popular last years due to its simplicity and effectiveness.

Mixing parameter $a=1/4$ can be viewed as an imitation of screening for bare Coulomb potential present in Hartree-Fock approximation.

Basic models in strongly correlated systems theory

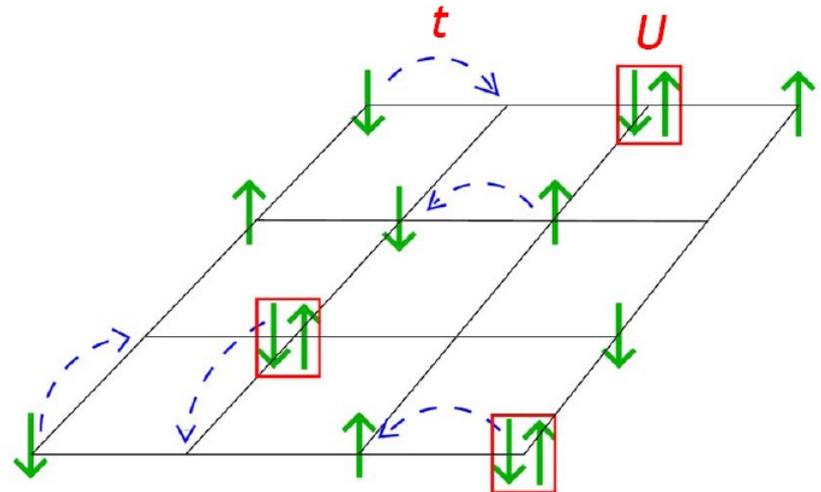
Hubbard model

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

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

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

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

$$J = 4t^2 / U \quad \text{Anderson kinetic exchange.}$$

S are local spin moments

tJ -model can be derived from Hubbard model in the limit $U \gg t$

Basic models in strongly correlated systems theory

Kondo lattice model

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

\mathbf{S} is spin operator for localized electrons,

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

Itinerant electrons spin operator.

Usually it 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)

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

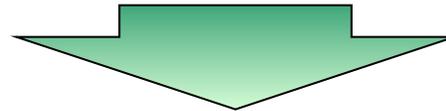
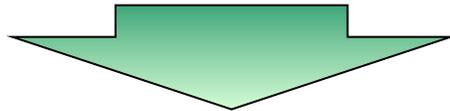
$$\hat{c}_{i\sigma} (\hat{c}_{i\sigma}^+) \text{ and } \hat{d}_{i\sigma} (\hat{d}_{i\sigma}^+)$$

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

V_{ij} s-d hybridization parameter.

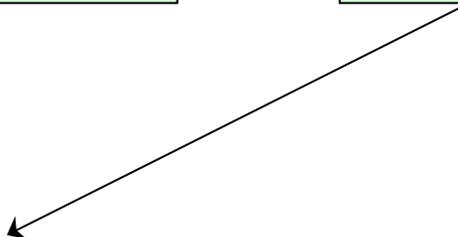
If hopping between d-electrons term is added to PAM then the most general model Hamiltonian is defined that gives complete description of any material.

“Dream” fully *ab-initio* method

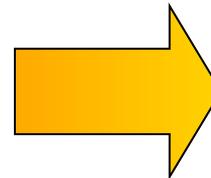


**General functionals
(electron density,
spectral density *et. ct.*)**

**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

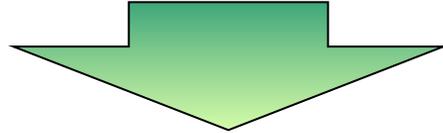
Self-energy operator for cubic systems:

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

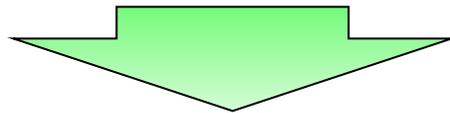
Green function:

$$\begin{aligned} G(\omega) &= \int_{IBZ} (\omega - \Sigma(\omega) - H_{LDA}^0(\mathbf{k}))^{-1} d\mathbf{k} = \\ &= G^0(\omega - \sigma(\omega)) = \int \frac{N^0(\epsilon)}{\omega - \sigma(\omega) - \epsilon} d\epsilon \end{aligned}$$

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

Wannier functions in real space [1]:

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

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

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

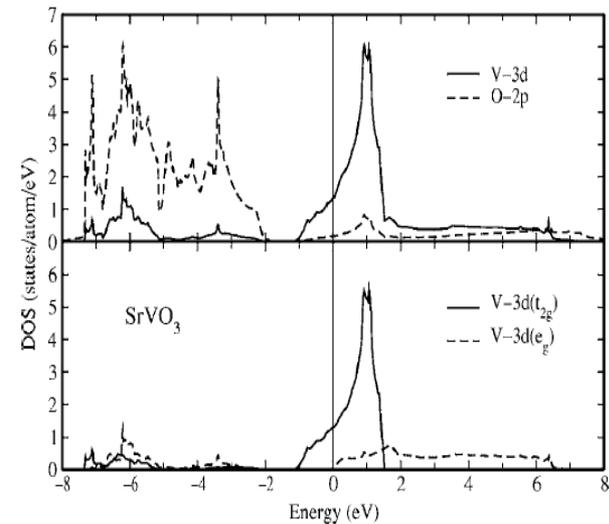
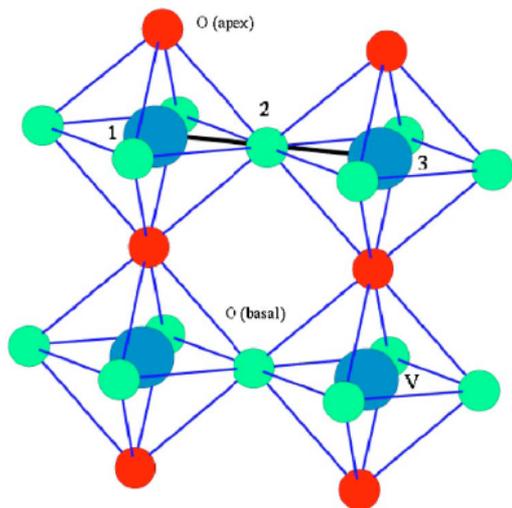
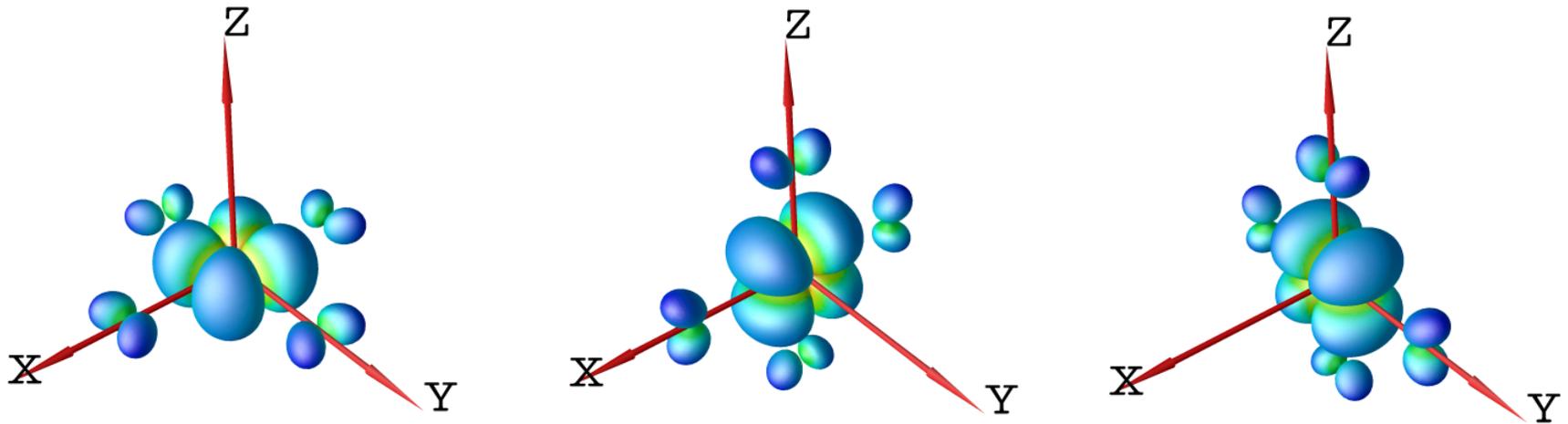
$$|\widetilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} \sum_j c_{ji}(\mathbf{k}) c_{ni}^*(\mathbf{k}) |\phi_j^{\mathbf{k}}\rangle = \sum_j \tilde{b}_{jn}^{\mathbf{k}} |\phi_j^{\mathbf{k}}\rangle$$

coefficients of WF expansion in LMTO-orbitals:

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

Example of WF in real space

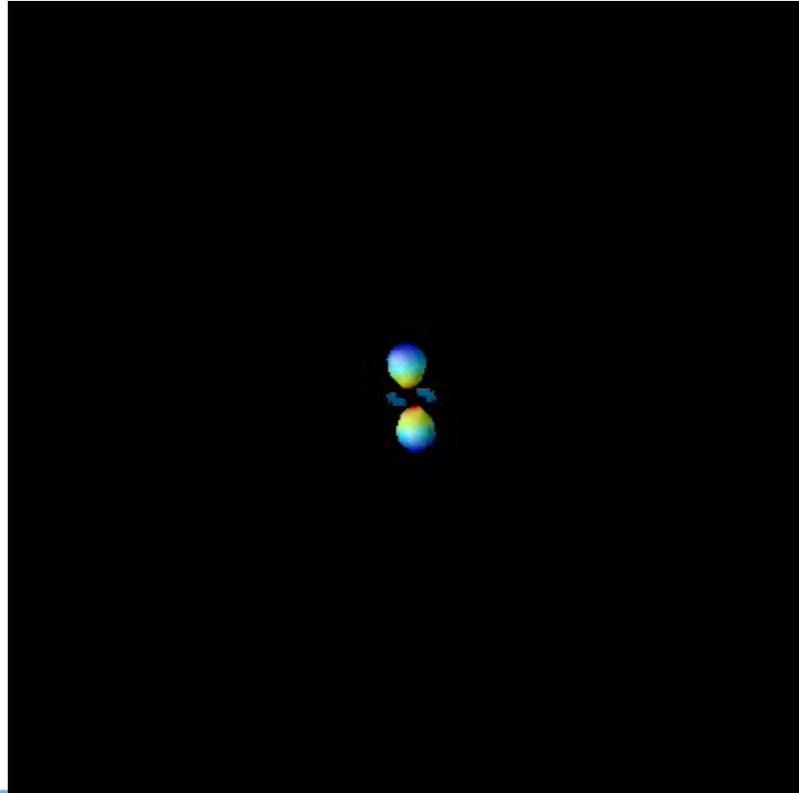
WF basis set for V-3d (t_{2g}) subband of SrVO_3 : XY , XZ , YZ - orbitals



Example of WF in real space

V-3d ($3z^2-r^2$) WF orbital for SrVO₃

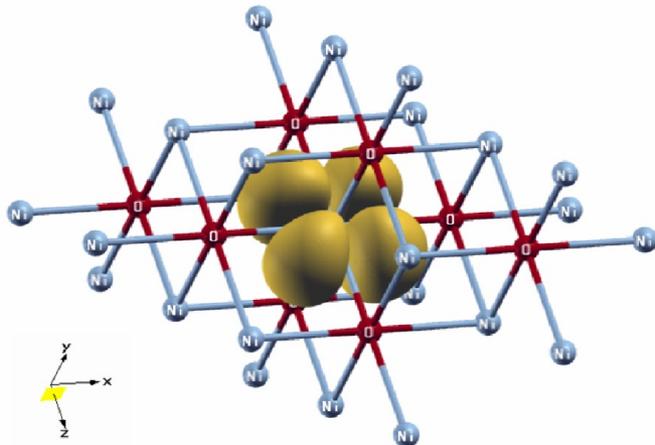
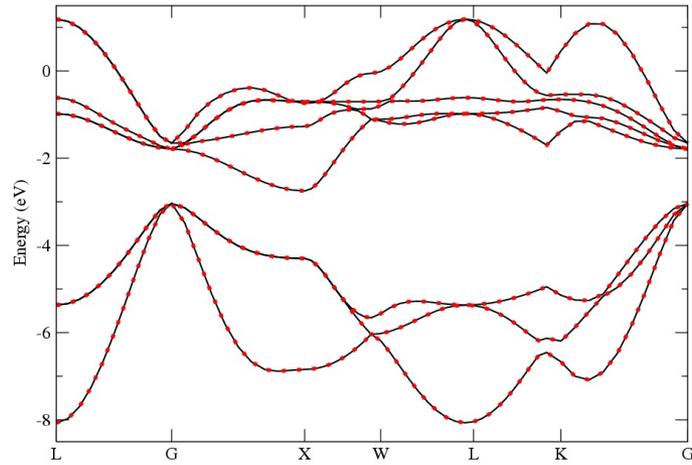
Max{|WF|} = 1



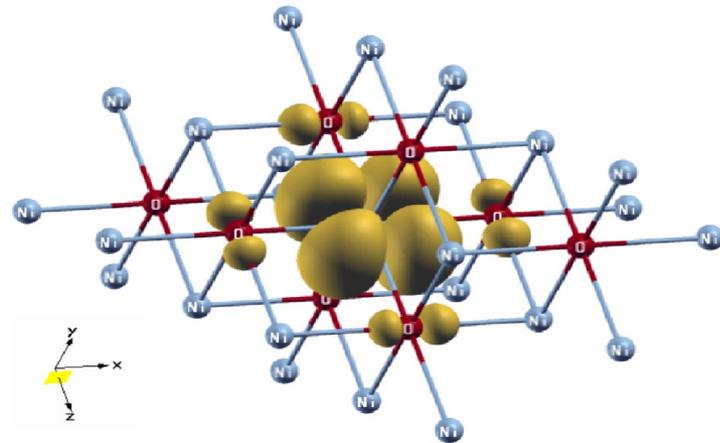
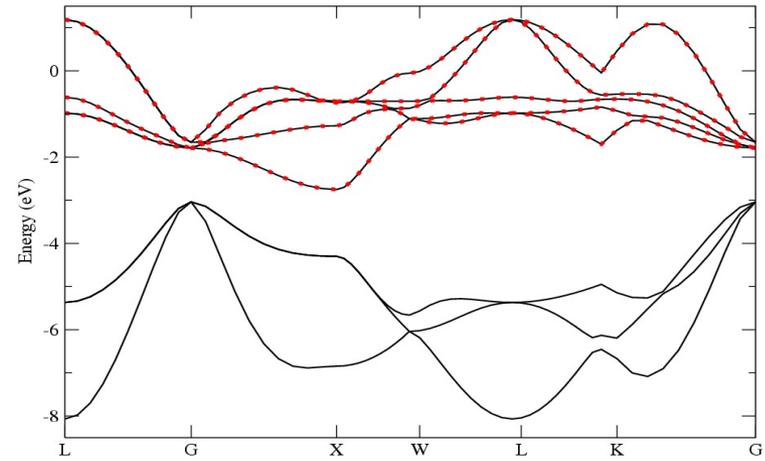
3D plot of WF isosurface:

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

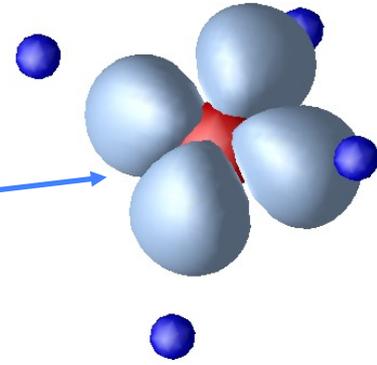
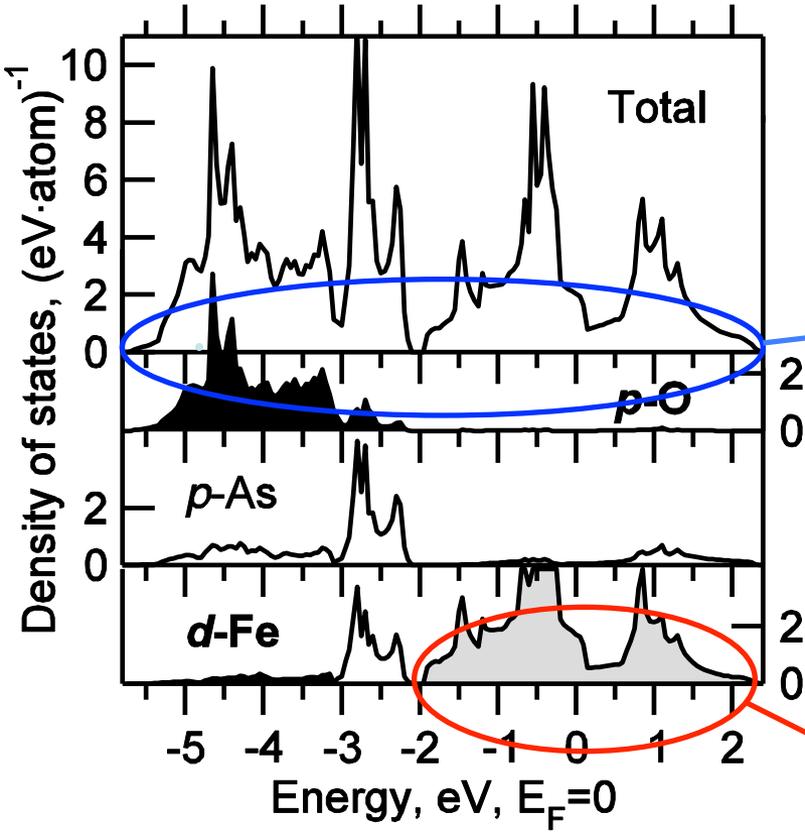


Full bands projection

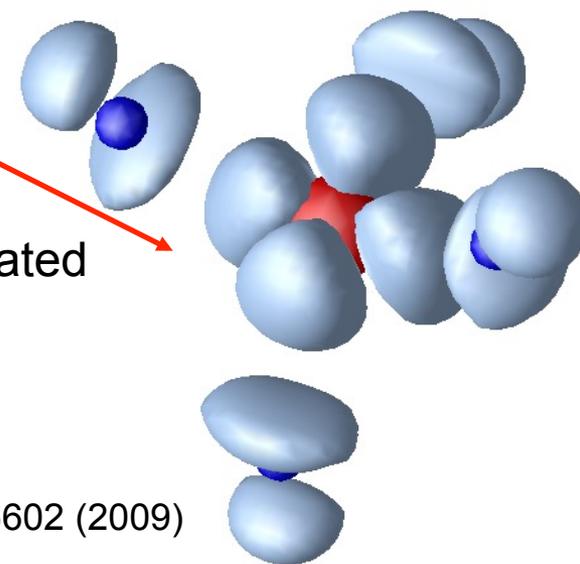


d-bands only projection

Novel superconductor LaOFeAs

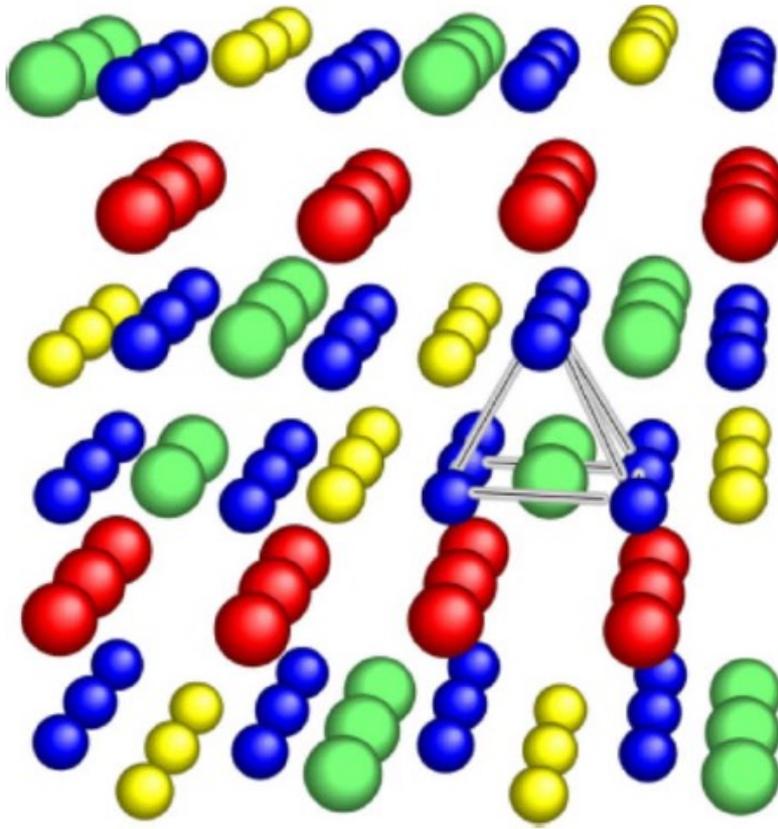


All bands WF
constrain DFT
 $U=3.5$ eV
 $J=0.8$ eV

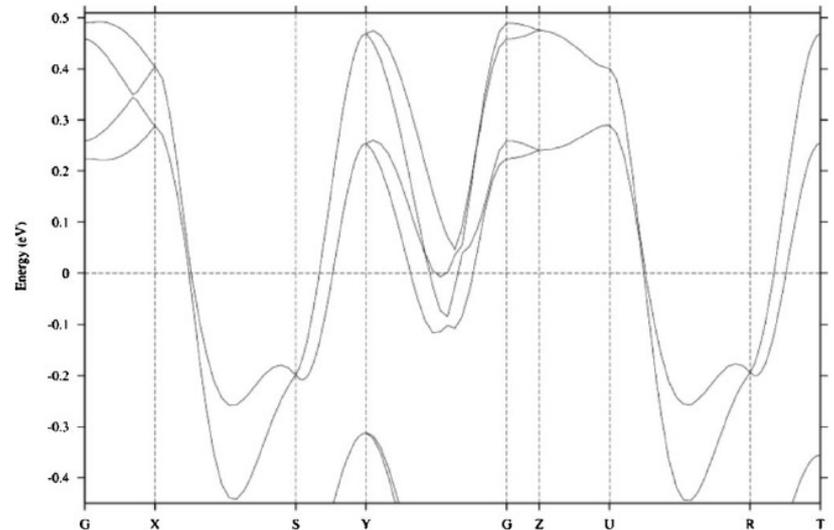


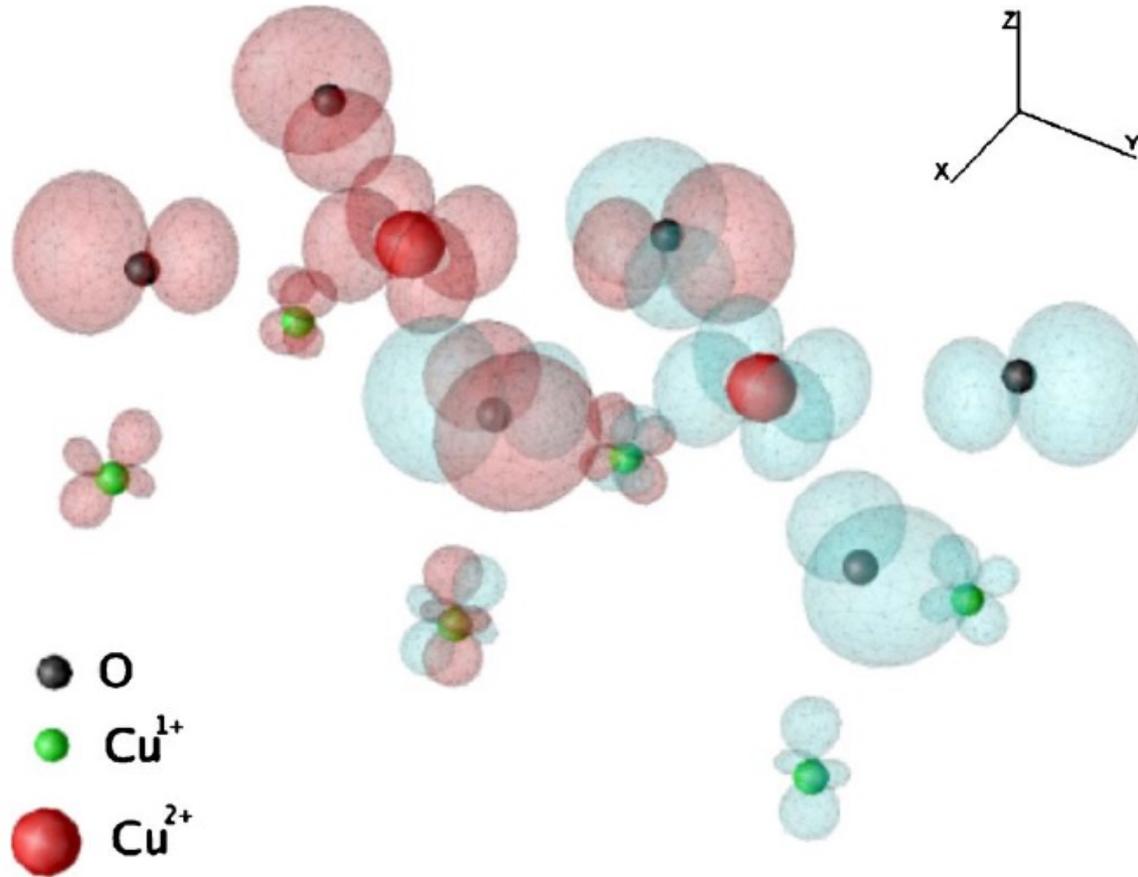
Fe3d band
only WF
constrain DFT
 $U=0.8$ eV
 $J=0.5$ eV

$d(x^2-y^2)$ Wannier functions (WF) calculated
for all bands (O2p,As4p,Fe3d) and
for Fe3d bands only

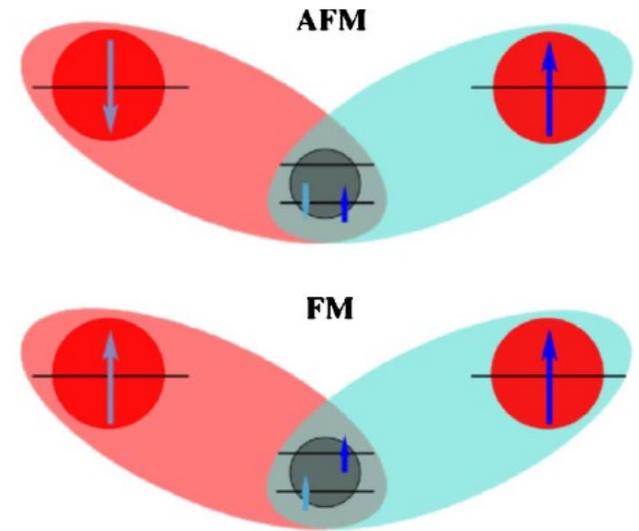
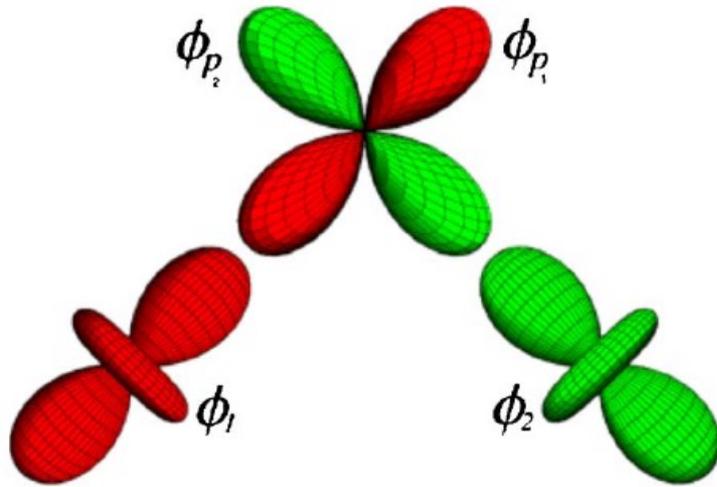


Crystal structure of LiCu_2O_2
Green, red, blue, black, and
yellow spheres are Cu^{2+} ,
 Cu^+ , O, and Li ions, respectively.



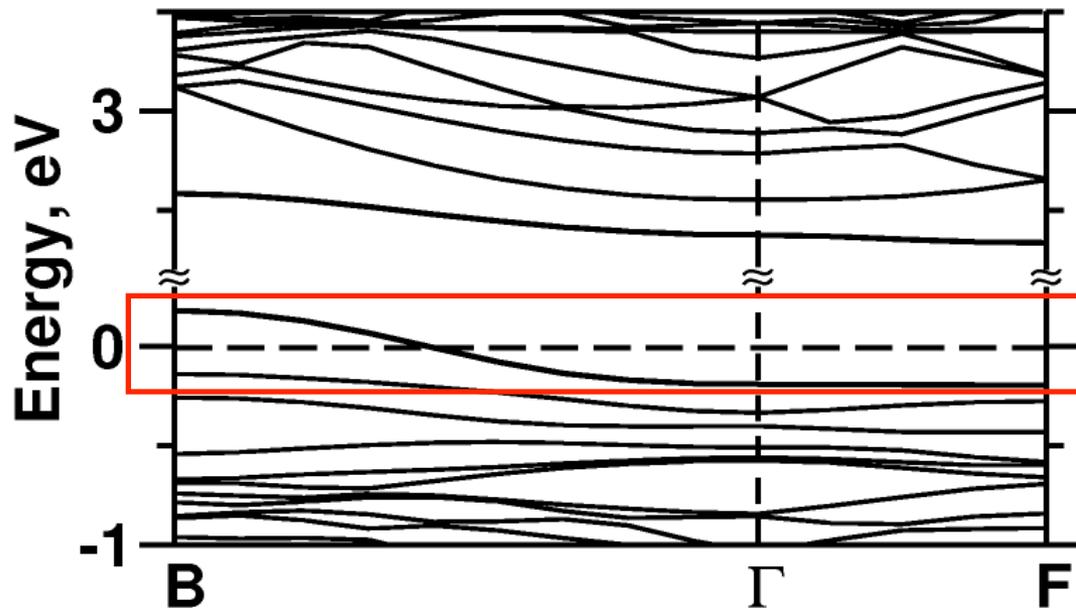
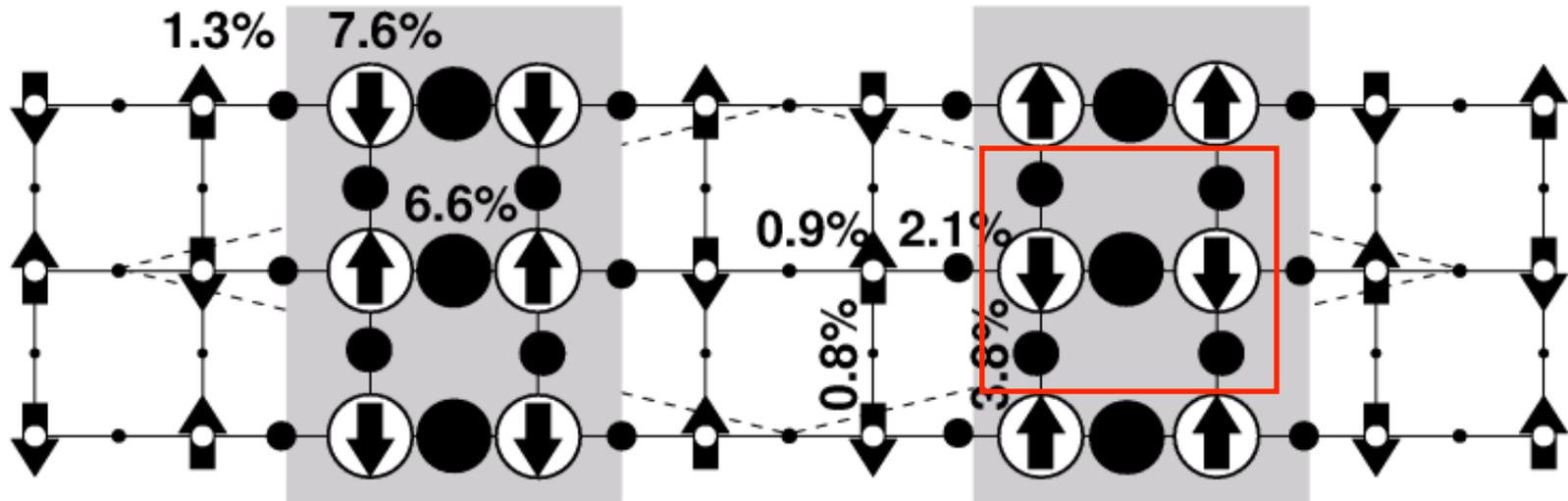


Wannier orbitals centered on neighboring copper atoms along the y axis.



90° 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

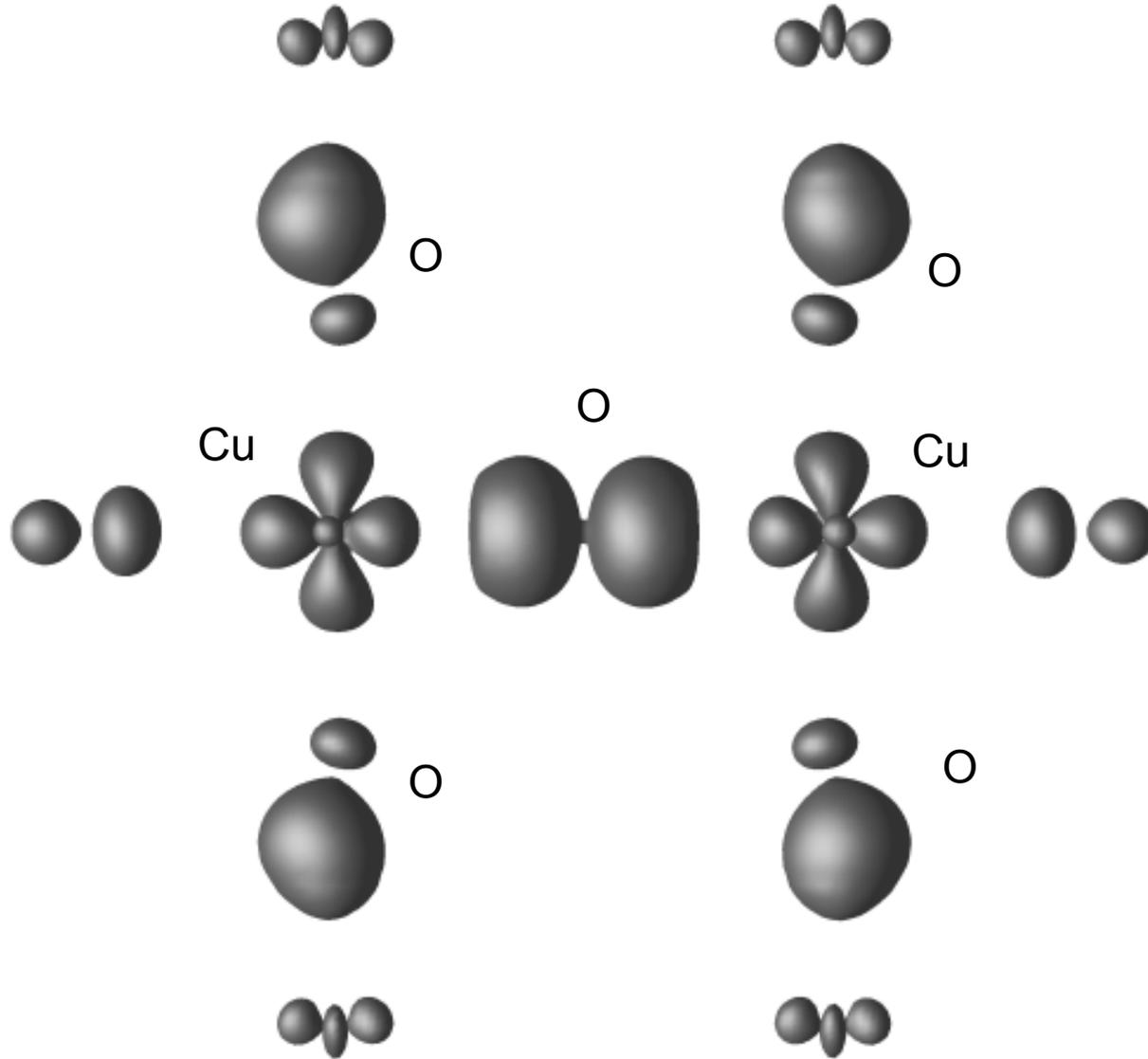
WF for stripe phase in cuprates



$\text{La}_{7/8}\text{Sr}_{1/8}\text{CuO}_4$

Half-filled band

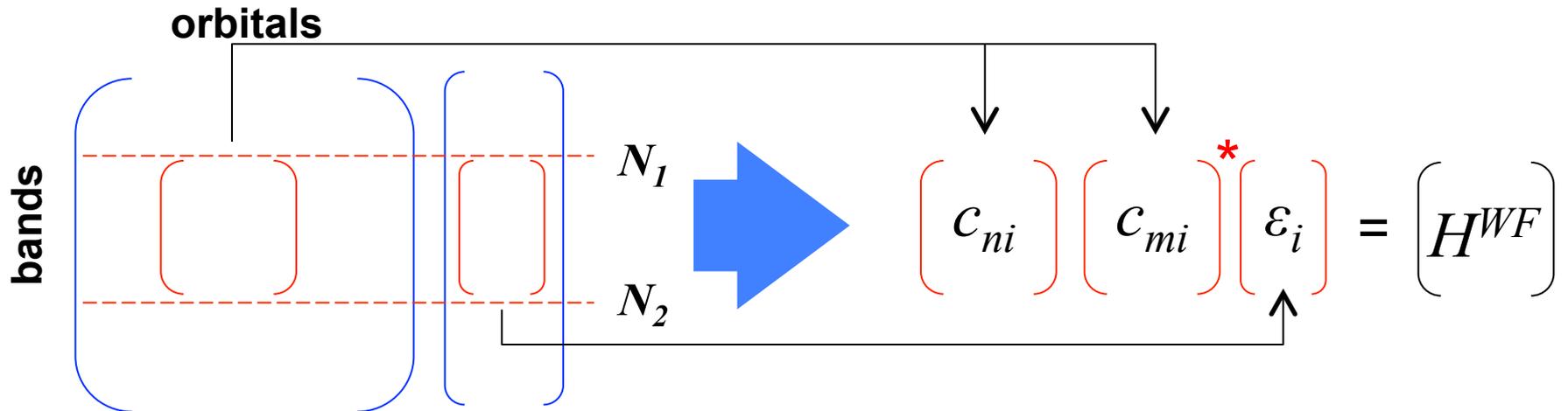
WF for stripe phase in cuprates



Projection procedure for Hamiltonian

Matrix elements of projected Hamiltonian:

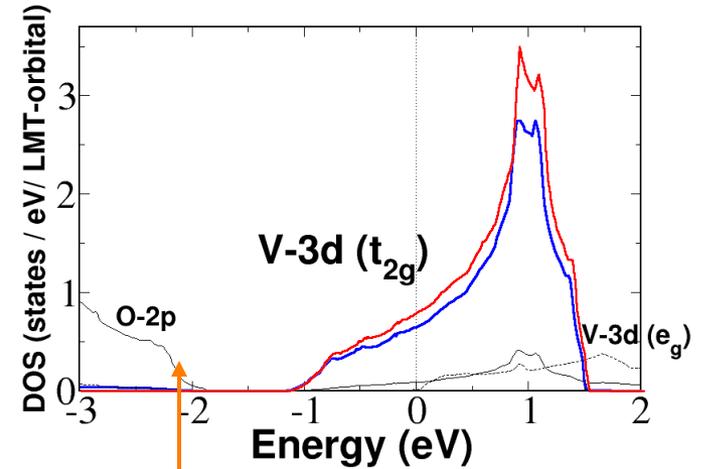
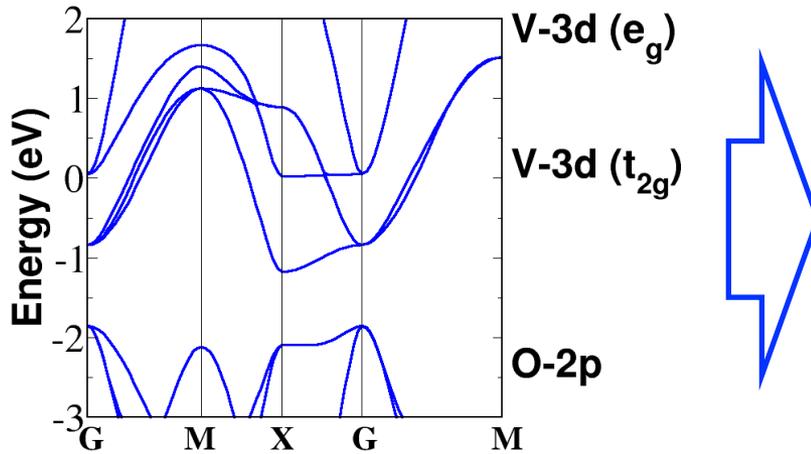
$$\widetilde{H}_{nm}^{WF}(\mathbf{k}) = \langle \widetilde{W}_{n\mathbf{k}} | \left(\sum_{i\mathbf{k}'} |\psi_{i\mathbf{k}'}\rangle \epsilon_i(\mathbf{k}') \langle \psi_{i\mathbf{k}'}| \right) | \widetilde{W}_{m\mathbf{k}} \rangle = \sum_{i=N_1}^{N_2} c_{ni}(\mathbf{k}) c_{mi}^*(\mathbf{k}) \epsilon_i(\mathbf{k})$$



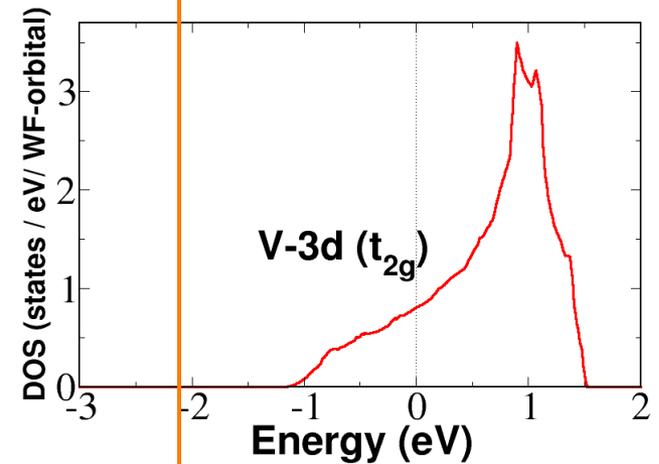
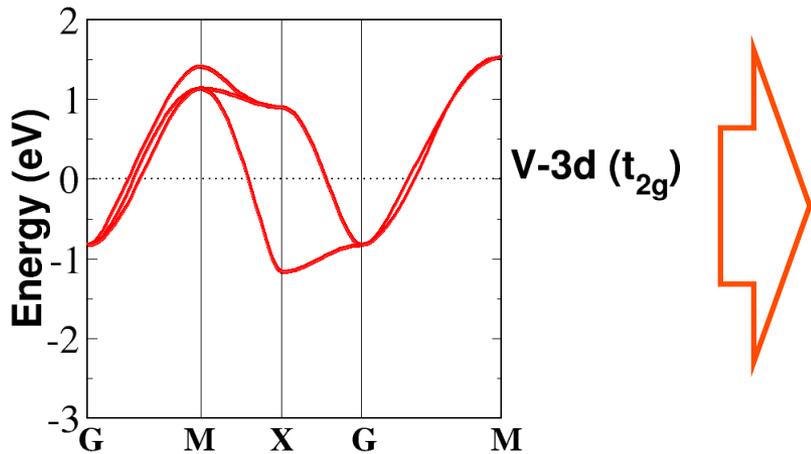
LMTO Eigenvectors, Eigenvalues

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:

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

Density matrix operator:

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



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:

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

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

In the absence of Self-energy:

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

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

Coincides with definition of WF using Bloch functions

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 $k = 0, 2, \dots, 2l$

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, $L=(l,m)$:

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

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

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

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 $1001/2025$.

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:

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

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

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: $\epsilon_d = \frac{\partial E_{DFT}}{\partial n_d} \longrightarrow U = \frac{\partial \epsilon_d}{\partial n_d}$

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: $Q_n = Q_{nn}^{WF}$

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

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 $|nlm\sigma\rangle$ 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.

Coulomb interaction Hamiltonian:

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

is particle number operator for electrons on orbital $|ilm\sigma\rangle$

Here we have introduced matrices of direct

$U_{mm'}$ and exchange $J_{mm'}$ Coulomb interaction:

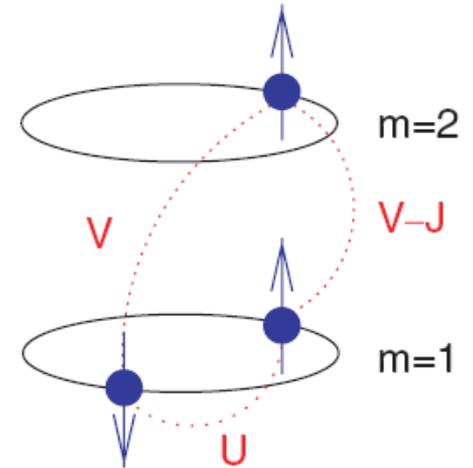
$$U_{mm'} \equiv \langle m, m' | V_{ee} | m, m' \rangle, \quad J_{mm'} \equiv \langle m, m' | V_{ee} | m', m \rangle$$

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:

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

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 :

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

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:

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

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

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

LDA+correlations Hamiltonian:

$$\hat{H}_{\text{LDA+correl}} = \hat{H}^0 + \hat{H}_{\text{Coulomb}}$$

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

Coulomb interaction term

$$\begin{aligned} \hat{H}^0 &= \hat{H}_{\text{LDA}} - \hat{H}_{\text{DC}} = \\ &= \sum_{\alpha\alpha'\sigma} \delta_{\alpha\alpha'} \epsilon_{\alpha}^0 \hat{n}_{\alpha}^{\sigma} + t_{\alpha\alpha'} \hat{c}_{\alpha}^{\sigma*} \hat{c}_{\alpha'}^{\sigma} \end{aligned}$$

Non-interacting Hamiltonian

Double-counting correction:

$$\epsilon_{\alpha}^0 = \frac{\partial}{\partial \mathbf{n}_{\alpha}} \left(\mathbf{E}_{\text{LDA}} - \frac{1}{2} \mathbf{U} \mathbf{n}_d (\mathbf{n}_d - \mathbf{1}) \right) = \epsilon_{\alpha} - \mathbf{U} (\mathbf{n}_d - \frac{1}{2})$$

LDA+U method: static mean-field approx.

Static mean-field decoupling of four Fermi operators product:

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

results in one-electron Hamiltonian:

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

$$\begin{aligned} V_{mm'}^\sigma = \sum_{\{m\}} & \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{m''m'''}^{-\sigma} + (\langle m, m'' | V_{ee} | m', m''' \rangle - \\ & - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{m''m'''}^\sigma \} - \bar{U} (n_d - \frac{1}{2}) \end{aligned}$$

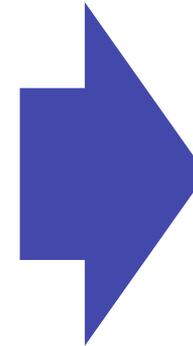
LDA+U method: static mean-field approx.

LDA+U functional:
$$\mathbf{E} = \mathbf{E}_{\text{LDA}} - \frac{1}{2} \mathbf{U} \mathbf{n}_d (\mathbf{n}_d - 1) + \frac{1}{2} \mathbf{U} \sum_{i \neq j} \mathbf{n}_i \mathbf{n}_j$$

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

Occupied states: $\mathbf{n}_i = 1 \Rightarrow \varepsilon_i = \varepsilon_{\text{LDA}} - \frac{\mathbf{U}}{2}$

Empty states: $\mathbf{n}_i = 0 \Rightarrow \varepsilon_i = \varepsilon_{\text{LDA}} + \frac{\mathbf{U}}{2}$



Mott-Hubbard gap

$$\mathbf{U} \equiv \frac{\partial \varepsilon_{\text{LDA}}}{\partial \mathbf{n}_d}$$

Coulomb interaction parameter

LDA+U functional:

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

Interaction term:

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

Double-counting term:

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

Non-local LDA+U potential operator:

$$\hat{H}_{LDA+U} = \hat{H}_{LSDA} + \sum_{mm'\sigma} |inlm\sigma\rangle V_{mm'}^\sigma \langle inlm'\sigma|$$

Potential correction matrix:

$$V_{mm'}^\sigma = \sum_{m''m'''} \{ U_{mm'm''m'''} n_{m''m}^{-\sigma} + (U_{mm'm''m'''} - J_{mm'm''m'''}) n_{m''m}^\sigma \} - U(n_d - \frac{1}{2}) + J(n_d^\sigma - \frac{1}{2})$$

Occupation matrix:

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

Exchange interaction couplings

Heisenberg Hamiltonian parameters:

$$\mathbf{E} = \sum_{ij} \mathbf{J}_{ij} \vec{\mathbf{S}}_i \vec{\mathbf{S}}_j \quad \mathbf{J}_{ij} = \frac{\partial^2 \mathbf{E}}{\partial \theta_i \partial \theta_j}$$

Calculation of J from LDA+U results:

$$\mathbf{J}_{ij} = \sum_{\{m\}} \mathbf{I}_{mm'}^i \chi_{mm'm''m'''}^{ij} \mathbf{I}_{m''m'''}^j \quad \mathbf{I}_{mm'}^i \equiv \mathbf{V}_{mm'}^{i\uparrow} - \mathbf{V}_{mm'}^{i\downarrow}$$
$$\chi_{mm'm''m'''}^{ij} = \sum_{kmm'} \frac{f_{nk\downarrow} - f_{n'k\uparrow}}{\epsilon_{nk\uparrow} - \epsilon_{n'k\downarrow}} \mathbf{c}_{nk\uparrow}^{ilm*} \mathbf{c}_{nk\uparrow}^{jlm''*} \mathbf{c}_{n'k\downarrow}^{ilm'} \mathbf{c}_{n'k\downarrow}^{jlm'''}$$

LDA+U eigenvalues
and eigenfunctions:

$$\epsilon_{nk\sigma}; \quad \Psi_{nk\sigma} = \sum_{ilm} \mathbf{c}_{nk\sigma}^{ilm} |ilm\rangle$$