Electronic structure calculations

Vladimir I. Anisimov

Institute of Metal Physics
Ekaterinburg, Russia
• 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
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
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
Electronic structure calculations

Many-electrons equations

\[ \hat{H} \Psi = E\Psi \]

where \( \Psi = \Psi(x_1, x_2, \ldots, x_N) \) is many electron wave function depending on \( x_1, x_2, \ldots, x_N \) coordinates of all \( N \) electrons.

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

\[ \hat{H} = \sum_{\mu=1}^{N} \hat{H}_\mu + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \frac{e^2}{|x_\mu - x_\nu|} \]
Electronic structure calculations

Many-electrons equations

\[ \hat{H}_\mu = -\frac{\hbar^2}{2m} \nabla_\mu^2 + V_Z(x_\mu) \]

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

\[ V_Z = -\frac{Ze^2}{|x_\mu|} \]

Electrons variables separation leads to one-electron approximation:

\[ \Psi(x_1, x_2, \ldots, x_N) = u_1(x_1)u_2(x_2)\ldots u_N(x_N) \]

\( u_\mu(x) \) is a one-electron wave function
Electronic structure calculations

Hartree-Fock approximation

\[ \Psi = \frac{1}{\sqrt{N}} \begin{vmatrix} u_1(x_1) & u_1(x_2) & \ldots & u_1(x_N) \\ u_2(x_1) & u_2(x_2) & \ldots & u_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ u_N(x_1) & u_N(x_2) & \ldots & u_N(x_N) \end{vmatrix} \]

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

Hartree-Fock equations

\[ H_\mu u_\mu (x_\mu) + \sum_{\nu=1}^{N} \int u^*_\nu (x_\nu) \frac{2}{|x_\mu - x_\nu|} \{u_\nu (x_\nu)u_\mu (x_\mu) - \delta_{\sigma(\mu),\sigma(\nu)} u^*_\nu (x_\mu)u_\mu (x_\nu)\}dx_\nu = \varepsilon_\mu u_\mu (x_\mu), \quad 1 \leq \mu \leq N \]

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

\[ H_\mu u_\mu(x_\mu) + \left( \sum_{\nu=1}^{N} \int u_\nu^*(x_\nu) \frac{2}{|x_\mu - x_\nu|} u_\nu(x_\nu) \, dx_\nu \right) u_\mu(x_\mu) - \]

\[ \delta_{\sigma(\mu), \sigma(\nu)} \sum_{\nu=1}^{N} \left( \int u_\nu^*(x_\nu) \frac{2}{|x_\mu - x_\nu|} u_\mu(x_\nu) \, dx_\nu \right) u_\nu(x_\mu) = \varepsilon_\mu u_\mu(x_\mu), 1 \leq \mu \leq N \]

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

\[ V_H(x) = \sum_{\nu} \int u_\nu^*(s) \frac{2}{|x - s|} u_\nu(s) \, ds = \int \rho(s) \frac{2}{|x - s|} \, ds \]

\[ \rho(s) = \sum_{\nu} u_\nu^*(s) u_\nu(s) \]

\[ \nabla^2 V_H = 8\pi \rho \]
Electronic structure calculations

Hartree-Fock equations

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

\[ V_{ex}^{\mu\nu}(x) = \int \frac{2}{|x-s|} u_\mu^*(s) u_\nu(s) ds \]

Hartree-Fock equations have a form:

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

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
Electronic structure calculations

Slater approximation for exchange potential

Exchange potential for homogeneous electron gas:

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

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

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

Decoupled one-electron equation with the same potential for all wave functions instead of the integral-differential equations system
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 $\rho(r)$:

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

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

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

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

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 for one-electron wave functions:
Density Functional Theory

**Kohn-Sham equations**

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

Here \(\mathbf{R}_I\) is position vector for nucleus with charge \(Z_I\); \(\varepsilon_i\) 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 \(\varepsilon_i\) 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!
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 \( \rho(r) \):

\[
E_{xc}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho(r)) \, dr
\]

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

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

\[
E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}] = \int \rho(r) \varepsilon_{xc}(\rho^{\uparrow}(r), \rho^{\downarrow}(r)) \, dr
\]
In Local Density Approximation (LDA) exchange-correlation potential in some space point \( r \) depends only on local value of electron density \( \rho(r) \):

\[
V_{xc}(r) = \frac{d}{d\rho}(\rho \varepsilon_{xc}(\rho))
\]

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

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

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

\[
V_{ex}(r) = -4 \left( \frac{3 \rho(r)}{8\pi} \right)^{\frac{1}{3}}
\]
In Local Spin Density Approximation (LDA) exchange-correlation energy depends on two spin densities:

\[ \mathcal{E}_{xc}(\rho_\uparrow, \rho_\downarrow) \]

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

\[ V_\sigma(\mathbf{r}) = \frac{d}{d\rho_\sigma}(\rho \mathcal{E}_{xc}(\rho_\uparrow, \rho_\downarrow)) \]

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

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

but also on electron density gradient \( \nabla n_\sigma \)

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

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

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

GGA sometimes corrects and sometimes overcorrects the LSDA predictions.
Density Functional Theory

DFT self-consistent calculation scheme

Initial electron density defines starting potential

\[ \rho_{in}(r) \Rightarrow V_{in}(r) \]

Kohn-Sham equations solution

\[ [ -\nabla^2 + V(r) ] \Psi(r) = E \Psi(r) \]

results in a set of eigenvalues and eigenfunctions

\[ E_i, \Psi_i(r) \]

That gives a new value of electron density

\[ \rho_{out}(r) = \sum_i | \Psi_i(r) |^2 \]

which is used as an input density on the next iteration

\[ \rho_{out}(r) \Rightarrow \rho_{in}(r) \]

Self-consistency condition:

\[ \int d\mathbf{r} (\rho_{out}(r) - \rho_{in}(r))^2 < \varepsilon \]
Kohn-Sham equations for periodic crystal (translational invariant potential \( V(r+l) = V(r) \), \( l \) is lattice translation vector):

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

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

\[
\psi(r) \equiv \psi_k(r) = u_k(r) \exp(ik \cdot r)
\]

Bloch function satisfies to relation:

\[
\psi_k(r + l) = \exp(ik \cdot l) \psi_k(r)
\]
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 into two major groups. One of them uses as a basis set atomic-like orbitals centered at atoms and decaying with increasing distance from the center, for example Muffin-tin orbital (MTO) in Linearized Muffin-Tin Orbitals (LMTO) method:

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

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

$R_l(|\mathbf{r}|, E)$ is radial variable dependent part of Kohn-Sham equation solution for spherically symmetric potential inside atomic sphere with radius $S$. 
Another group of DFT methods uses delocalized plane waves as a basis set:

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

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

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

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.
Systematic underestimations for energy gap value of band insulator materials.

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

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GTS</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>5.04</td>
<td>7.73</td>
<td>7.83(^a)</td>
</tr>
<tr>
<td>Si</td>
<td>0.44</td>
<td>1.04</td>
<td>1.17(^b)</td>
</tr>
<tr>
<td>NiO</td>
<td>0.11</td>
<td>3.76</td>
<td>4.0–4.3(^c)</td>
</tr>
<tr>
<td>BaBiO(_3)</td>
<td>0.15</td>
<td>0.51</td>
<td>0.48(^d)</td>
</tr>
</tbody>
</table>
DFT problems for real materials

Systematic overestimation for cohesive energy.
Example of silicon:

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.378</td>
<td>5.463</td>
<td>5.429</td>
</tr>
<tr>
<td>$B$ (Mbar)</td>
<td>0.965</td>
<td>0.882</td>
<td>0.978</td>
</tr>
<tr>
<td>$E_c$ (eV/atom)</td>
<td>6.00</td>
<td>5.42</td>
<td>4.63</td>
</tr>
</tbody>
</table>
Breakdown of LDA for strongly correlated systems

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

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

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 $i$:

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

$$\rho_i = |\psi_i(r)|^2$$ 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 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:

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

$$= \tilde{\epsilon}_i^{LDA} + \left(1/2 - \tilde{n}_i\right) \frac{\partial \tilde{\epsilon}_i}{\partial \tilde{n}_i} \bigg|_{\tilde{n}_i=1/2}$$

using:

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

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

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

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

dielectric matrix is expressed via polarization operator $P(r, r', \omega)$

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 meal 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:

\[ E_{xc}^{hyb} = (1 - a) E_{xc}^{DFT} + a E_x^{HF} \]

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

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

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**

\[
\mathcal{H} = t \sum_{ij\sigma} \tilde{c}_{i\sigma}^+ \tilde{c}_{j\sigma} + J \sum_{ij} (S_i^e S_j^e)
\]

\[
\tilde{c}_{i\sigma}^+ = \hat{c}_{i\sigma}^+ (1 - \hat{n}_{i-\sigma})
\]

Creation operator for correlated electrons,

\[
J = 4t^2 / U
\]

Anderson kinetic exchange.

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

\[ H = \sum_{k\sigma} \varepsilon_k \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + J \sum_i S_i S_i \]

\( S \) is spin operator for localized electrons,

\[ S_i = \sum_{\mu\nu} \hat{c}_{i\mu}^\dagger \sigma_{\mu\nu} \hat{c}_{i\nu} \]

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)**

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

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

**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:**

\[
\Sigma(\omega) = \begin{pmatrix}
\sigma(\omega) & 0 & \ldots & 0 \\
0 & \sigma(\omega) & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & \sigma(\omega)
\end{pmatrix}
\]

**Green function:**

\[
G(\omega) = \int_{IBZ} (\omega - \Sigma(\omega) - H^0_{LDA}(k))^{-1} dk =
\]

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

Low-symmetry systems?
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]:

$$W_i(r - T) = \sum_k e^{-i k T} \langle r | \psi_{ik} \rangle$$

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:

$$|\psi_{ik}\rangle = \sum_j U_{ji}^{(k)} |\psi_{jk}\rangle$$

Unitary matrix

**Wannier functions and projection**

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

\[
|\tilde{W}_{nk}\rangle = \sum_{i=N_1}^{N_2} |\psi_{ik}\rangle \langle \psi_{ik}| \phi_n\rangle
\]

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

\[
\psi_{ik}(\mathbf{r}) = \sum_j c_{ji}(\mathbf{k}) \phi_j^k(\mathbf{r})
\]

**coefficients** of WF expansion in LMTO-orbitals:

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

Example of WF in real space

WF basis set for V-3d ($t_{2g}$) subband of SrVO$_3$: $XY$, $XZ$, $YZ$ - orbitals

[Images of molecular structures and density of states plots showing orbitals and band structure of SrVO$_3$.]
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 \(|WF| = 0.5\)
Full bands projection
d-bands only projection

Novel superconductor LaOFeAs

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

Crystal structure of LiCu$_2$O$_2$
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.

$90^\circ$ 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
Projection procedure for Hamiltonian

Matrix elements of projected Hamiltonian:

\[ \overline{H}_{nm}^{WF}(k) = \langle \overline{W}_{nk} \left| \sum_{ik'} |\psi_{i,k'}\rangle \epsilon_i(k') \langle \psi_{i',k'}\rangle \right| \overline{W}_{mk} \rangle = \sum_{i=N_1}^{N_2} c_{ni}(k) c_{mi}^*(k) \epsilon_i(k) \]

LMTO Eigenvectors, Eigenvalues
Projection results for SrVO₃

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:

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

Density matrix operator:

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

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:**

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

where

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

**In the absence of Self-energy:**

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

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

Coincides with definition of WF using Bloch functions
Coulomb interaction Hamiltonian:

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

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, \( L=(l,m) \):

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

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

\[ \times \left[ \frac{(l+m)!(l-m)!}{(l''+m'')!(l''-m'')!(l'+m')!(l'-m')!} \right]^{\frac{1}{2}} \]
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 \( \sim 0.625 \) 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:

\[ U = \int drdr'|W_n(r)|^2U(r, r')|W_n(r')|^2 \]

Screened Coulomb potential:

\[ U = [1 - vP]^{-1}v \]

Unscreened Coulomb potential:

\[ v(r, r') = 1/(r - r') \]

Polarization operator:

\[ P(r, r') = \sum_{\text{occ}} \sum_{\text{unocc}} \psi_i(r)\psi_i^*(r')\psi_j^*(r)\psi_j(r) \left\{ \frac{1}{\epsilon_i - \epsilon_j + i0^+} - \frac{1}{\epsilon_j - \epsilon_i - i0^+} \right\} \]

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: 

\[ U = \frac{\partial^2 E_{DFT}}{\partial n_d^2} \]

Connection of one-electron eigenvalues and total energy in DFT: 

\[ \epsilon_d = \frac{\partial E_{DFT}}{\partial n_d} \quad \Rightarrow \quad U = \frac{\partial \epsilon_d}{\partial n_d} \]

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:** 

\[ Q_n = Q_{nn}^{WF} \]
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 \(|inl\sigma>\) 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

\[
\hat{H}_{Coulomb} = \frac{1}{2} \sum_{i=i_d,l=l_d} \sum_{m,m',\sigma} \left\{ U_{mm'} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\bar{\sigma}} + (U_{mm'} - J_{mm'}) \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma} \right\} - \\
- \frac{1}{2} \sum_{i=i_d,l=l_d} \sum_{m \neq m',\sigma} J_{mm'} \left\{ \hat{c}^+_{ilm\sigma} \hat{c}_{ilm\bar{\sigma}} \hat{c}^+_{ilm'\bar{\sigma}} \hat{c}_{ilm'\sigma} + \hat{c}^+_{ilm\sigma} \hat{c}^+_{ilm\bar{\sigma}} \hat{c}_{ilm'\sigma} \hat{c}_{ilm'\bar{\sigma}} \right\}. 
\]

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 \( |inlm\sigma> \)

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:

\[ \hat{H}_{\text{Coulomb}} = \frac{1}{2} \sum_{i=i_d,l=l_d} \sum_{m,m',\sigma} \{ U_{mm'} \hat{n}_{ilm\sigma} \hat{n}_{ilm’\bar{\sigma}} + (U_{mm'} - J_{mm'}) \hat{n}_{ilm\sigma} \hat{n}_{ilm’\sigma} \} \]
Kanamori parameterization is usually used where for the same orbitals \((m = m')\) direct Coulomb interaction \(U_{mm} \equiv U\), for different orbitals \((m \text{ non equal } m')\) \(U_{mm'} \equiv U'\) with \(U' \equiv U - 2J\) and exchange interaction parameter does not depend on orbital index \(J_{mm'} \equiv J\).

In this approximation Hamiltonian is:

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

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 $\epsilon_d$ 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 $\epsilon_{DC}$ can be determined as:

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

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

$$\hat{H}_{DC} = \sum_{inlm\sigma} \epsilon_{DC} \hat{n}_{inlm\sigma}$$
**LDA+correlations Hamiltonian:**

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

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

\[
\hat{H}^0 = \hat{H}_{\text{LDA}} - \hat{H}_{\text{DC}} = \sum_{\alpha\alpha', \sigma} \delta_{\alpha\alpha'} \epsilon^0_{\alpha} \hat{n}_{\alpha} + t_{\alpha\alpha'} \hat{c}_{\alpha}^\dagger \hat{c}_{\alpha'}^\dagger
\]

**Coulomb interaction term**

**Non-interacting Hamiltonian**

**Double-counting correction:**

\[
\epsilon^0_{\alpha} = \frac{\partial}{\partial n_{\alpha}} \left( E_{\text{LDA}} - \frac{1}{2} U n_d (n_d - 1) \right) = \epsilon_{\alpha} - U (n_d - \frac{1}{2})
\]
LDA+U method: static mean-field 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:

\[
\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 | \\

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})
\]
**LDA+U method: static mean-filed approx.**

**LDA+U functional:**

\[ E = E_{\text{LDA}} - \frac{1}{2} U n_d (n_d - 1) + \frac{1}{2} U \sum_{i \neq j} n_i n_j \]

**One-electron energies:**

\[ \varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon_{\text{LDA}} + U \left( \frac{1}{2} - n_i \right) \]

**Occupied states:**

\[ n_i = 1 \quad \Rightarrow \quad \varepsilon_i = \varepsilon_{\text{LDA}} - \frac{U}{2} \]

**Empty states:**

\[ n_i = 0 \quad \Rightarrow \quad \varepsilon_i = \varepsilon_{\text{LDA}} + \frac{U}{2} \]

**Coulomb interaction parameter:**

\[ U \equiv \frac{\partial \varepsilon_{\text{LDA}}}{\partial n_d} \]

**Mott-Hubbard gap**
LDA+U method: general formalism

LDA+U functional:

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

Interaction term:

\[ E_U[\{n^\sigma\}] = \frac{1}{2} \sum_{\{m\}\sigma} \{U_{mm'm''m''}n_{mm'}^\sigma n_{m''m''}^{-\sigma} + (U_{mm'm''m''} - J_{mm'm''m''})n_{mm'}^\sigma n_{m''m''}^\sigma \} \]

Double-counting term:

\[ E_{\text{DC}}[\{n^\sigma\}] = \frac{1}{2} Un_d(n_d - 1) - \frac{1}{2} J[n_d^\uparrow(n_d^\uparrow - 1) + n_d^\downarrow(n_d^\downarrow - 1)] \]

Non-local LDA+U potential operator:

\[ \hat{H}_{LDA+U} = \hat{H}_{LSDA} + \sum_{mm'\sigma} \left| inlm\sigma > V_{mm'}^{\sigma} < inlm'\sigma \right| \]

Potential correction matrix:

\[ V_{mm'}^{\sigma} = \sum_{m'm''m} \{ U_{mm'm''m} n^{-\sigma}_{m''m} + (U_{mm'm''m} - J_{mm'm''m}) n^\sigma_{m''m} \} - U(n_d - \frac{1}{2}) + J(n^\sigma_d - \frac{1}{2}) \]

Occupation matrix:

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

Heisenberg Hamiltonian parameters:

\[ E = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j \]

\[ J_{ij} = \frac{\partial^2 E}{\partial \theta_i \partial \theta_j} \]

Calculation of J from LDA+U results:

\[ J_{ij} = \sum_{\{m\}} I^i_{mm'} \chi^{ij}_{mm'm''} I^j_{m'm''} \quad I^i_{mm'} \equiv V^i_{mm'} - V^i_{mm'} \]

\[ \chi^{ij}_{mm'm''} = \sum_{kmn'} \frac{f_{nk\downarrow} - f_{n'k\uparrow}}{\varepsilon_{nk\uparrow} - \varepsilon_{n'k\downarrow}} c^{ilm\ast}_{nk\uparrow} c^{jlm'}_{nk\uparrow} c^{ilm'}_{n'k\downarrow} c^{jlm''}_{n'k\downarrow} \]

LDA+U eigenvalues and eigenfunctions:

\[ \varepsilon_{nk\sigma}; \quad \Psi_{nk\sigma} = \sum_{ilm} c^{ilm}_{nk\sigma} |ilm> \]