Density Functional and Dynamical Mean-Field Theory (DFT+DMFT) method and its application to real strongly correlated materials

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Method formulation:

Dynamical Mean-Field Theory (DMFT)

Wannier functions as localized orbitals basis

Determination of Hamiltonian parameters

“Constrained DFT” calculations for Coulomb interaction parameters

DFT+DMFT calculation scheme
Results of DFT+DMFT calculations:

Strongly correlated metal Sr(Ca)VO$_3$
Metal-insulator transition in V$_2$O$_3$
Heavy fermions in d-system Li$_2$VO$_4$
Charge transfer insulator NiO
Metal-insulator transition with pressure in MnO
Correlated covalent insulators FeSi and FeSb$_2$
Novel superconductor LaOFeAs
Jahn-Teller distortions in KCuF$_3$
f-electrons localization in Ce
Dynamical Mean-Field Theory

Hubbard model:
Simplest lattice fermions model

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

D=2,3: unsolvable many-body problem

- reliable approximations?
- non-perturbative energy scale?

Static mean-field (DFT+U) does not describe correlated metal and paramagnetic insulator

Correlation phenomena:
Metal-insulator transition
Ferromagnetisms,...
Single-impurity Anderson Model:

Non-interacting conduction (s-) electrons

+ Single $d$-orbital ("impurity")

with interaction $U$

+ $s,d$-hybridization

\[
\hat{H}_{\text{SIAM}} = \sum_{k,\sigma} \epsilon_k \hat{c}^\dagger_{k,\sigma} \hat{c}_{k,\sigma} + U \hat{n}_d \hat{n}_d + \sum_{k,\sigma} (V_k d^\dagger_\sigma c_{k,\sigma} + h.c.)
\]

many-body problem: solve with QMC, NRG,…

- Characteristic 3-peak structure
- non-perturbative energy scale ("Kondo physics")
**Dynamical Mean-Field Theory**

Mapping impurity Anderson model on lattice Hubbard model

Hubbard model:

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

- proper time resolved treatment of local electronic interactions
- includes all many-body correlations!

"single-impurity Anderson model" + self-consistency

Georges and Kotliar (1992)

dynamic mean-field (hybridization function):

\[ \Delta(\omega) = \sum_k \frac{|V_k|^2}{\omega - \epsilon_k} \]

self-consistency condition:

\[ G[\Delta(\omega)] = \sum_k \{\omega - \Sigma[\Delta(\omega)] - t_k\}^{-1} \]

\[ \Sigma[\Delta(\omega)] \equiv \Delta(\omega) - G^{-1}(\Delta(\omega)) + \omega \]

Effective impurity model defined by hybridization function is solved with an "impurity" solver, e.g., QMC, NRG, ED,…
Including material specific details

Model Hamiltonians:
- input parameters $(t, U, \ldots)$ unknown
- systematic many-body approach

Density Functional Theory:
- material specific: “ab initio”
- fails for strong correlations

Anisimov et al. (1997)
Lichtenstein, Katsnelson (1998)
Kotliar, Vollhardt (2004)

DFT+DMFT

- DFT band structure:
  \[ \varepsilon_{lml'm'}(k) \rightarrow \hat{H}_{LDA} \]
- + Coulomb $U$
  \[ \rightarrow \hat{H}_{LDA+corr} \]
- solve $\hat{H}_{LDA+corr}$ by DMFT
Wannier functions as orbitals basis set

Wannier functions in real space [1]:

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

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:

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

**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):**

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

\[
|\tilde{W}_{nk}\rangle = \sum_{i=N_1}^{N_2} \sum_j c_{ji}(k) c_{ni}^*(k) |\phi_j^k\rangle = \sum_j \tilde{b}_{jn}^k |\phi_j^k\rangle
\]

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

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

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

d-bands only projection

WF for stripe phase in cuprates

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

Half-filled band

WF for stripe phase in cuprates
Matrix elements of projected Hamiltonian:

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

LMTO Eigenvectors, Eigenvalues
Projection results for SrVO$_3$

Eigenvalues of full-orbital and projected Hamiltonians are the same.

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

\[ U \equiv \frac{\partial E_n}{\partial Q_n} \]
Local Green function:

\[
G^{\text{loc}}_{n,n'}(\varepsilon) = \frac{1}{V_{\text{IBZ}}} \int d\mathbf{k} \left( \left[ (\varepsilon + E_f^{(N)})1 - H_{0W}^{WF}(\mathbf{k}) - \Sigma(\varepsilon) \right]^{-1} \right)_{n,n'}
\]

Dyson equation defines bath Green function:

\[
G^{-1} = (G^{\text{loc}})^{-1} + \Sigma
\]

Self-consistent condition:

\[
G^{\text{loc}} = G^{\text{imp}} \Rightarrow \Sigma_{\text{new}}
\]

Impurity problem defined bath Green function is solved by QMC
Strongly correlated metal SrVO$_3$

$V^{+4}$ (d$^1$) ion in cubic perovskite crystal structure

One electron in partially filled t$_{2g}$ band

Strongly correlated metal \( \text{SrVO}_3 \)

LDA+DMFT(QMC) results

\( V_{3d(t_{2g})} \) orbitals

\( \bar{U} = 3.55 \text{ eV}, J = 1.0 \text{ eV} \)

Strongly correlated metal with pronounced Lower Hubbard band (LHB)
Strongly correlated metal $\text{SrVO}_3$

Spectral function $A(k, \omega) = -\frac{1}{\pi} \text{Im} \text{Tr} \left[ \omega - \Sigma(\omega) - H_0(k) \right]^{-1}$
Strongly correlated metal SrVO$_3$

Effective electron mass
\[
\frac{m^*}{m} = 1 - \frac{\partial \text{Re} \Sigma(\omega)}{\partial \omega} \bigg|_{\omega=0} \approx 2
\]

Bands narrowing
\[
\tilde{\varepsilon}(k) = \left( \frac{m^*}{m} \right)^{-1} \varepsilon_0(k)
\]
Prototypical Mott insulator. Iso-structural paramagnetic metal to paramagnetic insulator transition with small volume change due to chemical negative pressure.
Mott insulator $V_2O_3$

$V^{+3} (d^2)$ ion in trigonal symmetry corundum crystal structure. Two electrons in $t_{2g}$ band ($W \sim 2.5$ eV). Trigonal crystal field splitting $\sim 0.3$ eV leads to orbital polarization in DMFT.
Paramagnetic metal to paramagnetic insulator transition with small change in corundum crystal structure parameters

Heavy-fermions without f-electrons: linear specific heat coefficient $g=420 \text{ mJ/molK}^2$, effective electron mass $m^*/m =25$ below $T_K \sim 28 \text{ K}$

Cubic spinel crystal structure with local trigonal symmetry
Heavy fermions material LiV$_2$O$_4$

Sharp quasiparticle peak above the Fermi for $T=0$ limit (PQMC)

XPS => Quasiparticle peak 10 meV width
4 meV above the Fermi

Charge transfer insulator in paramagnetic phase.
Ni$^{+2}$ ($d^8$) ion in cubic rock salt crystal structure

Holes in charge transfer insulator have predominantly oxygen 2p character.
Band structure of charge transfer insulator combines dispersive (itinerant states) and flat bands (localized states).

Metal-insulator transition (paramagnetic insulator to paramagnetic metal) with pressure in MnO accompanied with high-spin to low-spin state transition.

Metal-insulator transition in MnO

High-spin state (HS) - $t_{2g}^3 e_{2g}^2$ configuration

Low-spin state (LS) - $t_{2g}^5 e_{0g}^0$ configuration
Decreasing volume with pressure increases crystal field splitting $\Delta_{cf}$ competing with exchange energy $J$ that results in HS $\rightarrow$ LS transition with volume collapse.
Transition from non-magnetic semiconductor to paramagnetic metal with temperature increase in FeSi and FeSb$_2$. Electron doping in Fe$_{1-x}$Co$_x$Si results in ferromagnetic metallic state.
Effective one-orbital per Fe ion model corresponding to covalent insulator

Temperature increase results in transition from nonmagnetic covalent insulator to bad metal with local moments. Electron doping leads to divergence of susceptibility for low T indicating ferromagnetic instability.
Pnictide superconductor LaOFeAs

$T_c = 26K$ for F content $\sim 11\%$

Pnictide superconductor LaOFeAs

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

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

V.Anisimov et al, cond-mat/0807.0547
DMFT results for Hamiltonian and Coulomb interaction parameters calculated with Wannier functions for Fe3d bands only
U=0.8 eV
J=0.5 eV

Weakly correlated regime!
DMFT results for Hamiltonian and Coulomb interaction parameters calculated with Wannier functions for all bands (O2p, As4p, Fe3d)

\( U = 3.5 \ \text{eV} \)

\( J = 0.8 \ \text{eV} \)

**Weakly correlated regime!**
**KCuF\textsubscript{3}: a prototype \( e_g \) \((3d^9)\) Jahn-Teller system**

Crystal structure and Orbital order (OO):

- pseudo cubic perovskite \textit{l}4/mcm
- cooperative JT distortion below 1000 K
- \textit{Neel} temperature \(\sim38\) K
- \(d_{x^2-y^2}\) hole antiferroorbital ordering

**d-level scheme:**

- Free ion
- Cubic
- Tetragonal \((c/a < 1)\)

**GGA (Cu 3d) density of state:**

- Metallic solution -> inconsistent with exp
KCuF$_3$: GGA+DMFT results

Total energy:

$U = 7.0$ eV, $J = 0.9$ eV

GGA:
- metallic solution
- total energy almost const for JT distortion < 4 %
- no JT distortion (orbital order) for $T > 100$ K !

GGA+DMFT:
- paramagnetic insulator
- energy gain of ~ 175 meV
- antiferro-orbital order
- optimal JT distortion at 4.2 %
- JT distortion persists up to 1000 K (melting tem-re)

→ inconsistent with experiment

→ in good agreement with exp

Leonov et al., cond-mat/0804.1093, accepted to PRL
f-electrons localization in Ce

Ce a-g transition with 15% volume change. Kondo temperature $T_K$ 1000K (a), 30K (g)

• Dynamical mean-field theory (DMFT) is a powerful tool to study correlation effects

• *Ab-initio* definition of correlated orbitals and interaction strength (U) between them based on Wannier functions formalism results in “first-principles” DFT+DMFT calculations scheme

• DFT+DMFT method was successful in describing paramagnetic Mott insulators, correlated metals, charge transfer insulators, metal-insulator transitions with pressure and temperature, cooperative Jahn-Teller lattice distortions