

Electronic Structure Calculations with Dynamical Mean Field Theory

S. Y. Savrasov


Department of Physics, University of California, Davis

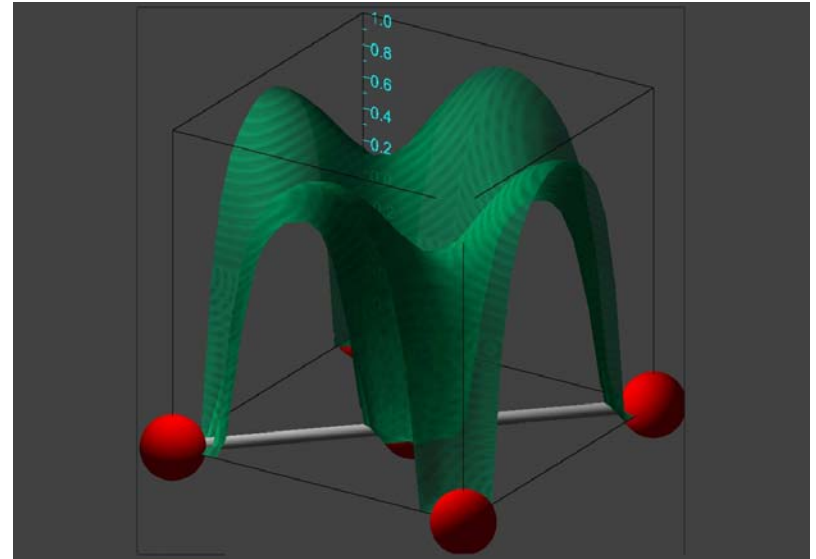


Supported by NSF, DOE

Electronic Structure

□ DFT considers total energy E as a functional of the density ρ and reduces the problem to solving single particle Kohn Sham equations with energy independent potential

$$(-\nabla^2 + V_{DFT})\psi_k = \epsilon_k \psi_k$$




From here various properties can be deduced with spectacular accuracies

Band structures ϵ_k

Single particle spectra
Densities of states
Photoemission & Optics
Transport & Superconductivity

Density ρ

Magnetic Moments
Bonding & Covalency
Static Response Functions

Energy E

Crystal structures
Equations of State
Phonon and Magnon Spectra

Problems with Strongly Correlated Systems

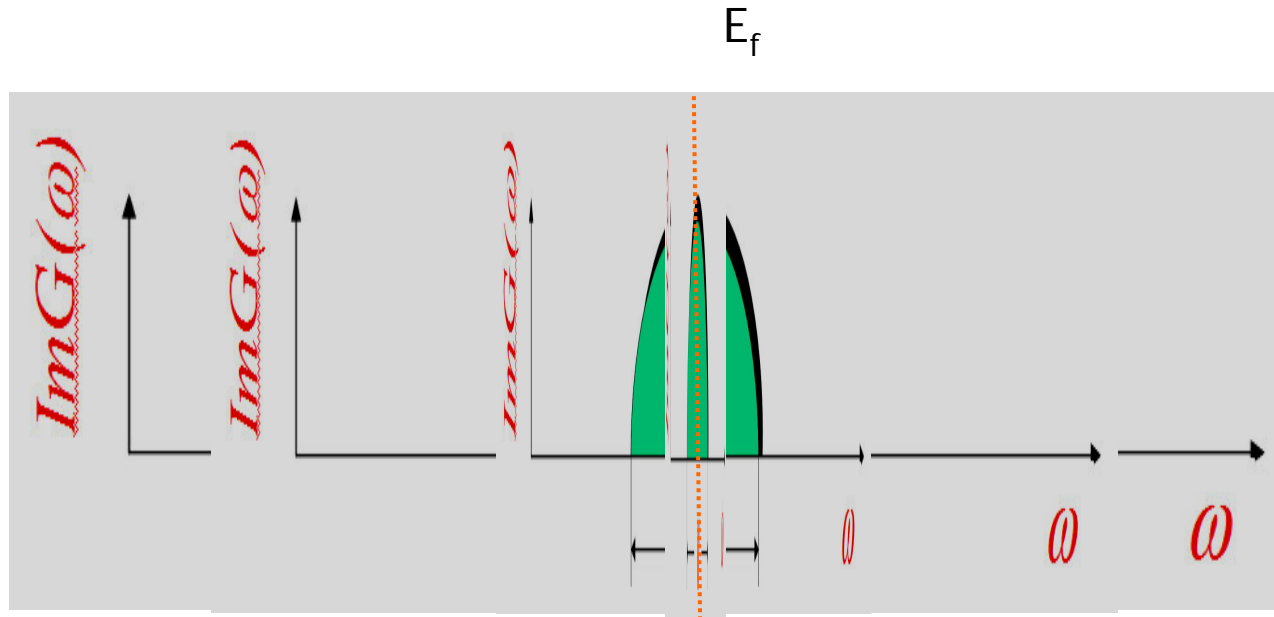
Density functional calculations using local density approximation (LDA) grossly fail for materials with strong correlations:

- ❑ Ground state volume of δ -Pu is 30% too small within LDA.
- ❑ Multiplet transitions seen in many lanthanides and actinides cannot be resolved by DFT-LDA calculation.
- ❑ Kondo and mixed valence physics is missing.
- ❑ Mott physics, paramagnetic insulating behavior cannot be modeled by DFT.

Mott Transition is not here!

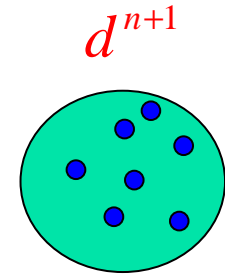
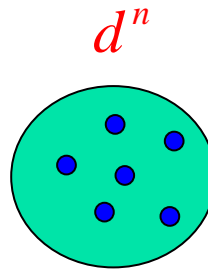
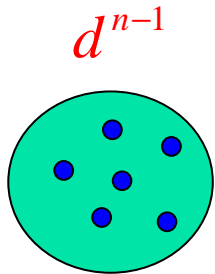
Paramagnetic Mott insulators at high temperatures cannot be understood based on standard band theory argument.

According to the band theory a material with partially filled band will remain metallic at all interatomic distances



Atomic limit is not correctly described.

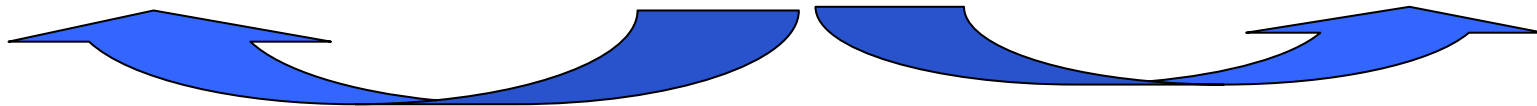
Excitations in Atoms



$$E_n = \varepsilon_d n + \frac{1}{2} U n(n-1)$$

$$E_{n-1} = \varepsilon_d (n-1) + \frac{1}{2} U (n-1)(n-2)$$

$$E_{n+1} = \varepsilon_d (n+1) + \frac{1}{2} U (n+1)n$$

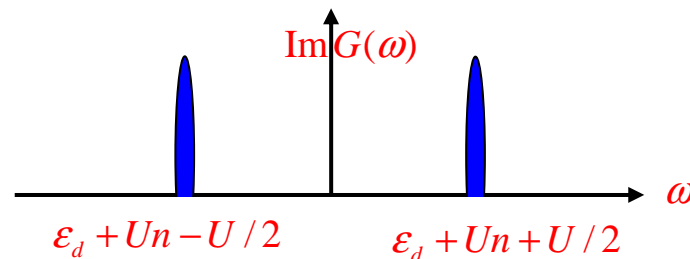


Electron Removal Spectrum

$$E_n - E_{n-1} = \varepsilon_d + U n - U / 2$$

Electron Addition Spectrum

$$E_n - E_{n+1} = \varepsilon_d + U n + U / 2$$



Atomic Self-Energies have singularities

Ground state energies for configurations d^n , d^{n+1} , d^{n-1} give rise to electron removal $E_n - E_{n-1}$ and electron addition $E_n - E_{n+1}$ spectra. Atoms are always insulators!

$$E_n - E_{n-1} = \tilde{\varepsilon}_d - U/2$$

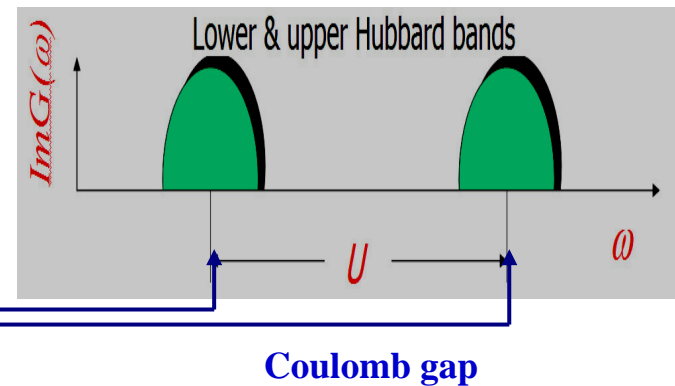
Electron removal

$$E_n - E_{n+1} = \tilde{\varepsilon}_d + U/2$$

Electron addition

or two poles in one-electron Green function

$$G(\omega) = \frac{1/2}{\omega - \tilde{\varepsilon}_d + U/2} + \frac{1/2}{\omega - \tilde{\varepsilon}_d - U/2}$$



Self-energy with **a pole** is required:

$$G(\omega) = \frac{1}{\omega - \tilde{\varepsilon}_d - \boxed{\Sigma(\omega)}} = \frac{1}{\omega - \tilde{\varepsilon}_d - \boxed{\frac{U^2}{4(\omega - \tilde{\varepsilon}_d)}}}$$

This is missing in DFT effective potential or LDA+U orbital dependent potential

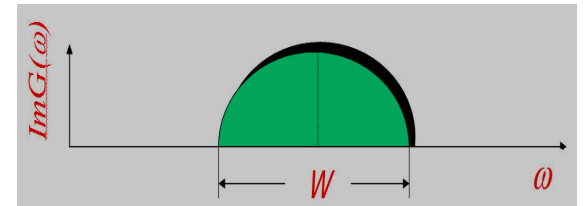
Mott Insulators as Systems near Atomic Limit

Classical systems: MnO (d^5), FeO (d^6), CoO (d^7), NiO (d^8).

Neel temperatures 100-500K. Remain insulating both below and above T_N

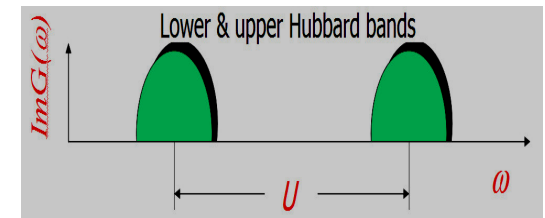
LDA/LDA+U, other static mean field theories, cannot access paramagnetic insulating state.

$$G_{LDA}(\omega) = \frac{1}{\omega - \epsilon_d - V_{LDA}}$$



Frequency dependence in self-energy is required:

$$G_{Hubbard1}(k\omega) = \frac{1}{\omega - \epsilon(k) - \Sigma_d(\omega)} = \frac{1}{\omega - \epsilon(k) - \frac{U^2}{4(\omega - \epsilon_d)}} = \frac{1/2}{\omega - \epsilon(k) + U/2} + \frac{1/2}{\omega - \epsilon(k) - U/2}$$

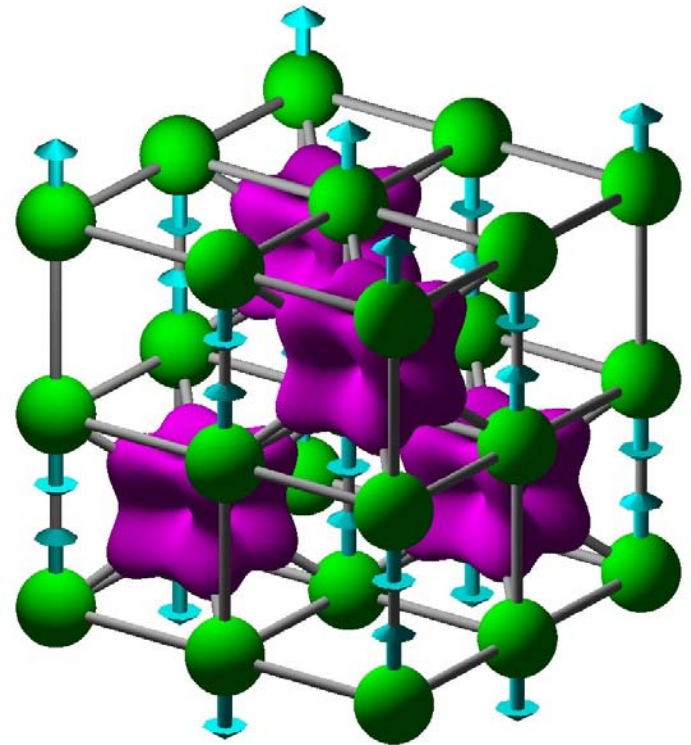


Sometimes bringing spin dependence helps however!

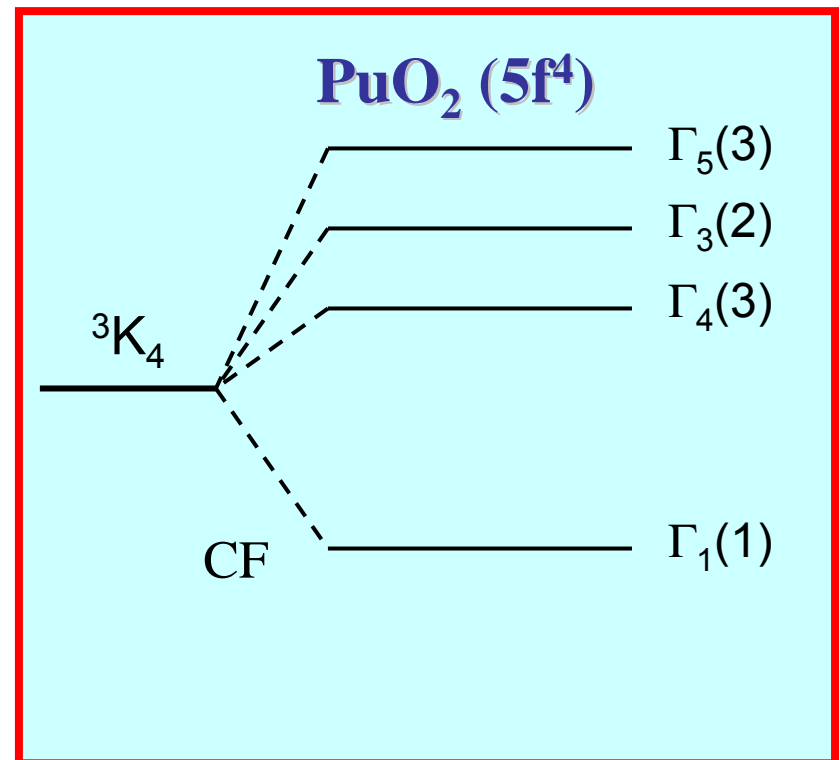
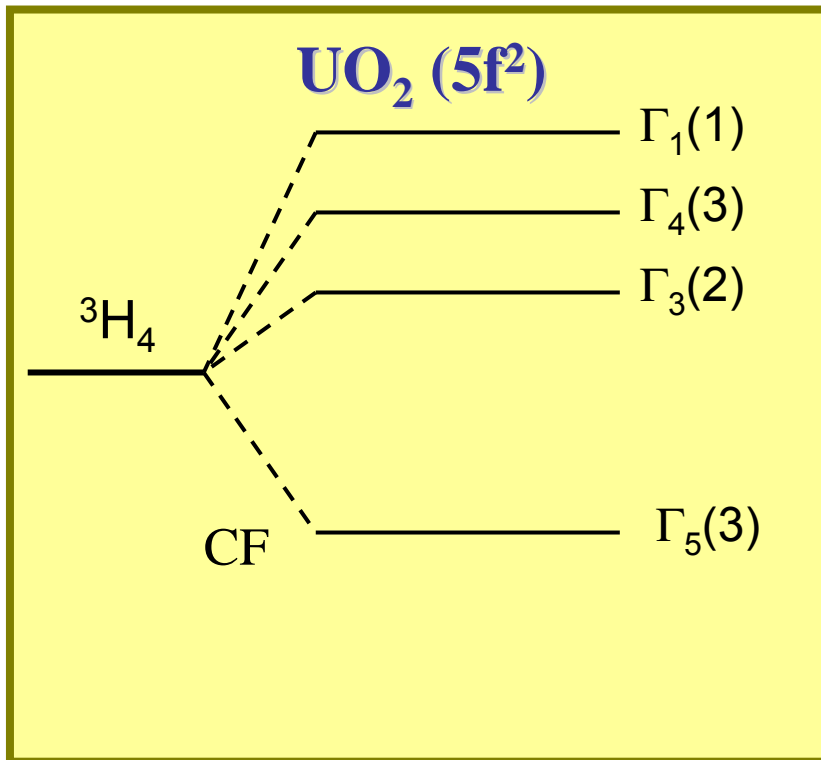
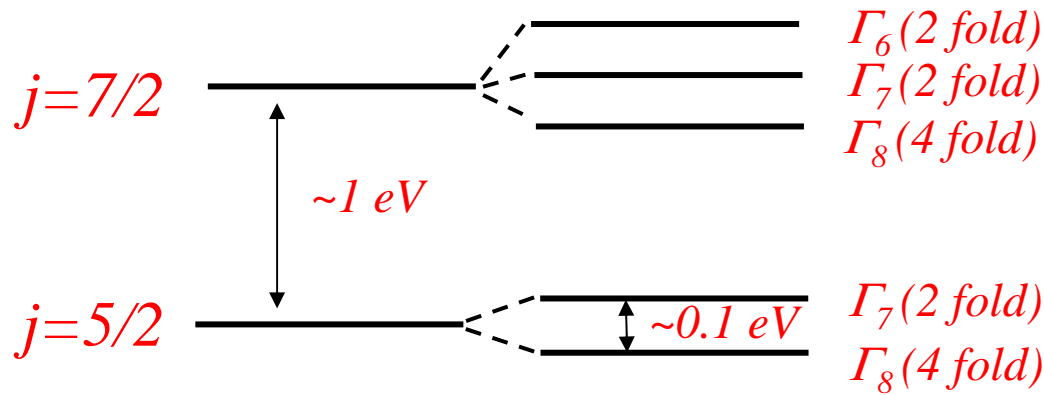
Properties of UO_2 & PuO_2

UO_2 (UOX) or its mixture with PuO_2 (MOX)

- Both are Mott-Hubbard insulators, $E_g \sim 2$ eV.
- UO_2 is AFM with $T_N = 30\text{K}$, while PuO_2 is non-magnetic.



Ground states for f-electrons



Localized electrons: Dynamical Mean Field Approach

Electronic structure is found by solving Dyson equation

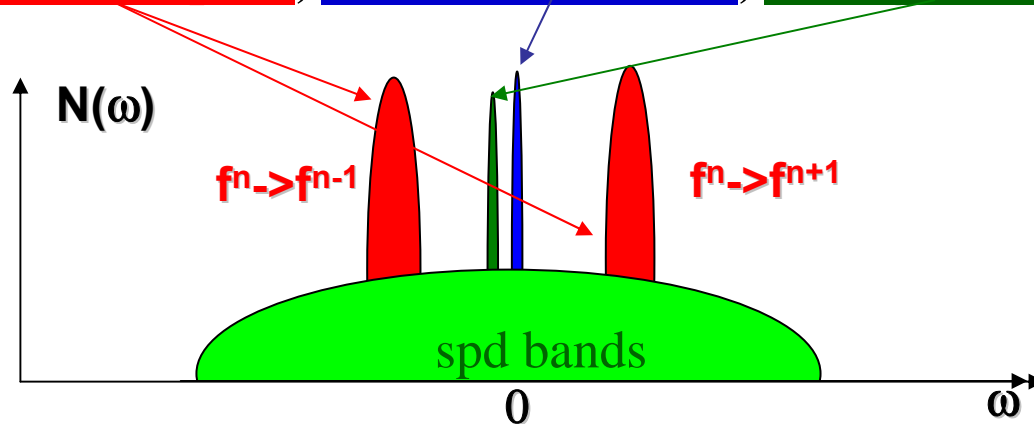
$$[-\nabla^2 + \Sigma(\omega)]\psi_k(r, \omega) = \varepsilon_k(\omega)\psi_k(r, \omega)$$

where **dynamical self-energy** for f-electrons is extracted by solving Anderson impurity model

$$\hat{\Sigma}_f(\omega) = \omega - \varepsilon_f - [\hat{G}_{imp}(\omega)]^{-1} - \sum_k \frac{V_{kf}^2}{\omega - \varepsilon_k}$$

Poles of the Green function $G(k, \omega) = \frac{1}{\omega - \varepsilon_k(\omega)}$

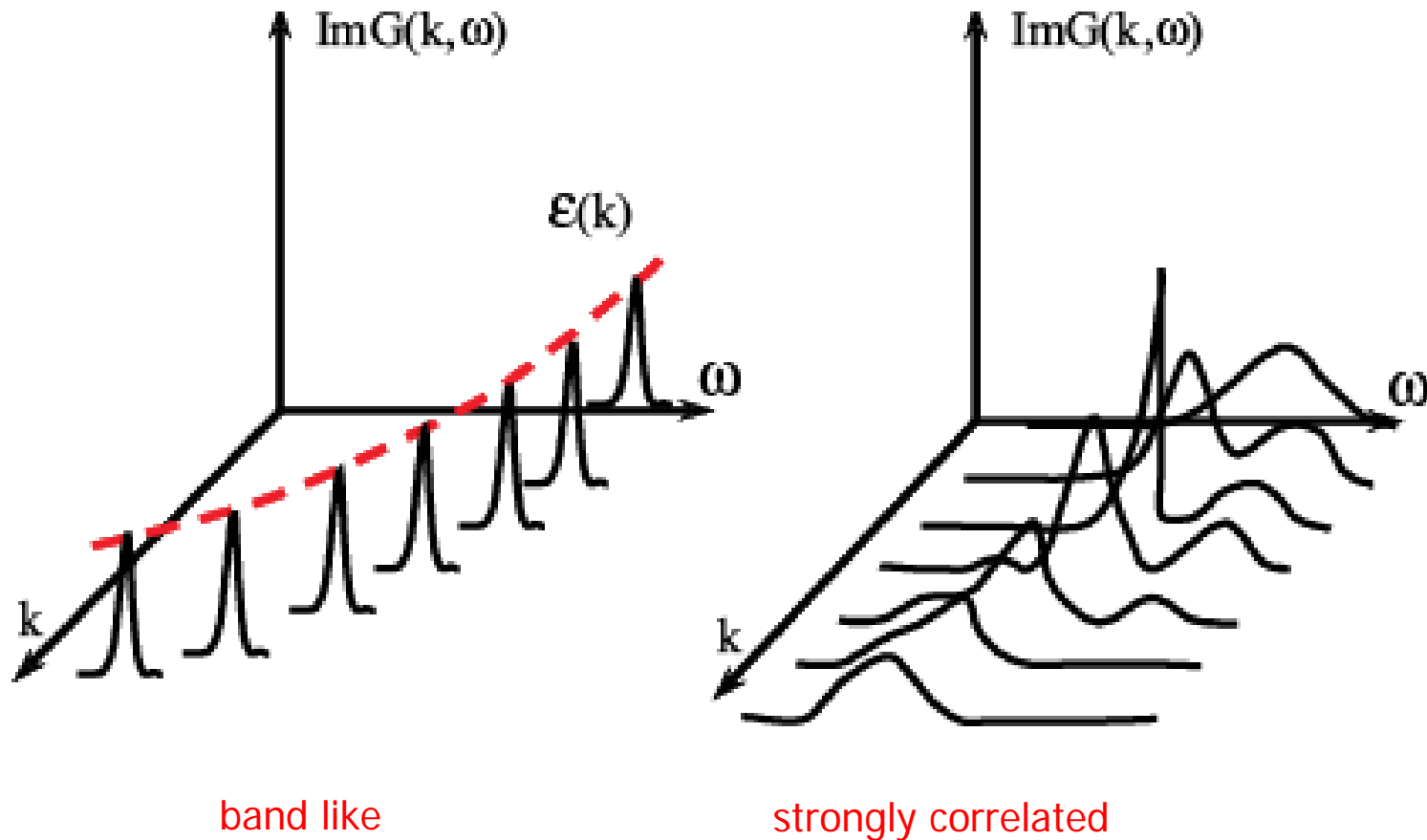
describe atomic multiplets, Kondo resonances, Zhang-Rice singlets, etc.



Better description compared to DFT-LDA is obtained

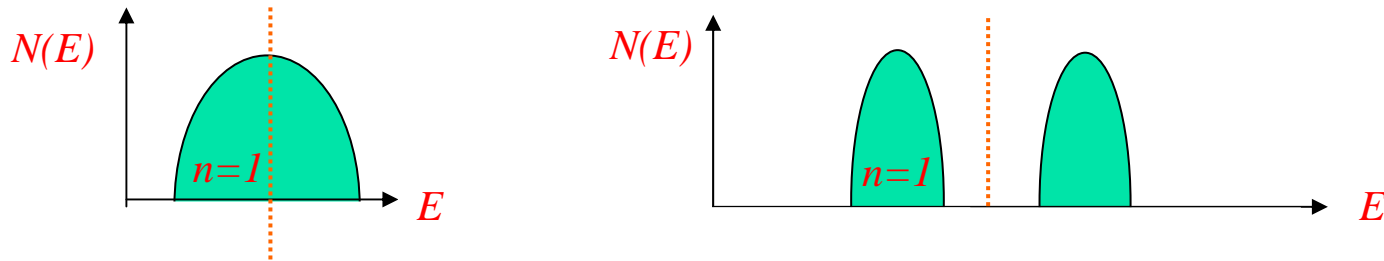
Strongly Correlated Materials

Not well described by a “standard model” based on band theories: Fermi liquid theory, Kohn Sham DFT, GW, where QPs are a reference system.



Spectral Density Functional as alternative to DFT

Density is not a good variable to describe total energies of strongly correlated system



Formulate a functional where electronic spectral function is a variable. This will predict both energetics and spectra.

A functional where local spectral function $N(E)$ is at the center of interest is based on **Dynamical Mean Field Theory**.

Can be entitled as

Spectral Density Functional

(Kotliar, SS, Haule, Udovenko, Parcolett, Marianetti,

Reviews of Modern Physics, 2006)

Green Function Theory

Effective action formulation (*Chitra, Kotliar, PRB 2001*) $x = (r, \tau)$

$$S = \int dx \psi^\dagger(x) [\partial_\tau - \nabla^2 + V_{ext}(x)] \psi(x) + \int dx dx' \psi^\dagger(x) \psi^\dagger(x') v_C(x-x') \psi(x) \psi(x')$$

□ Adding an auxiliary source field to the system $J(x, x')$ to probe Green function

$$S[J] = S + \int dx dx' J(x, x') \psi(x') \psi^\dagger(x)$$

$$W[J] = -\ln \int D[\psi^\dagger \psi] \exp(-S'[J])$$

□ Eliminate source in favor of conjugate field using Legendre transform, obtain **Free Energy Baym-Kadanoff Functional**

$$\Gamma_{BK}[G] = W[J] - Tr[JG]$$

Freedom to construct functionals

Choosing various source fields, various **functionals** can be obtained:

Example 1. Static local source $J(x)=J(r) \delta(\tau)$

$$S[J] = S + \int dr J(r) \psi(r) \psi^+(r)$$

probes the density => **Density Functional** $\Gamma_{DFT}[\rho]$ is obtained.

Example 2,3,4... Choose appropriate source – obtain TD-DFT, Spin Polarized DFT, LDA+U, ...

In all cases free energy of the system is accessed in extremum.
(Kotliar, Savrasov, in *New Theoretical Approaches to Strongly Correlated Systems*, 2001)

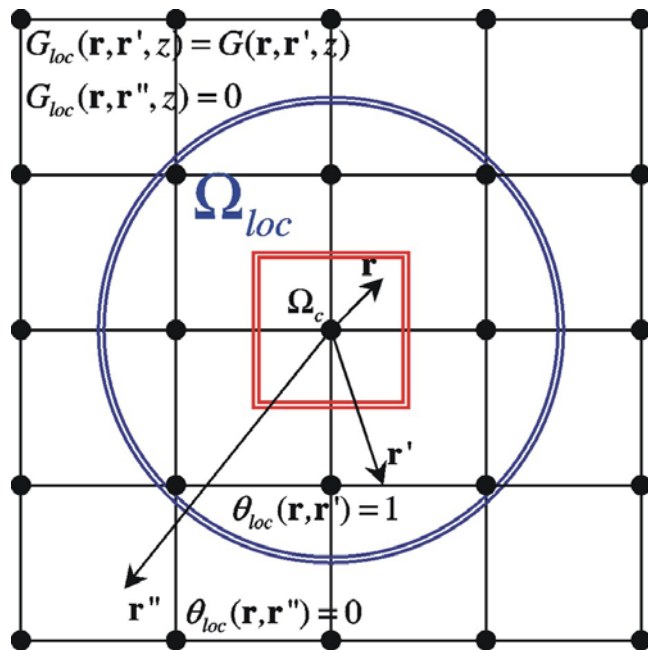
Spectral Density Functional Theory

Spectral Density Functional Theory is obtained using local source

$$J_{loc}(x, x') = J(x, x')\theta(r, r')$$

which probes local Green function

$$G_{loc}(r, r', i\omega) = G(r, r', i\omega)\theta(r, r')$$



Total Free Energy is accessed

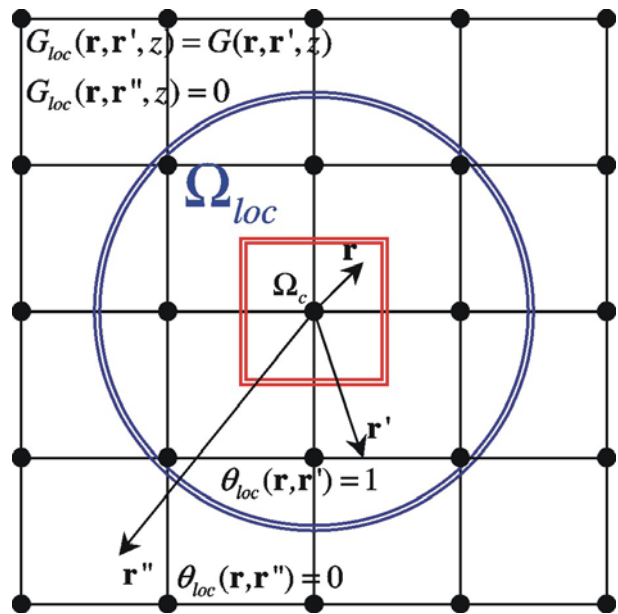
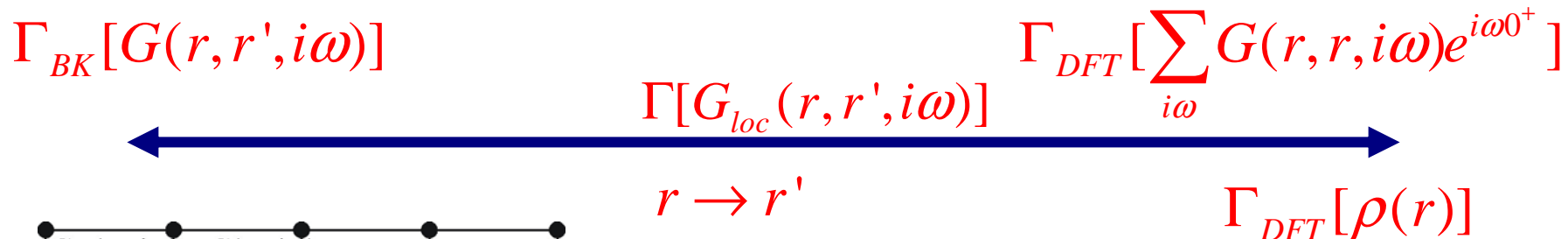
$$\Gamma_{SDF}[G_{loc}]$$

$$\frac{\delta \Gamma_{SDF}}{\delta G_{loc}} = 0$$

Local Green function Functionals

$$\rho(r) = \sum_{i\omega} G(r, r, i\omega) e^{i\omega 0^+} = \sum_{i\omega} G_{DFT}(r, r, i\omega) e^{i\omega 0^+}$$

Family of Functionals



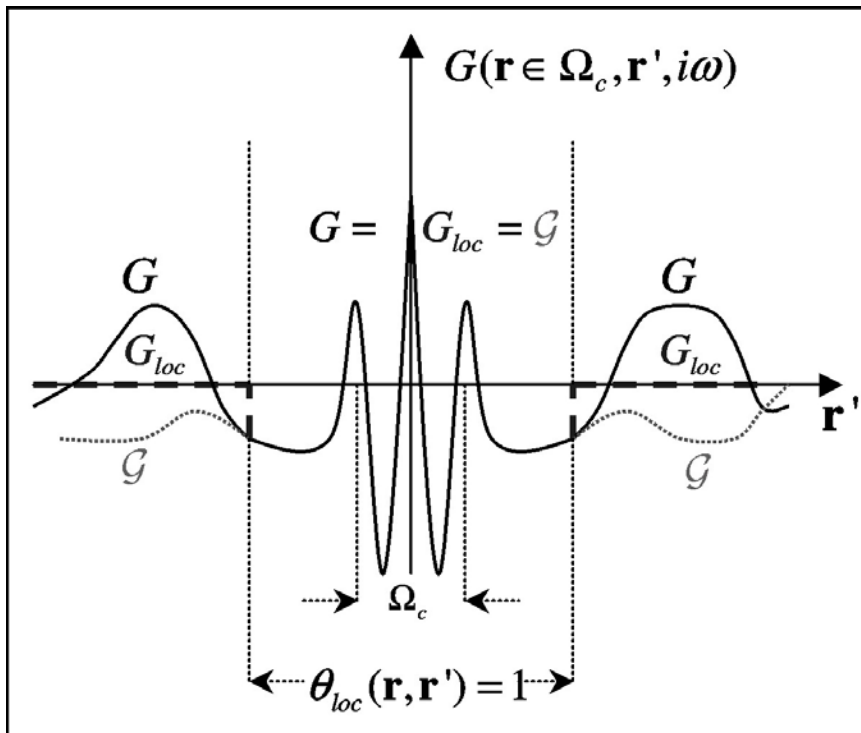
$$G_{loc}(r, r', i\omega) = G(r, r', i\omega) \theta(r, r')$$

Kinetic energy & generalization of Kohn-Sham Idea

To obtain kinetic functional:

$$\Gamma_{SDF}[G_{loc}] = K_{SDF}[G_{loc}] + \Phi_{SDF}[G_{loc}]$$

introduce **fictitious** particles which describe local Green function:



$$\mathcal{G}(r, r', \omega) = \sum_{kj} \frac{\psi_{kj\omega}(r)\psi_{kj\omega}^\dagger(r')}{\omega - E_{kj\omega}}$$

$$K_{SDF}[G_{loc}] \rightarrow K_{SDF}[\mathcal{G}]$$

Exactly as in DFT:

$$G_{KS}(r, r', \omega) = \sum_{kj} \frac{\psi_{kj}(r)\psi_{kj}^*(r')}{\omega - E_{kj}}$$

$$K_{DFT}[\rho] \rightarrow K_{DFT}[G_{KS}]$$

Local Self-Energy of Spectral Density Functional

- Spectral Density Functional looks similar to DFT

$$\Gamma[\psi_{kj\omega}] = \sum_{kj} \sum_{i\omega} f_{kj\omega} \epsilon_{kj\omega} - \sum_{i\omega} \int \mathcal{M}_{eff}(r, r', i\omega) \mathcal{G}(r, r', i\omega) dr dr'$$

$$+ \int \rho(r) V_{ext}(r) dr + E_H[\rho] + \Phi_{xc}[G_{loc}] \quad f_{kj\omega} = \frac{1}{(i\omega + \mu - E_{kj\omega})}$$

- Effective mass operator is local by construction and plays auxiliary role exactly like Kohn-Sham potential in DFT

$$\mathcal{M}_{eff}(r, r', \omega) = [V_{ext}(r) + V_H(r)] \delta(r - r') + \frac{\delta \Phi_{xc}}{\delta G_{loc}(r, r', \omega)}$$

- Energy dependent Kohn-Sham (Dyson) equations give rise to energy-dependent band structure

$$-\nabla^2 \psi_{kj\omega}(r) + \int \mathcal{M}_{eff}(r, r', \omega) \psi_{kj\omega}(r') dr' = E_{kj\omega} \psi_{kj\omega}(r)$$

- $E_{kj\omega}$ have physical meaning in contrast to Kohn-Sham spectra.
are designed to reproduce **local spectral density**

Local Dynamical Mean Field Approximation

□ Exchange-correlation functional $\Phi_{xc}[G_{loc}]$ is unknown

□ **Local dynamical mean field approximation** for $\Phi_{xc}[G_{loc}]$

Sum of diagrams constructed with local Green function G_{loc} and bare Coulomb interaction v_C

□ Remarkably, that sum can be performed by mapping onto auxiliary quantum impurity model subjected to self-consistency condition (*Georges, Kotliar, 1991*)

$$S_{imp} = \int_{\Omega_{loc}} dx \psi^\dagger(x) \mathcal{G}_0^{-1}(x, x') \psi(x) + \int_{\Omega_{loc}} dx dx' \psi^\dagger(x) \psi^\dagger(x') v_C(x-x') \psi(x) \psi(x')$$
$$\mathcal{G}_0^{-1}(x, x') = G_{loc}^{-1}(x, x') + \mathcal{M}_{int}(x, x')$$

Dynamically Screened Interaction

- Interaction functional in Baym-Kadanoff theory (*Chitra, Kotliar, 2001*)

$$\Phi_{BK}[G] = E_H - \frac{1}{2} \text{Tr} \ln W + \frac{1}{2} \text{Tr} [v_C^{-1} - W^{-1}] W + \Psi_{BK}[G, W]$$

obtained via introducing another source coupled to $\psi^+(x)\psi^+(x')\psi(x)\psi(x')$
Functional $\Gamma_{BK}[G, W]$ is extremized both over G and over W

$$G = G_0 - G_0 \Sigma_{\text{int}} G$$

$$W = v_C - v_C \Pi W$$

- Interaction functional in spectral density functional theory is obtained via introducing a **local** source which probes $\psi^+(x)\psi^+(x')\psi(x)\psi(x')$ in **part** of the space:

$$W_{loc}(r, r', \omega) = W(r, r', \omega) \theta(r, r')$$

May be a formal way to define on-site “U”

Local Interaction & "Kohn-Sham" interaction

□ Do the same Kohn-Sham trick to find a "non-interacting" functional (Chitra, Kotliar, 2001) Introduce auxiliary interaction $\mathcal{W}(r, r', \omega)$

$$\mathcal{W}(r, r', \omega) = W(r, r', \omega) = W_{loc}(r, r', \omega), r \in \Omega_c, r' \in \Omega_{loc}$$

$$\mathcal{W}(r, r', \omega) \neq W(r, r', \omega), W_{loc}(r, r', \omega) = 0, r \in \Omega_c, r' \notin \Omega_{loc}$$

□ Interaction Functional in Spectral Density Functional Theory

$$\Phi_{SDF}[G_{loc}, \mathcal{W}] = E_H - \frac{1}{2} \text{Tr} \ln \mathcal{W} + \frac{1}{2} \text{Tr}[v_C^{-1} - \mathcal{W}^{-1}] \mathcal{W} + \Psi_{SDF}[G_{loc}, \mathcal{W}]$$

Functional $\Gamma_{BK}[\mathcal{G}, \mathcal{W}]$ is extremized both over \mathcal{G} and over \mathcal{W}

$$\mathcal{G} = G_0 - G_0 \mathcal{M}_{int} \mathcal{G}$$

$$\mathcal{W} = v_C - v_C \mathcal{P} \mathcal{W}$$

□ \mathcal{P} is an auxiliary susceptibility (similar to mass operator \mathcal{M})

\mathcal{P} is manifestly local within Ω_{loc}

Extended Dynamical Mean Field Theory

□ Reduction to impurity model (*Si, Kotliar, 1995, Chitra, Kotliar 2001*)

$$S_{imp} = \int_{\Omega_{loc}} dx \psi^\dagger(x) \mathcal{G}_0^{-1}(x, x') \psi(x) + \int_{\Omega_{loc}} dx dx' \psi^\dagger(x) \psi^\dagger(x') \mathcal{V}_0(x - x') \psi(x) \psi(x')$$

leads to definitions of bath Green function and bath interaction which is input to impurity model

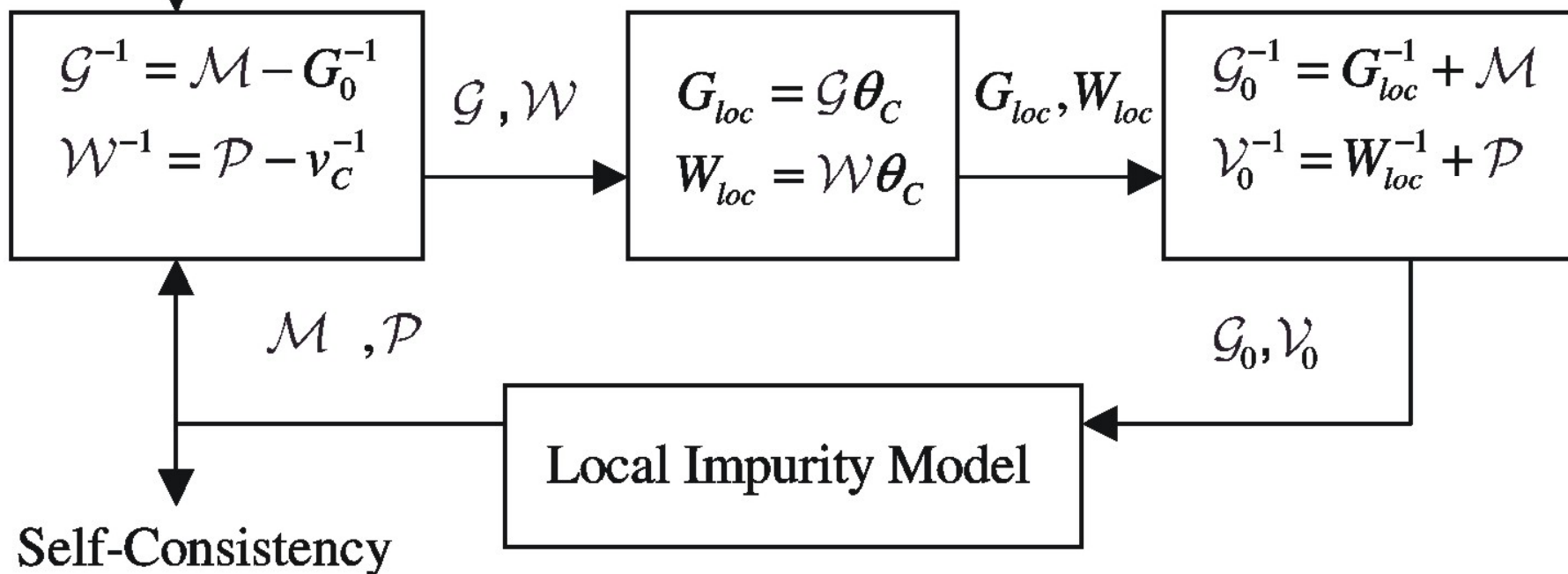
$$\mathcal{G}_0^{-1}(x, x') = G_{loc}^{-1}(x, x') + \mathcal{M}_{int}(x, x')$$

$$\mathcal{V}_0^{-1}(x, x') = W_{loc}^{-1}(x, x') + \mathcal{P}(x, x')$$

Self-Consistency

Spectral Density Functional Theory within Local Dynamical Mean Field Approximation

Input \mathcal{M}, \mathcal{P}





Further Approximations

□ LDA+DMFT method and its static limit: LDA+U

(Anisimov et.al, 1990, Anisimov+Kotliar team, 1997,
Held+Nekrasov+Vollhard, 2001, McMahan+Held+Scalettar, 2001)

Why not think of LDA as most primitive impurity solver?

Divide electrons onto light and heavy. Apply LDA for light electrons.

Use more intelligent solution of impurity problem for heavy electrons.

□ Local GW approximation

(Kotliar+SS, 2001, Zein+Antropov 2002)

Solves impurity model using GW diagram: $M_{xc} = -G_{loc} W_{loc}$

□ GW+DMFT Method

(George+Aryasetyavan+Bierman, 2002, Zein+SS+Kotliar, 2006)

Eliminates problems of input “U” and double counting.

LDA+DMFT as natural extension of LDA+U

In LDA+U correction to the potential

$$\Delta V_{LDA+U}^{\sigma} = \sum_{atomic}^{\sigma} (\omega \rightarrow \infty) - V_{DC} = \sum_{atomic, HF}^{\sigma} - V_{DC}$$

is just the Hartree-Fock value of the exact atomic self energy.

Why don't use exact atomic self-energy itself instead of its Hartree-Fock value? This is so called Hubbard I approximation to the electronic self-energy.

$$\text{LDA+U} \longrightarrow \text{LDA+} \sum_{atomic, HF} \longrightarrow \text{LDA+} \sum_{atomic} (\omega)$$

Next step: use self-energy from atom allowing to hybridize with conduction bath, i.e. finding it from the Anderson impurity problem.

$$\text{LDA+} \sum_{atomic} (\omega) \longrightarrow \text{LDA+} \sum_{impurity} (\omega)$$

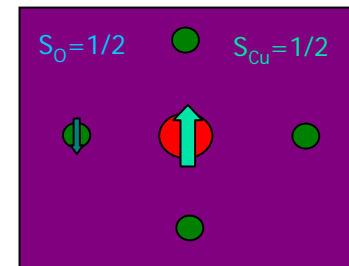
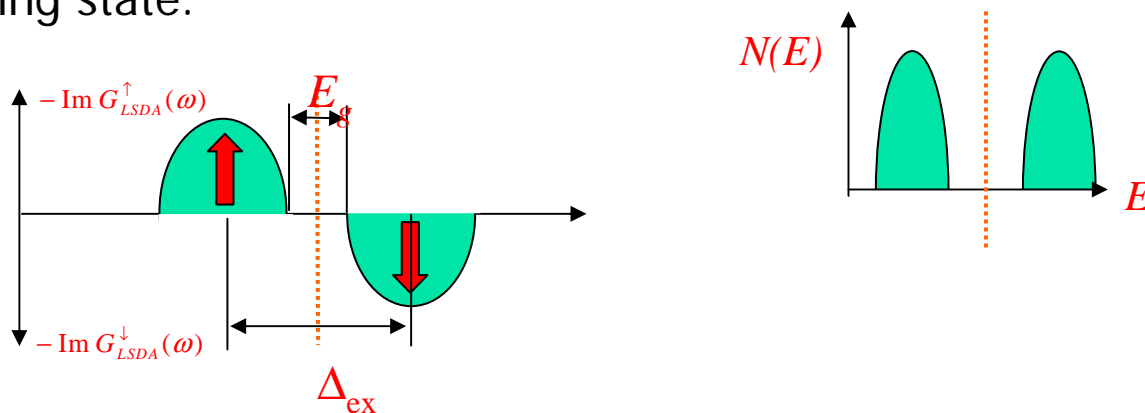
Impose self-consistency for the bath: full dynamical mean field theory is recovered.

$$\text{LDA+} \sum_{impurity} (\omega) \equiv \text{LDA+DMFT}$$

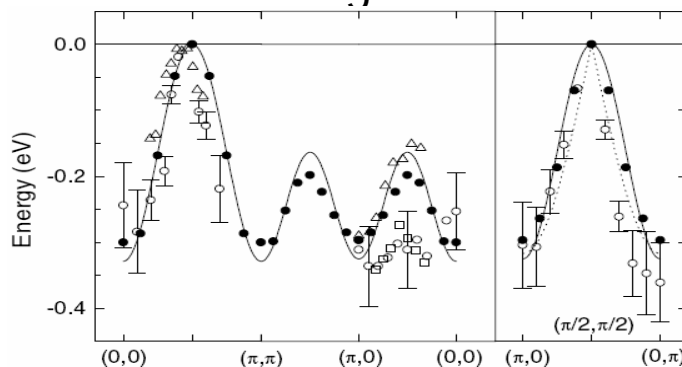
Excitations in Mott Insulators

Classical systems: MnO (d^5), FeO (d^6), CoO (d^7), NiO (d^8); parent materials for HTSCs: CaCuO₂, La₂CuO₄ (d^9). Neel temperatures 100-500K. Energy gaps 20,000+ K. Remain insulating both below and above T_N

LDA/LDA+U, other static mean field theories, cannot access paramagnetic insulating state.



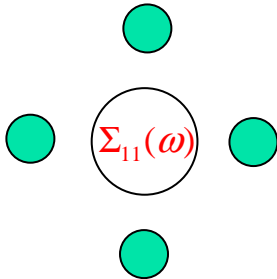
Cannot explain the existence of Zhang-Rice states



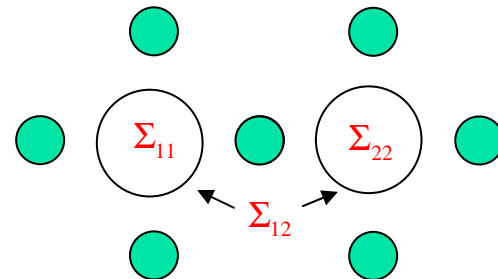
Cannot explain waterfalls, disappearance of spectral weight and so on. KITP, D y of California Davis

LDA+DMFT for HTSCs: Dispersion of Zhang-Rice singlet

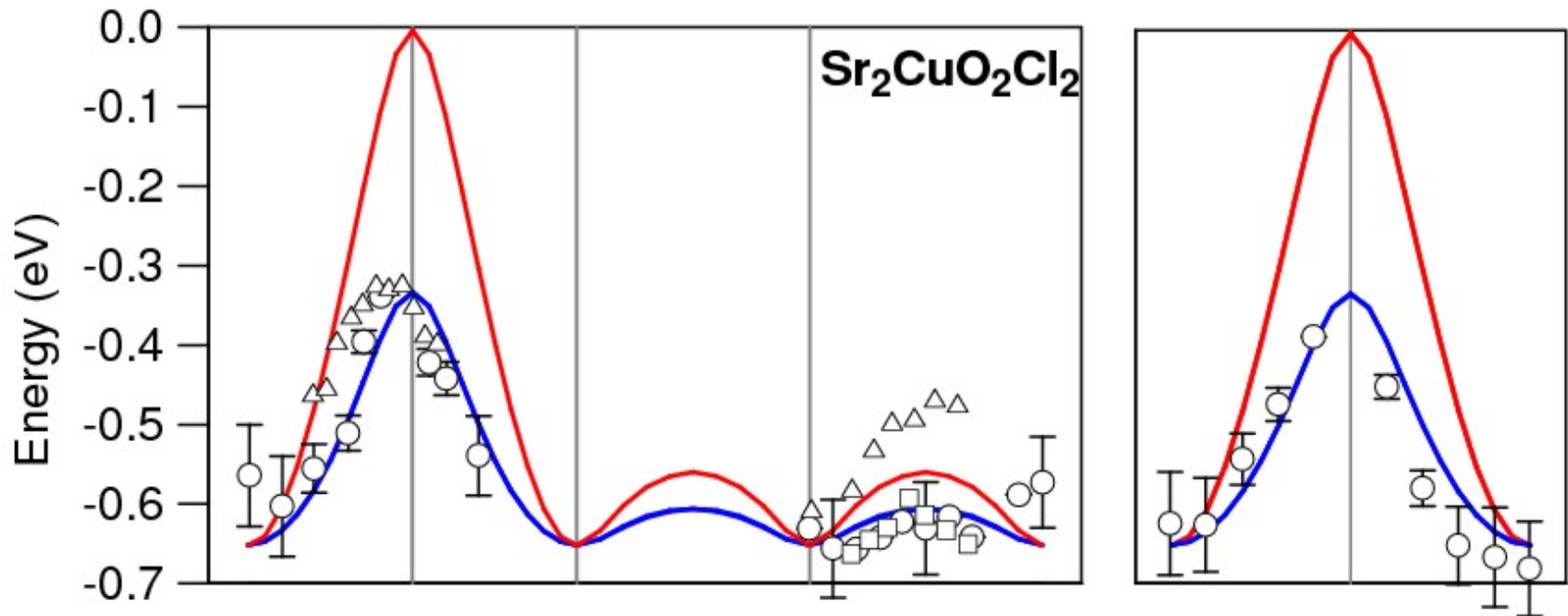
Single-site DMFT



Two-site Cluster ED



$$\Sigma(k, \omega) = \Sigma_{11}(\omega) + \Sigma_{12}(\omega)[\cos(k_x) + \cos(k_y)]$$



Yin, Gordienko, Wan, SS, PRL 2008

Waterfalls in HTSCs: Main Features

Features of recent ARPES data:

- Doping-independent Fermi velocities
- Disappearance of spectral weight at Gamma
- Existence of two energy scales

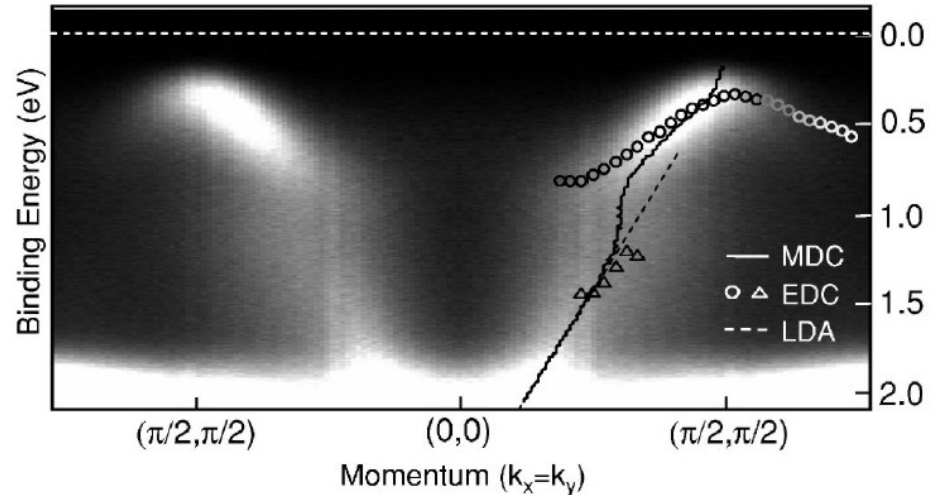
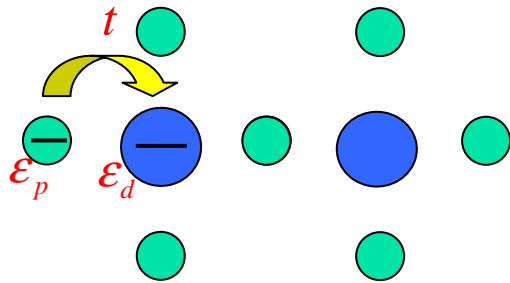
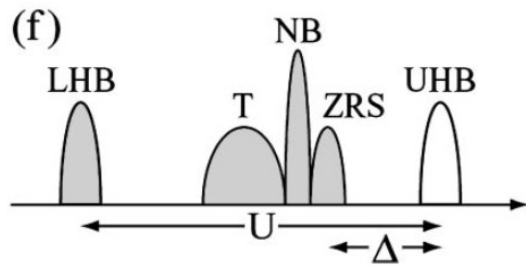


FIG. 2. Intensity plot of data shown in Fig. 1 as functions of the binding energy and momentum. The data was symmetrized around the Γ point. Also shown on the plot are the dispersions obtained by following the peak positions of the MDCs (solid line) and the EDCs (circles and triangles). The results are compared with the shifted dispersion from the LDA calculation (dashed line).

Ronning et.al PRB 2005

Tight-Binding Picture



k-dependent hybridization

$$V_{pd}(k) = \sum_R e^{ikR} V_{pd}(R) = 2t[\sin(k_x a) + \sin(k_y a)]$$

disappears at Γ point

$$V_{pd}(k=0) = 0$$

Assume two-pole approximation:

$$\Sigma(\omega) = \frac{W_1}{\omega - P_1} + \frac{W_2}{\omega - P_2}$$

One-electron Green Function:

$$G(k, \omega) = \begin{pmatrix} \omega - \epsilon_d - \Sigma(\omega) & -V_{pd}(k) & -V_{pd}(k) \\ -V_{pd}(k) & \omega - \epsilon_p & 0 \\ -V_{pd}(k) & 0 & \omega - \epsilon_p \end{pmatrix}^{-1}$$

Spectrum of Excitations from effective 5x5 Hamiltonian:

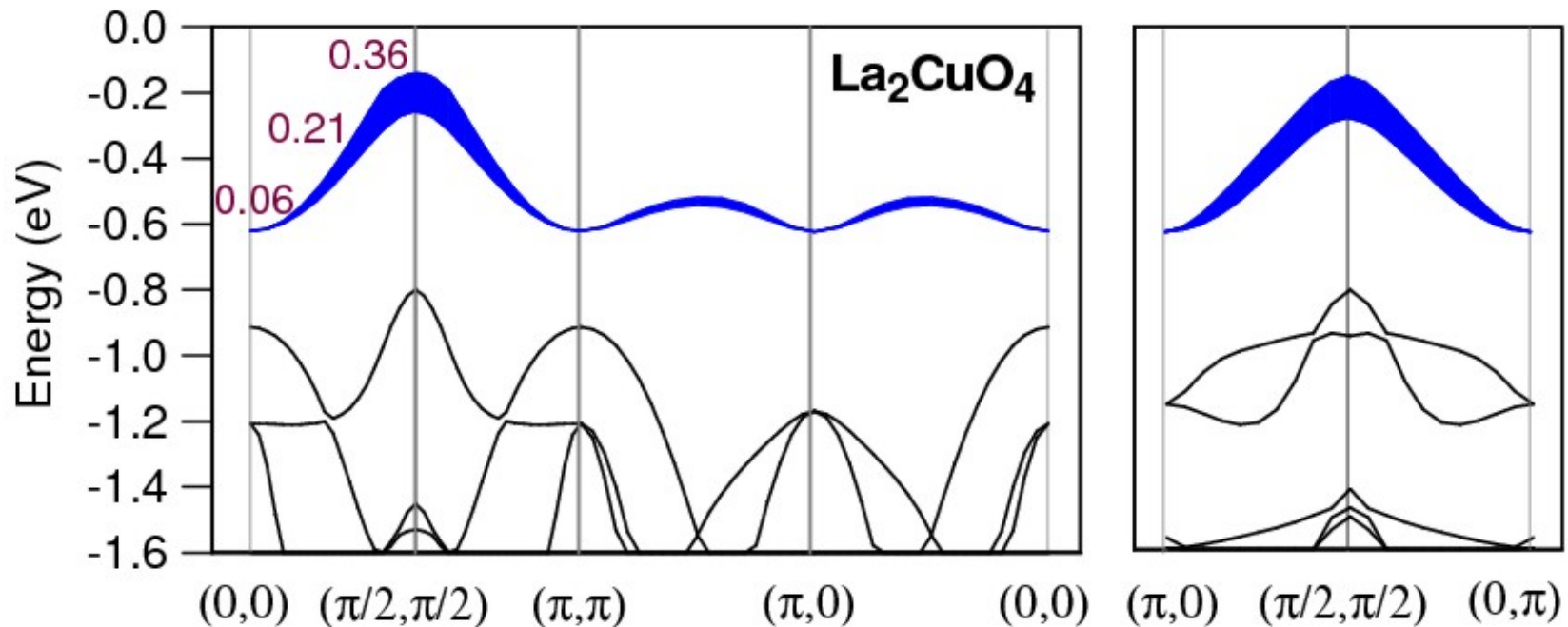
$$H_{aux} = \begin{pmatrix} \epsilon_d & V_{pd}(k) & V_{pd}(k) & \sqrt{W_1} & \sqrt{W_2} \\ V_{pd}(k) & \epsilon_p & 0 & 0 & 0 \\ V_{pd}(k) & 0 & \epsilon_p & 0 & 0 \\ \sqrt{W_1} & 0 & 0 & P_1 & 0 \\ \sqrt{W_2} & 0 & 0 & 0 & P_2 \end{pmatrix}$$

Waterfalls in HTSCs: Oxygen Content in ZR singlet

C-DMFT calculations with three pole approximated self-energies:

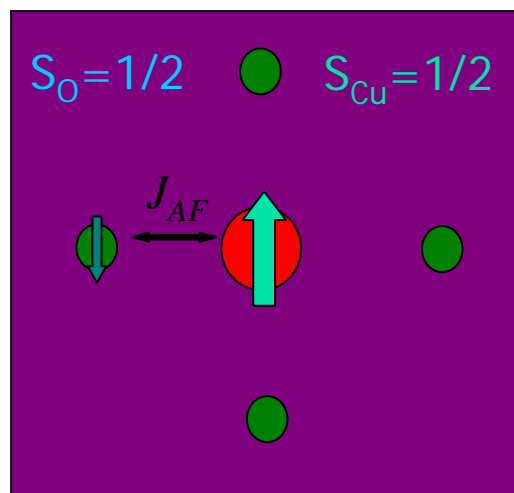
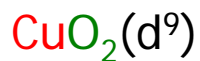
Blue fat lines show the amount of oxygen in the ZR band

Numbers show actual number of electrons in the ZR band

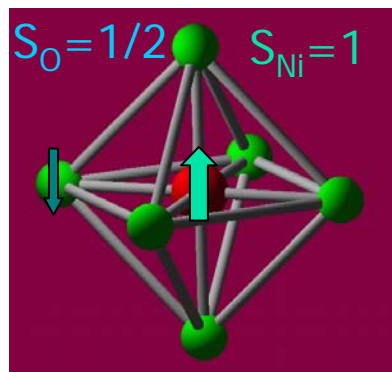
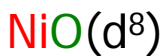


Yin, Gordienko, Wan, SS, PRL 2008

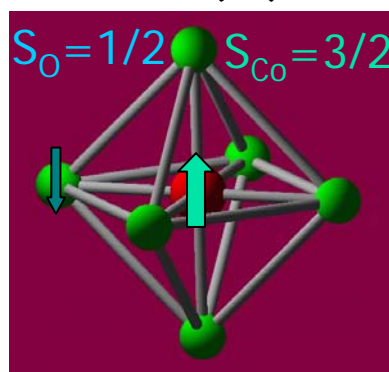
Generalized Zhang-Rice Physics



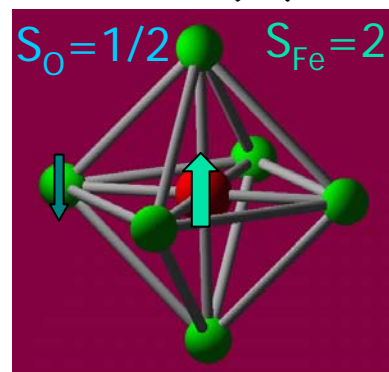
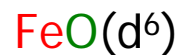
Zhang-Rice Singlet ($S_{\text{tot}}=0$)



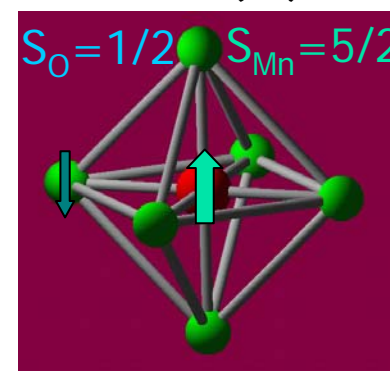
Doublet ($S_{\text{tot}}=1/2$)



Triplet ($S_{\text{tot}}=1$)

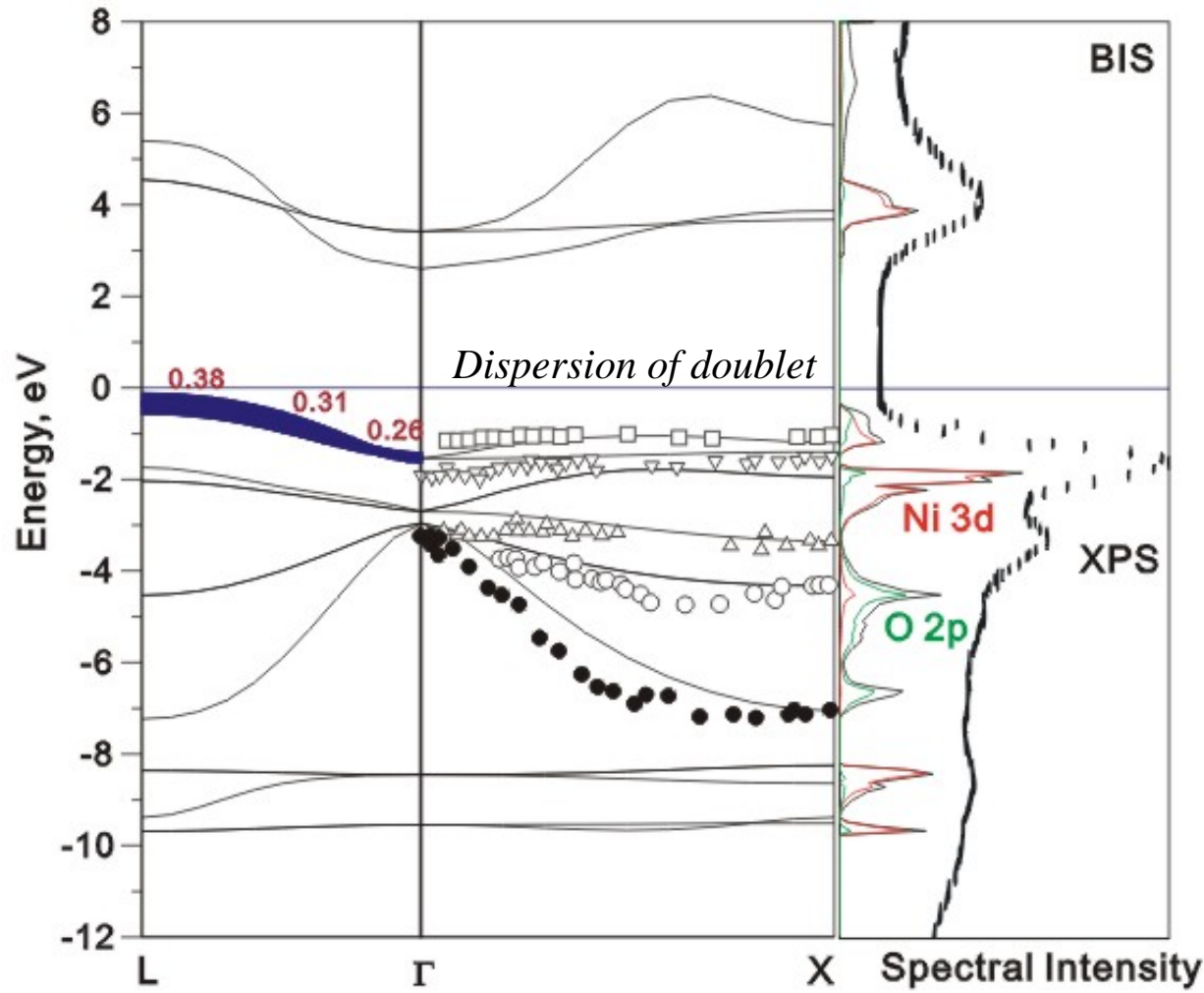


Quartet ($S_{\text{tot}}=3/2$)



Quintet ($S_{\text{tot}}=2$)

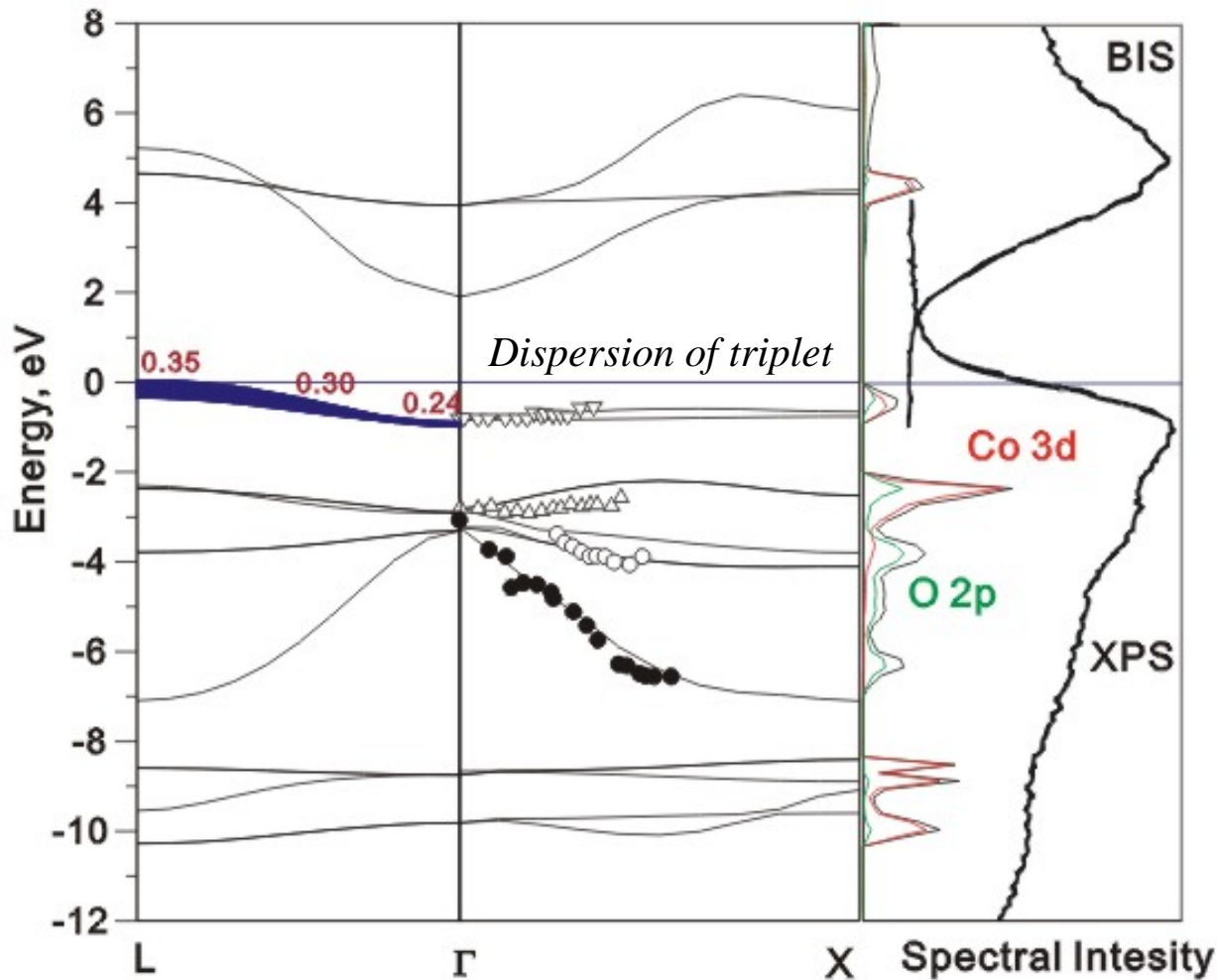
NiO: LDA+DMFT compared with ARPES



Paramagnetic state of NiO: The blue linewidth and the numbers show the oxygen content and the amount of electrons in the ZR band.

Q. Yin, A. Gordienko, X. Wan. SS, PRL 2008; Exp from G. A. Sawatzky et.al, Phys. Rev. Lett. 53, 2339 (1984).

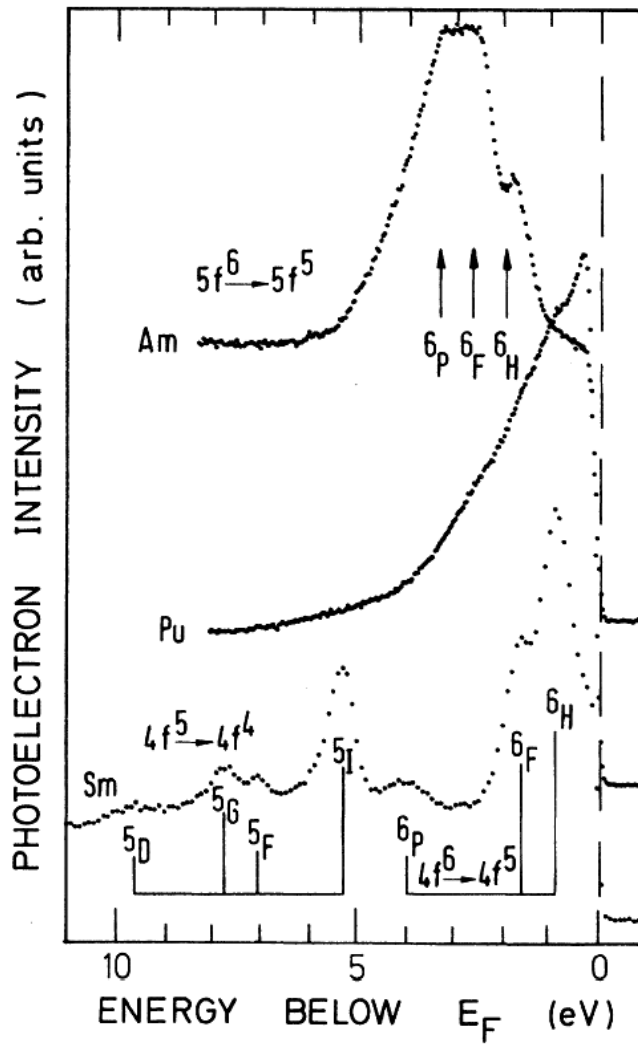
CoO: LDA+DMFT compared with ARPES



Paramagnetic state of CoO: The blue linewidth and the numbers show the oxygen content and the amount of electrons in the ZR band.

Q. Yin, A. Gordienko, X. Wan. SS, PRL 2008; Exp. from Z.-X. Shen et.al, Phys. Rev. B 42, 1817 (1990).

Atomic Multiplets in Photoemission of Americium



Atomic multiplet structure

emerges from measured photoemission spectra in **Am** ($5f^6$), **Sm** ($4f^6$) -

Signature for f electrons localization.

after J. R. Naegele, *Phys. Rev. Lett.* (1984).

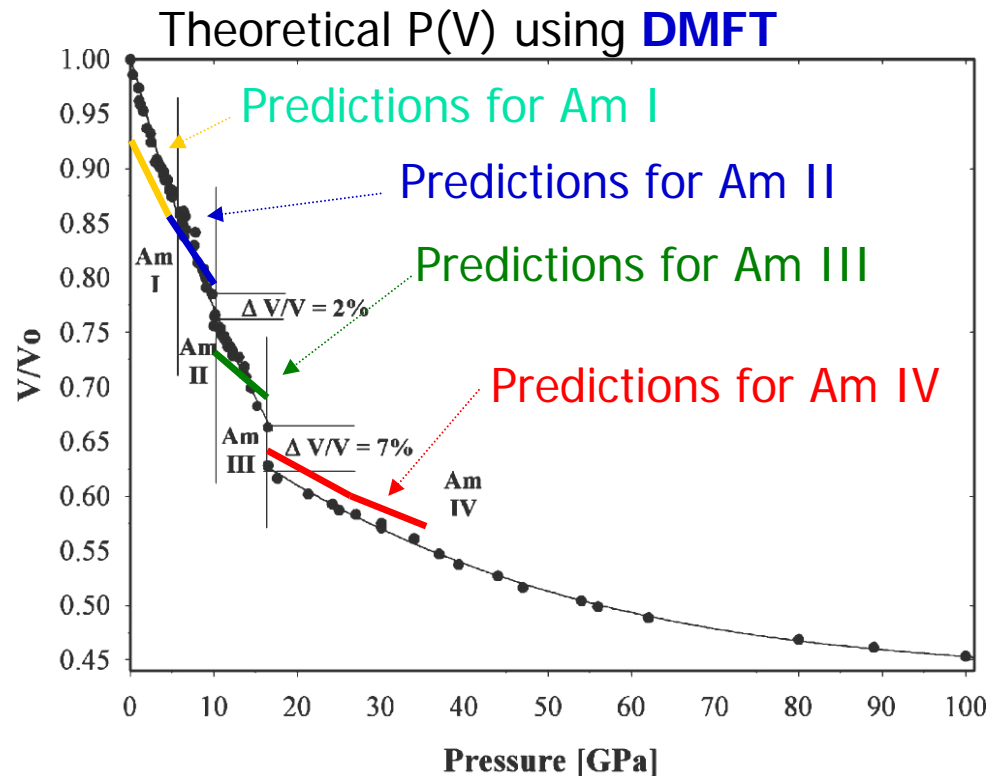
Am Equation of State: DMFT Predictions

Self-consistent evaluations of total energies with **DMFT** using exact diagonalization for f-shells

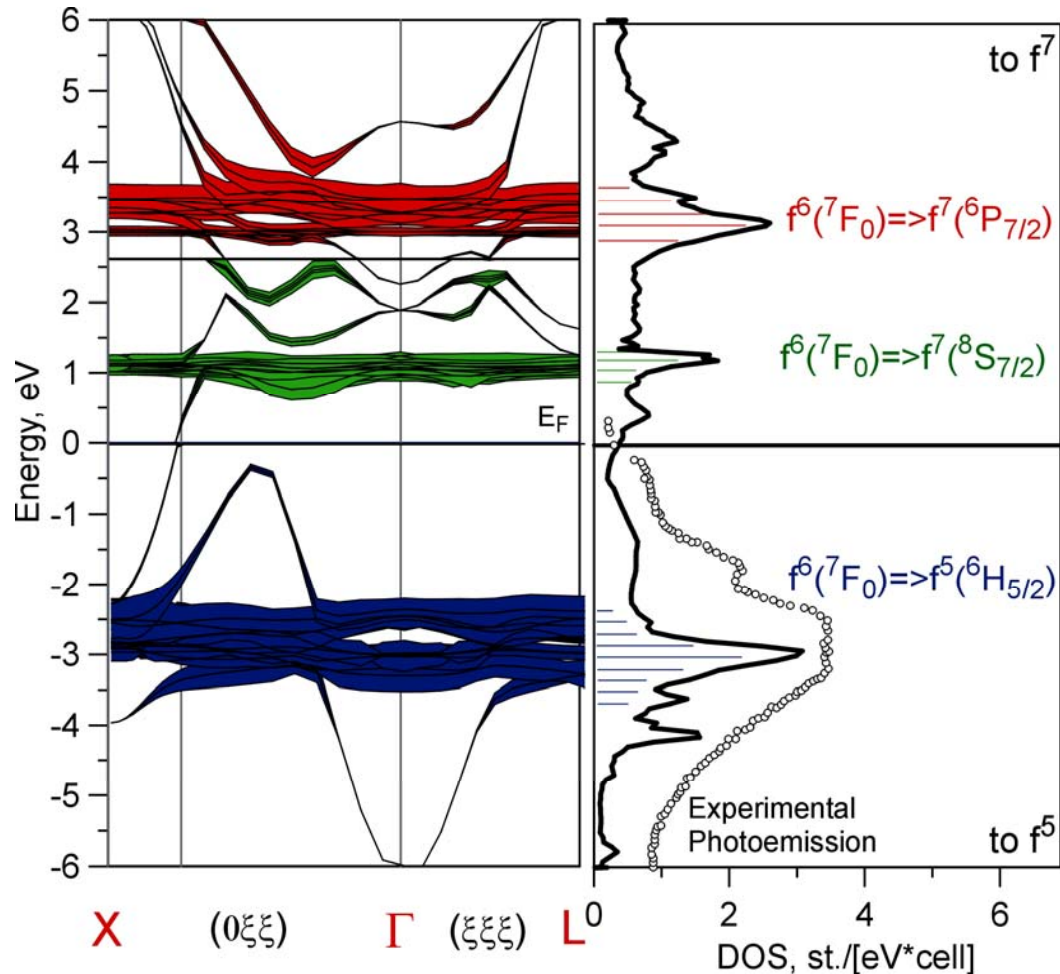
Accounting for full atomic multiplet structure using Slater integrals:
 $F^{(0)}=4.5 \text{ eV}$, $F^{(2)}=8 \text{ eV}$, $F^{(4)}=5.4 \text{ eV}$, $F^{(6)}=4 \text{ eV}$

DMFT predictions are much better than **DFT-LDA**:

- ❑ Non magnetic f^6 ground state with $J=0$ (7F_0)
- ❑ Equilibrium Volume: $V_{\text{theory}}/V_{\text{exp}}=0.93$
- ❑ Bulk Modulus: $B_{\text{theory}}=47 \text{ GPa}$
Experimentally $B=40\text{-}45 \text{ GPa}$

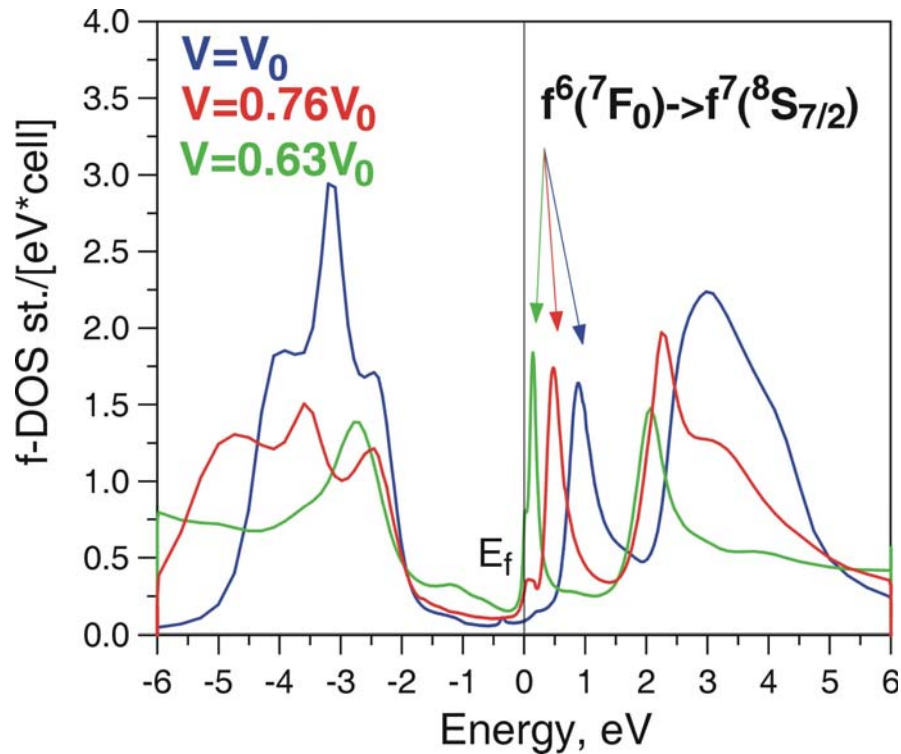


Many Body Electronic Structure for ${}_{7}\text{F}^0$ Americium



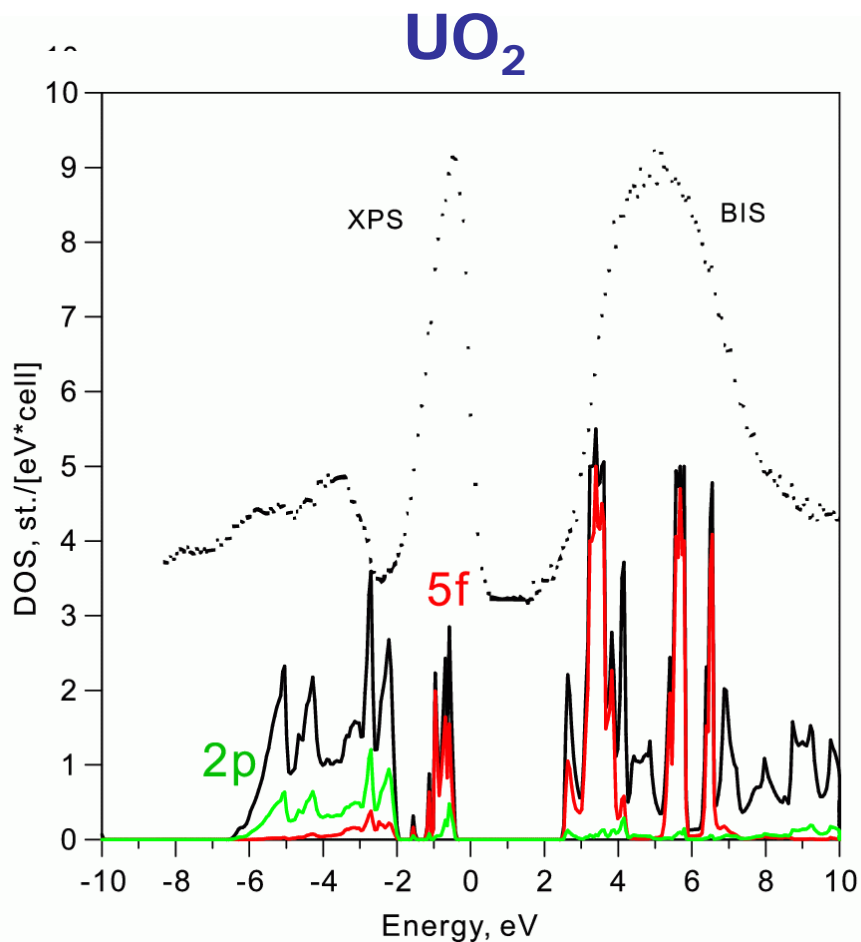
Experimental Photoemission Spectrum *after J. Naegele et.al, PRL 1984*

Signature of Mixed Valence

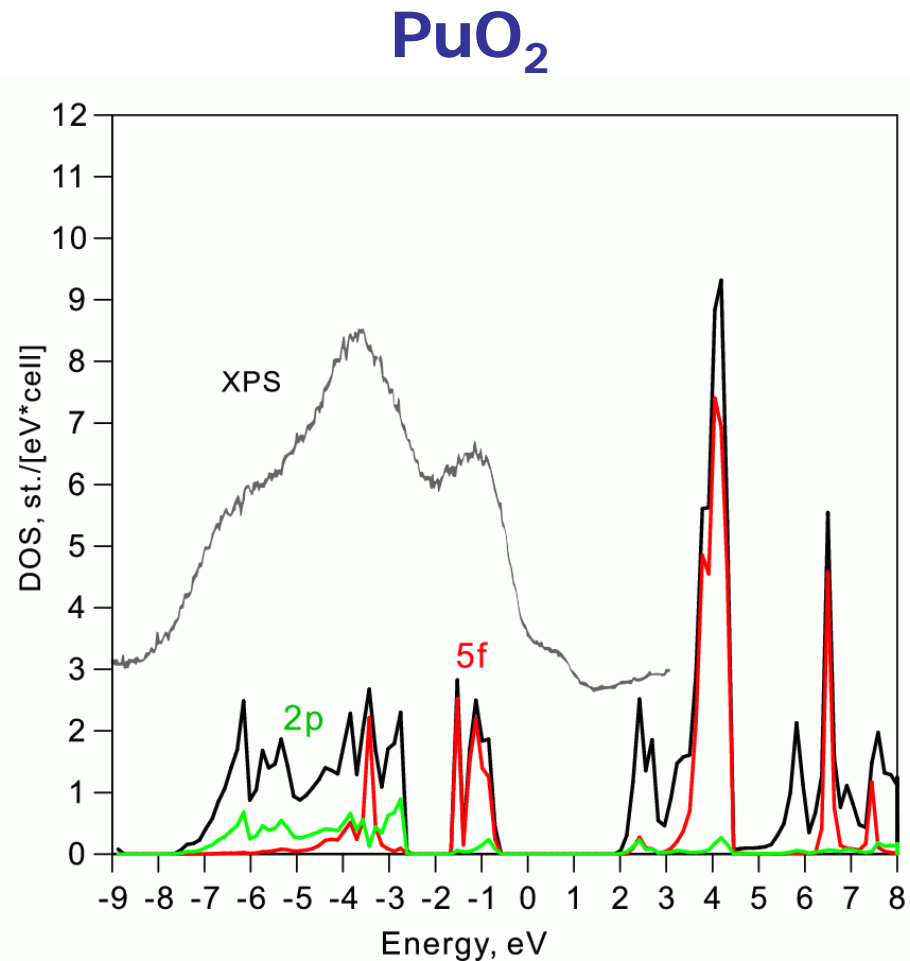


Insights from DMFT: Under pressure energies of f^6 and f^7 states become degenerate which drives Americium into mixed valence regime. Explains anomalous growth in resistivity, confirms ideas pushed forward recently by *Griveau, Rebizant, Lander, Kotliar, Physical Review Letters (2005)*

Calculated Electronic Structure using DMFT



XPS & BIS data after Veal and Lam,
Solid State Communications 33, 885 (1980)



XPS data after Butterfield et al,
Surface Science 571, 74 (2004)

Calculating Kondo Exchange Energy

Minimal Hamiltonian for heavy fermion superconductors – Kondo lattice

$$H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + J_K \sum_i S_i (\sum_{\sigma\sigma'} c_{i\sigma}^+ \tau_{\sigma\sigma'} c_{i\sigma'})$$

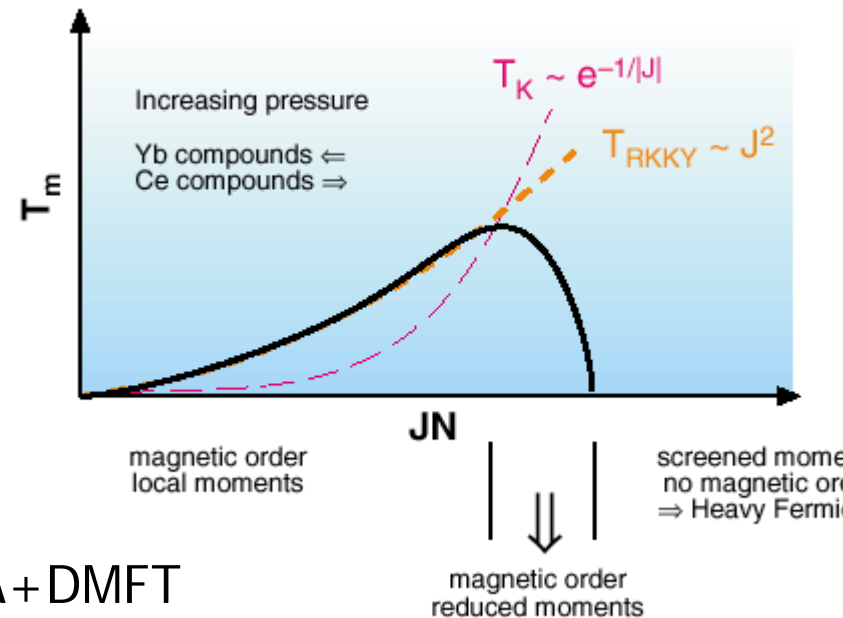
Solutions can be obtained accurately using Continuous Time Quantum Monte Carlo Method and Dynamical Mean Field Theory

Ce-122 and Ce-115 compounds

Antiferromagnetism competes with superconductivity (T_c 's ~ 1-4K).

Specific heat values range from 250 to 750 mJ/mol*K².

PuCoGa₅ has superconducting $T_c \sim 18.5$ K



Needs for Material Specific Input from LDA+DMFT calculation.

Describing Kondo systems with LDA+DMFT

Framework of the realistic simulation

For given materials, e.g. CeX_2Si_2 $\text{X}=\text{Rh,Pd,Au,Ag,Cu,Ru}$

LDA+DMFT (Hubbard I)

Hybridization function $\Delta(\epsilon) = \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$

Schrieffer-Wolff transformation

Kondo coupling J_K

+ crystal-field, spin-orbit splittings

Realistic Kondo (Coqblin-Schrieffer) lattice model

DMFT with CT-QMC as the impurity solver

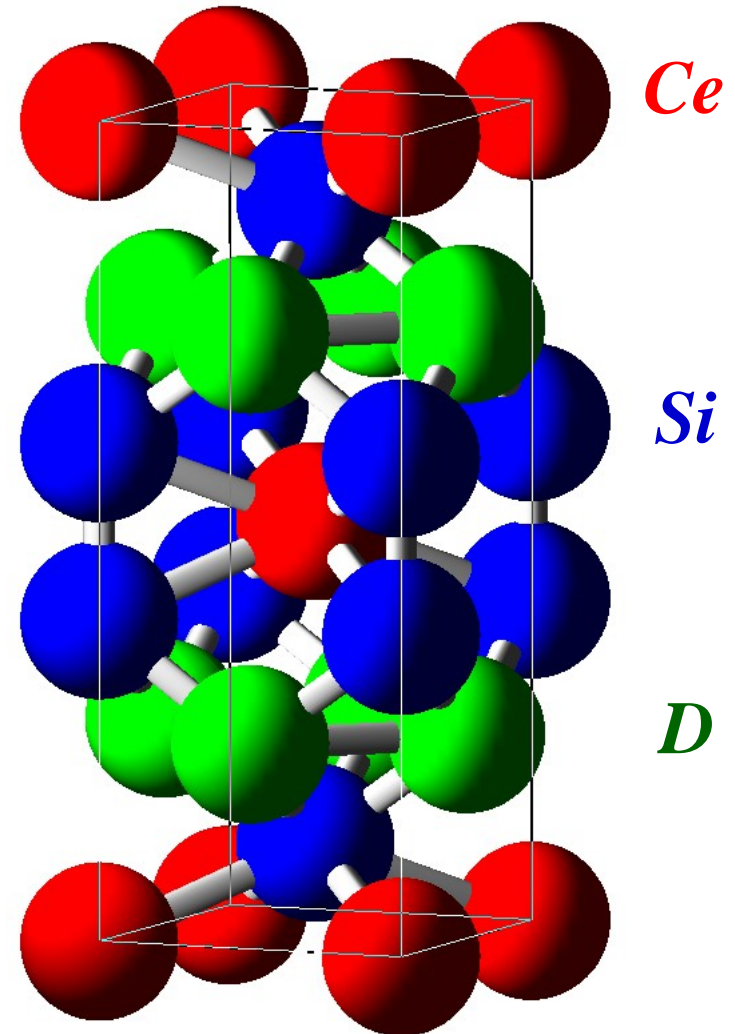
First-principle result for heavy fermions!

Kondo Coupling Strength Ce 122 Compounds

CeD₂Si₂ where
D=Mn,Fe,Co,Ni,Cu – 3d
D=Ru,Rh,Pd,Ag – 4d
D=Os,Au – 5d

Most widely studied, in particular
due to discovery of heavy fermion
superconductivity in **CeCu₂Si₂**
(*F. Steglich, et.al. Phys. Rev. Lett. 1979*)

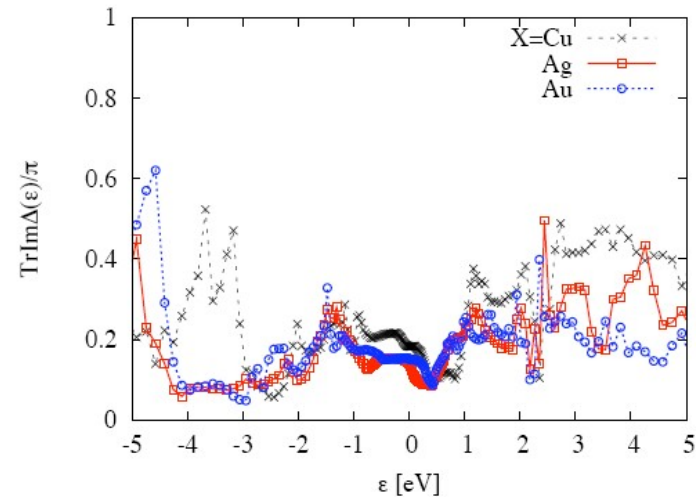
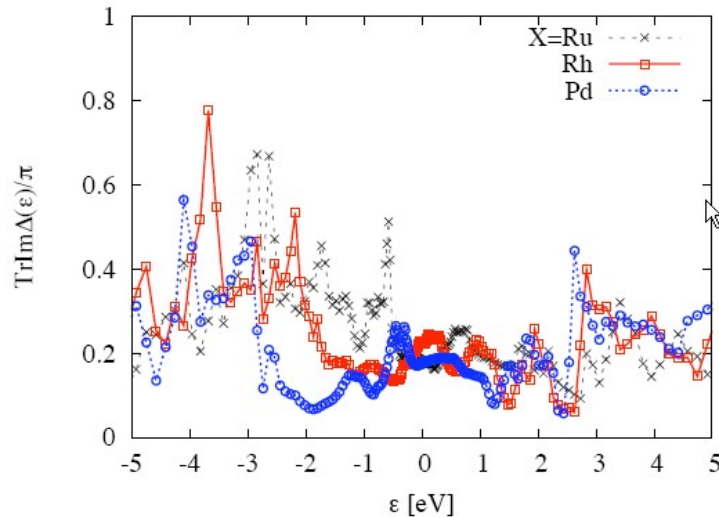
Ag,Au,Pd - 10K AFM, **Rh** – 40K AFM
Cu,Co,Fe,Ni,Ru,Os - PM
Mn – 379K AFM due to **Mn** moments



Calculated Hybridization for Ce 122 Compounds

Inputs to CT-QMC calculated by LDA for CeX_2Si_2

$$\Delta(\epsilon) = \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$$



Schrieffer-Wolff transformation

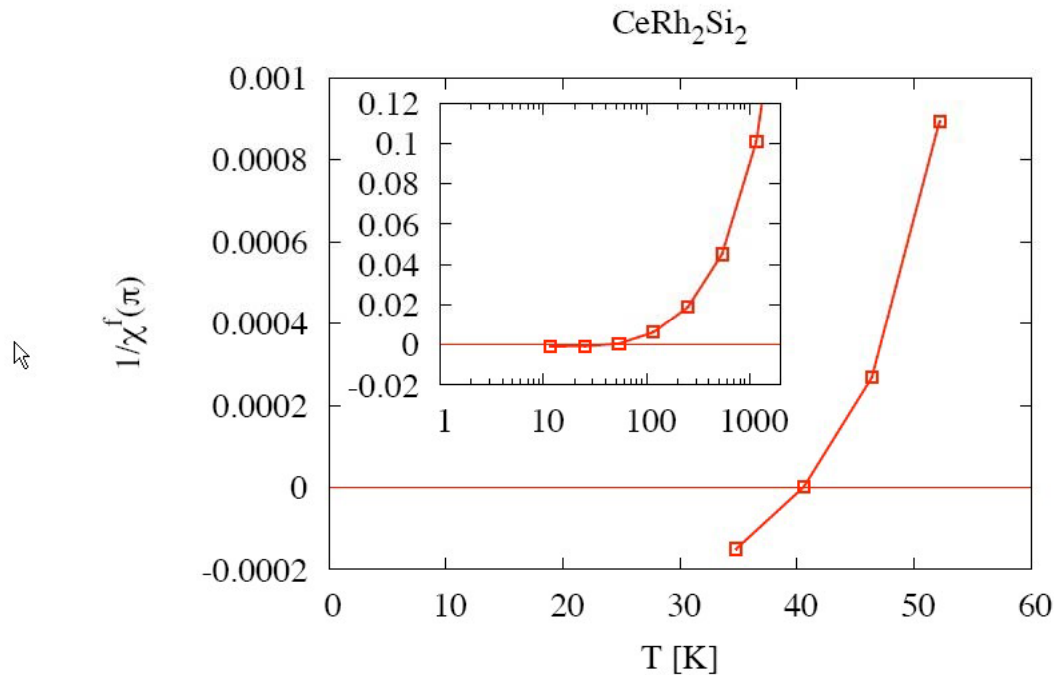
$$J_K = \frac{1}{\pi} \frac{\text{Tr} \int_{-D}^D d\epsilon \text{Im}\Delta(\epsilon)}{N_d} \left(\frac{1}{|\epsilon_f|} + \frac{1}{\epsilon_f + U} \right)$$

$$\epsilon_f = -2.5[\text{eV}], U = 5[\text{eV}] \quad D = 5[\text{eV}]$$

“conduction-band” Green’s function

$$G_c(i\omega_n) = \frac{1}{\pi} \frac{1}{N_d} \int_{-D}^D d\epsilon \frac{\text{TrIm}\Delta(\epsilon)}{i\omega_n - \epsilon} \frac{1}{\int_{-D}^D d\epsilon \text{TrIm}\Delta(\epsilon)/\pi N_d}$$

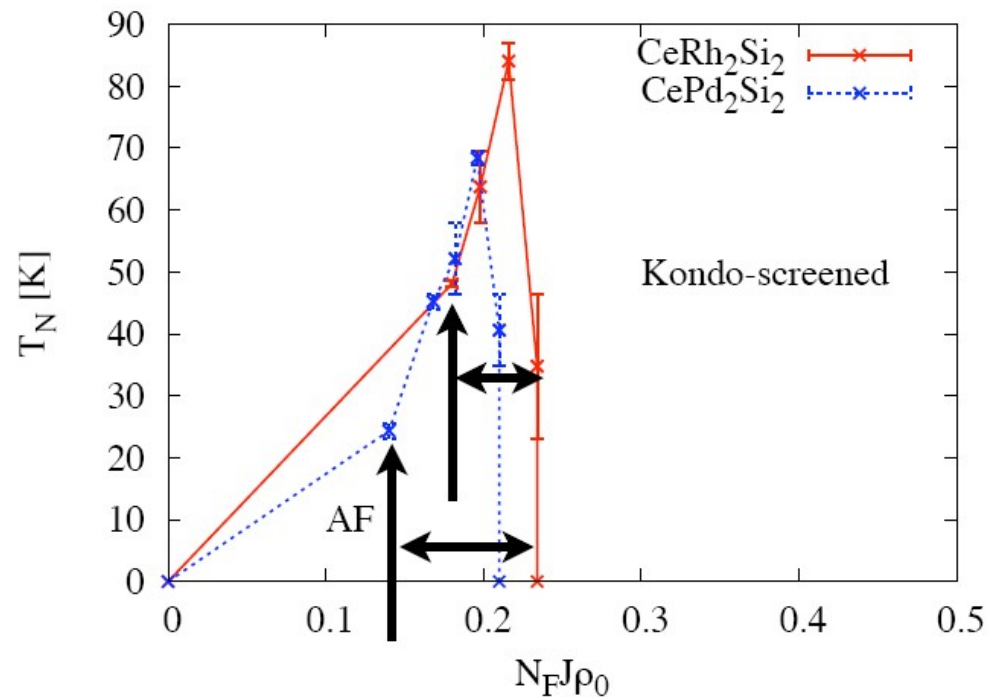
Tracking a magnetic phase transition of CeRh₂Si₂



Néel temperature $T_N = 41$ [K]

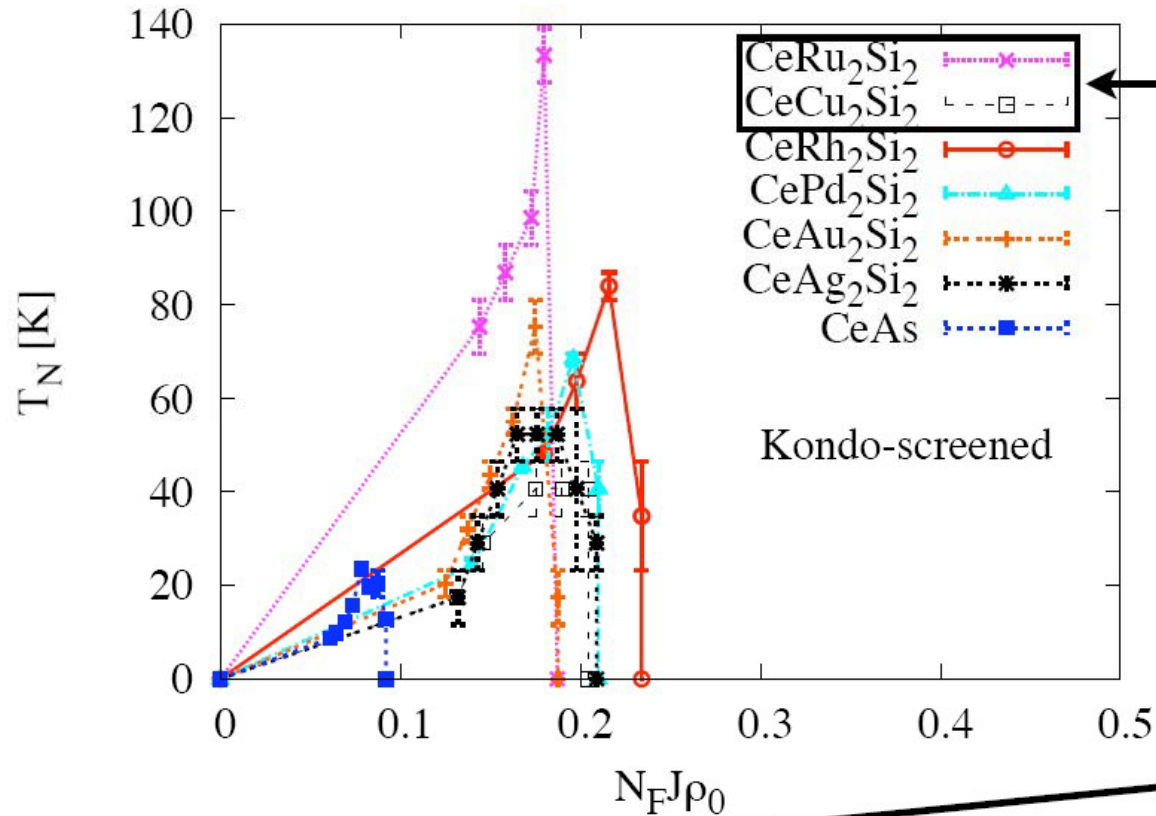
Material-specific Doniach phase diagram

Artificially rescale the Kondo coupling (qualitatively imitating the pressure experiments)



CeRh_2Si_2 is closer to the quantum critical point than CePd_2Si_2

Summarizing the material-specific Doniach phase diagrams

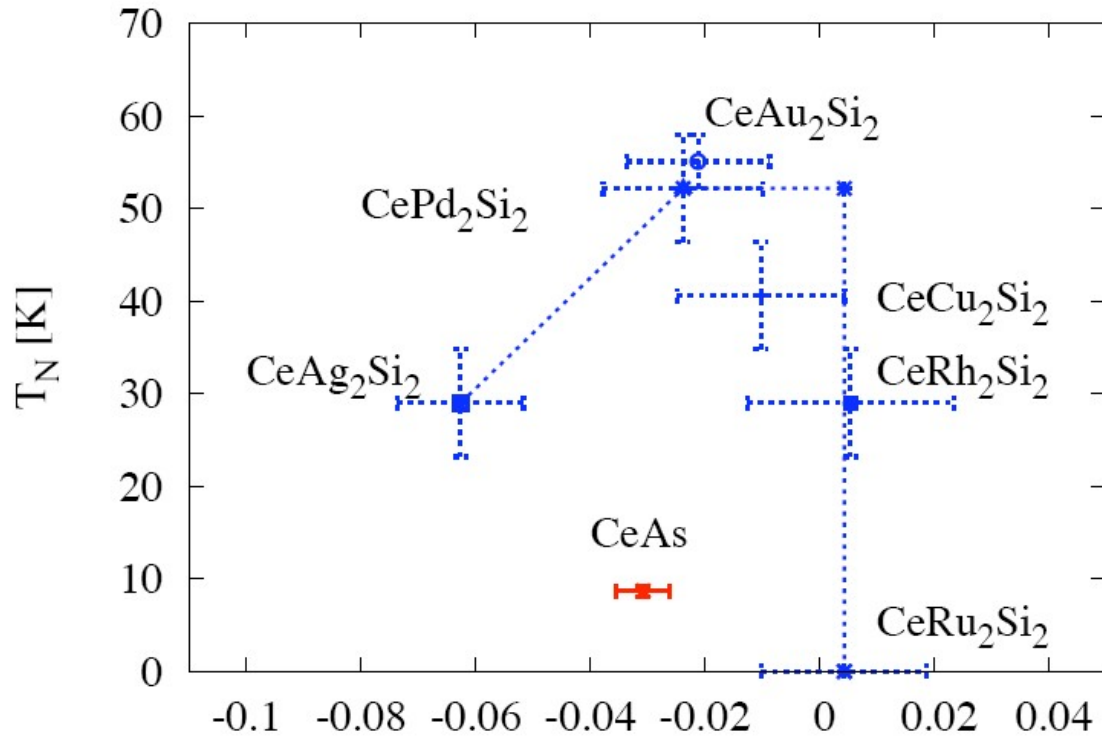


heavy fermion materials are close to the quantum critical point

The materials align like from the right to the left:

(quantum critical point) > CeRh₂Si₂ > CePd₂Si₂ ~ CeAu₂Si₂ > CeAg₂Si₂ > CeAs

Restoring the universal Doniach phase diagram

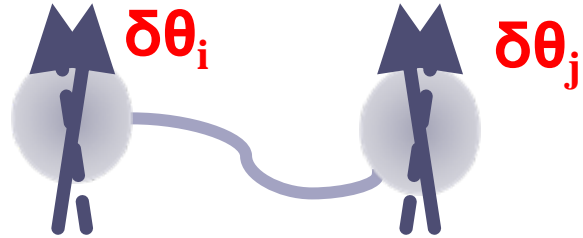


$$N_F J \rho_0 - (N_F J \rho_0)(qcp)$$

Hund coupling effects in f^2 states
give us a factor of $\sim 30\%$ in the Kondo coupling

taken as the point where the
Neel temperature vanishes

Calculations of RKKY Interactions



2d order perturbation theory for Kondo impurity hamiltonian

$$H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + J_K \sum_i S_i \left(\sum_{\sigma\sigma'} c_{i\sigma}^+ \tau_{\sigma\sigma'} c_{i\sigma'} \right)$$

$$\mathcal{H} = -\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

produces the scaling $J_{RKKY} \approx J_K^2 N(0)$

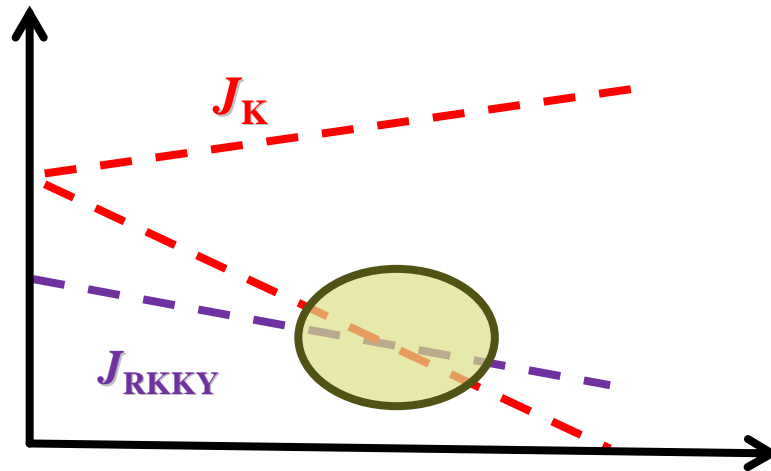
More general expression for exchange constants is obtained using magnetic force theorem: (Lichtenstein et.al 1987)

$$J_{\tau R \tau' R'}^{\alpha\beta} = \sum_{\mathbf{q}} \sum_{\mathbf{k} j j'} \frac{f_{\mathbf{k}j} - f_{\mathbf{k}+\mathbf{q}j'}}{\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}+\mathbf{q}j'}} \langle \psi_{\mathbf{k}j} | [\boldsymbol{\sigma} \times \mathbf{B}_{\tau}]_{\alpha} | \psi_{\mathbf{k}+\mathbf{q}j'} \rangle \langle \psi_{\mathbf{k}+\mathbf{q}j'} | [\boldsymbol{\sigma} \times \mathbf{B}_{\tau'}]_{\beta} | \psi_{\mathbf{k}j} \rangle e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}')} \quad (2)$$

Important to understand interplay between Kondo and RKKY interactions for heavy fermion systems using realistic electronic structures.

Scaling Kondo Exchange by Pressure or Doping

Material design: Once Kondo exchange J_K and local moment interaction (J_{RKKY}) are computed one can apply pressure or doping.



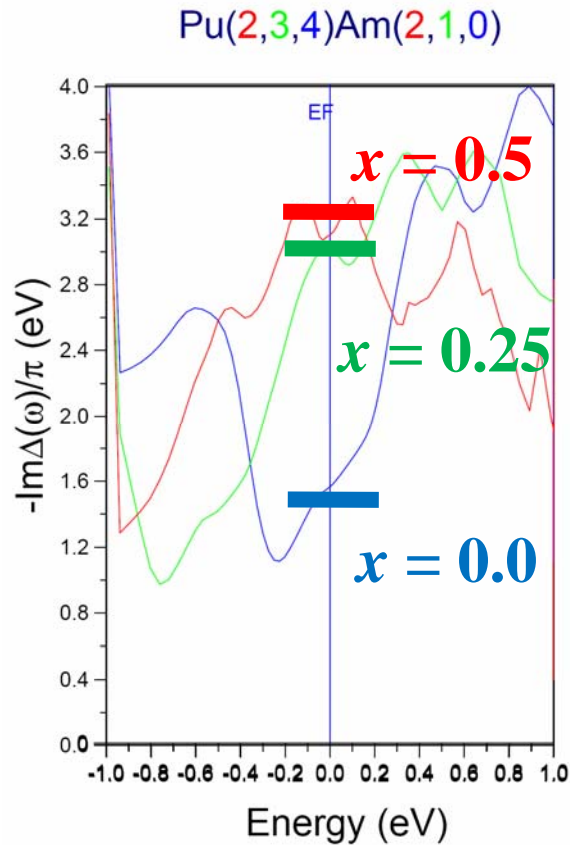
Quantum criticality?
Superconductivity?

Am ratio, x
($\text{Pu}_{1-x} \text{Am}_x$)

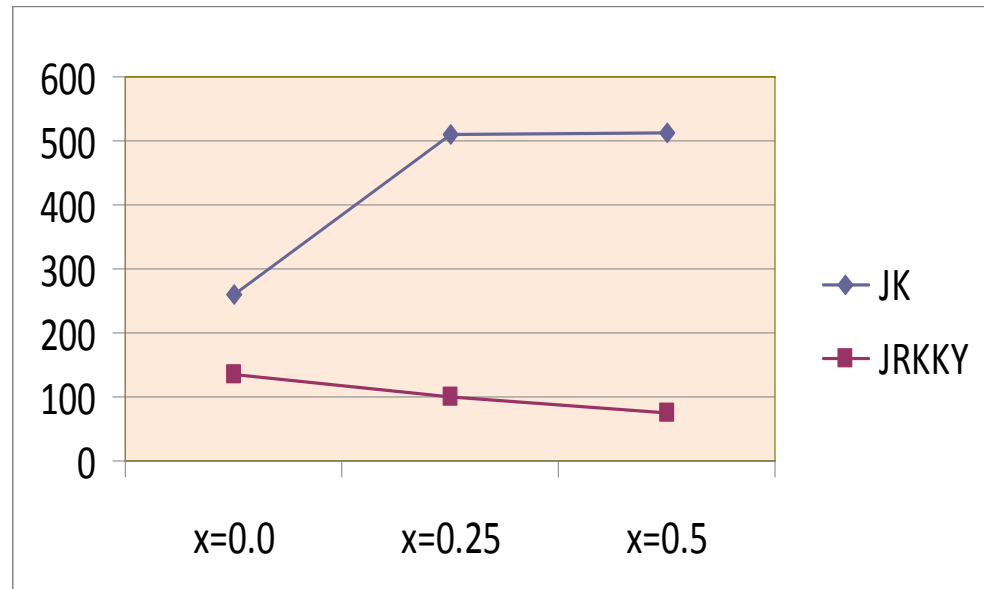
Searching for magnetism in Plutonium:

- * Pu is non magnetic: $f^5 + \text{Kondo?}$ (*Shim, Nature 2007*), f^6 (*Shick, PRB 2006*)
- * Mixing with Am expands the lattice up to 20%, can Pu moment be seen?

J_K vs J_{RKKY} in $\text{Pu}_{1-x}\text{Am}_x$



(MJ. Han, X. Wan, *SS*, *PRB* 2008
 J. Shim, K. Haule, *SS*, G. Kotliar, *PRL* 2008)



$J_K > J_{RKKY}$ for $0.0 \leq x \leq 0.5$

- No moment due to Kondo screening
- No quantum criticality and superconductivity



Conclusion

Combination of **electronic structure** and **many body** dynamical mean field methods open new avenues in **studying strongly correlated systems**:

- It allows to simulate structural phases, equations of states, volume expansions and collapses.
- It allows to resolve Kondo resonances, atomic multiplet spectra and mixed valence regimes.
- It allows to study Doniach phase diagrams and quantum critical behavior.

Collaborators

M.-J. Han, M. Matsumoto, Q. Yin



K. Haule, G. Kotliar, J.-H. Shim



J. Otsuki

Tohoku University, Japan