The LDA+DMFT Approach to Correlated Electron Systems

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I Introduction to LDA+DMFT
local density approximation + dynamical mean-field theory

II Difficulties and simplifications for transition metal oxides

III Technical details of V_2O_3 calculation

V_2O_3: kh, Keller, Eyert, Vollhardt, Anisimov PRL 84, 5168 (2001)
LDA+DMFT: kh, Nekrasov, Keller, Eyert, Blümer, McMahan, Scalettar, Pruschke, Ansimov, Vollhardt cond-mat/0112079

LDA band structure calculation

Ab initio electronic Hamiltonian:

$$\hat{H} = \underbrace{\underbrace{\int d^3r\ \hat{\Psi}^+(\mathbf{r})[-\Delta + V^{\text{ion}}(\mathbf{r})]\hat{\Psi}(\mathbf{r})}_{\hat{H}_{\text{kin}}}}_{\text{Crystal structure}} + \underbrace{\frac{1}{2}\int d^3r d^3r'\ \hat{\Psi}^+(\mathbf{r})\hat{\Psi}^+(\mathbf{r}')V^{ee}(\mathbf{r}-\mathbf{r}')\hat{\Psi}(\mathbf{r}')\hat{\Psi}(\mathbf{r})}_{\hat{H}_{e^-e^-}}$$

Hohenberg-Kohn: $E = E(\rho)$; $\partial E(\rho)/\partial\rho = 0 \rightarrow$ Kohn-Sham equations.
LDA band structure: Interpret ε_i (Lagrange parameter) as physical one-particle energies, i.e.,

$$\hat{H} = \underbrace{\int d^3r\ \hat{\Psi}^+(\mathbf{r})\left[-\Delta + V^{\text{ion}}(\mathbf{r}) + \int d\mathbf{r}'\rho(\mathbf{r}')V^{ee}(\mathbf{r}-\mathbf{r}') + \frac{\partial E_{xc}^{\text{LDA}}(\rho(\mathbf{r}))}{\partial\rho}\right]\hat{\Psi}(\mathbf{r})}_{\hat{H}_{\text{LDA}}} + \hat{H}_{\text{corr}}$$

For an actual calculation, expand WF in basis Φ_{ilm} (LMTO, APW ...):

$$\hat{\Psi}^+(\mathbf{r}) = \sum_{ilm}\hat{c}^+_{ilm}\Phi_{ilm}(\mathbf{r})\ ; \quad \hat{H}_{\text{LDA}} = \sum_{ilm,jl'm',\sigma} t_{ilm,jl'm'}\hat{c}^{\sigma+}_{ilm}\hat{c}^{\sigma}_{jl'm'}$$

How to deal with $\hat{H}_{\text{corr}}$ for a correlated systems?

LDA + local Coulomb correlations

$$\hat{H} = \hat{H}_{\rm LDA} + \underbrace{\hat{H}^{\rm local}_{\rm corr.}}_{\frac{1}{2}\sum_{il=l_d,m\sigma m'\sigma'} U^{\sigma\sigma'}_{mm'}\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma'}} - \underbrace{H^{\rm corr.}_{\rm LDA}}_{\frac{1}{2}Un_d(n_d-1)} + \hat{H}_{\rm res.}$$

Ab initio correlated electron model $\hat{\mathcal{H}} = \hat{H}^0_{\rm LDA} + \hat{H}^{\rm local}_{\rm corr.}$

Note:

- Leading $1/d$ contribution of non-local density-density interaction is Hartree term (already within LDA).
- Need basis where interacting orbitals can be identified: LMTO (Andersen'75)
- U can be calculated via constraint LDA: $U = \frac{\partial^2 E_{\rm LDA}(n_d)}{\partial n_d^2}$ (Gunnarsson et al'89)
- Hund's rule coupling can be calculated similarly

LDA+U: Solve $\hat{\mathcal{H}}$ with Hartree-Fock (Anisimov, Zaanen, Andersen'91)
LDA+DMFT: Solve $\hat{\mathcal{H}}$ with DMFT (Anisimov et al'97)

LDA+DMFT

Anisimov et al'97

Solve correlated electron problem $\hat{\mathcal{H}}$ by DMFT

Single site problem
$\oplus$ Dyson equation

Metzner, Vollhardt'89, Georges Kotliar'92, Jarrell'92

(i) Single site problem $\equiv$ multi-band Anderson impurity model:

$$G = -\frac{1}{Z}\int \mathcal{D}[\psi\psi^*]\psi\psi^* e^{\psi^*[G^{-1}+\Sigma]\psi + U\psi^*\psi\psi^*\psi}$$

(ii) k-integrated Dyson equation:

$$G^{\sigma}_{lm,l'm'}(\omega) = \int \frac{{\rm d}^3k}{v_{\rm BZ}}\left[\omega+\mu-[\epsilon-\epsilon^{\rm corr}]_{lm,l'm'}(\mathbf{k})-\Sigma^{\sigma}_{lm,l'm'}(\omega)\delta_{l,d}\right]^{-1}$$

Employ QMC to solve Anderson impurity model
Lichtenstein, Katsnelson'98

NCA, IPT show quantitative differences at a Mott transition
Nekrasov et al'00

II Difficulties and simplifications for transition metal oxides

How to determine U, J, double counting?

Standard approach — Anisimov et al.'91

Atomic limit:

$$E^U_{AL} = \frac{1}{2}\bar{U} n_d(n_d - 1) - \frac{1}{2}J \sum_\sigma n_{d\sigma}(n_{d\sigma} - 1)$$

Assuming $E^U_{\rm LDA} = E^U_{AL} \Rightarrow$ Double counting correction

$$\varepsilon^0_{im} \equiv \frac{\mathrm{d}}{\mathrm{d}n_{im}}(E_{\rm LDA} - E^U_{\rm LDA}) = \varepsilon_{im} - \bar{U}(n_d - \frac{1}{2}) + \frac{J}{2}(n_d - 1)$$

Constraint LDA calculation gives U,J — Gunnarsson et al.'89

$$\begin{aligned}\bar{U} &= \varepsilon_{im\uparrow}\left(n_{d\uparrow} = \frac{n_0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n_0}{2}\right) \\ &\quad -\varepsilon_{im\uparrow}\left(n_{d\uparrow} = \frac{n_0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n_0}{2} - 1\right)\end{aligned}$$

$$\begin{aligned}J &= \varepsilon_{im\uparrow}\left(n_{d\uparrow} = \frac{n_0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n_0}{2} - \frac{1}{2}\right) \\ &\quad -\varepsilon_{im\downarrow}\left(n_{d\uparrow} = \frac{n_0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n_0}{2} - \frac{1}{2}\right)\end{aligned}$$

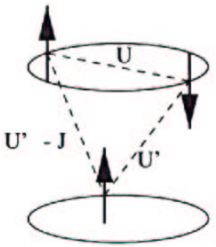
Works for $4f$ electrons – difficulties for TMO

1) Large uncertainties in $\bar{U}$ of O(0.5eV)
depends on basis, orthogonalization ...

2) Above formula for Hund's rule coupling holds for

$$\hat{H} = \bar{U}\hat{n}_d\hat{n}_d - J\sum_{\sigma}\hat{n}_{d\sigma}\hat{n}_{d\sigma} \qquad (1)$$

Nature and LDA+DMFT Hamiltonian have other form!



$$\hat{H} = U\sum_{m}\hat{n}_{m\uparrow}\hat{n}_{m\downarrow} + \sum_{m\neq\tilde{m}\,\sigma\tilde{\sigma}}(U' - \delta_{\sigma\tilde{\sigma}}J)\,\hat{n}_{m\sigma}\hat{n}_{\tilde{m}\tilde{\sigma}} + \text{spin-flip} \qquad (2)$$

$$U' = U - 2J$$

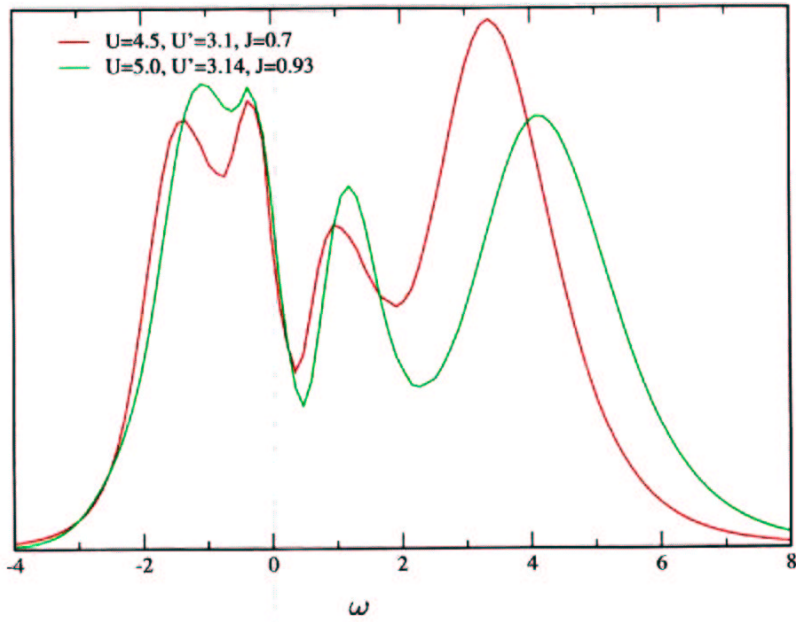
E.g., energies for t_{2g} electrons (V^{3+})

$E_{n_{d\uparrow}=n_{d\downarrow}=1} - E_{n_{d\uparrow}=2,n_{d\downarrow}=0} = -J$ for Hamiltonian (1)
$E_{n_{d\uparrow}=n_{d\downarrow}=1} - E_{n_{d\uparrow}=2,n_{d\downarrow}=0} = -\frac{4}{3}J$ for Hamiltonian (2)

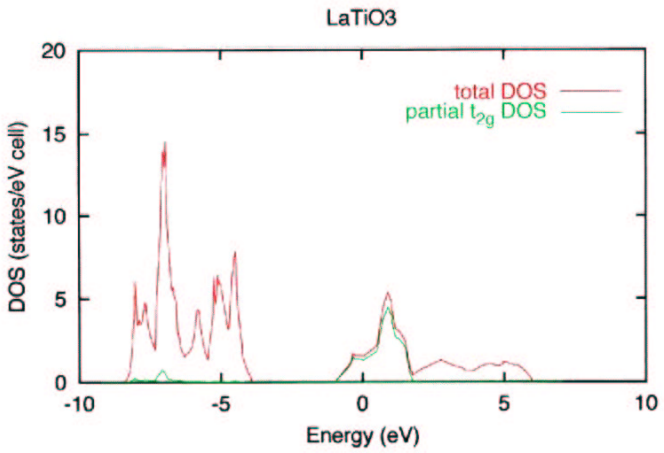
Constraint LDA — atomic line spectrum — constraint LDA×3/4
$J = 0.9$ eV $J = 0.69$ eV $J = 0.675$ eV

⇒ get J from atomic line spectra or analysis via Hamiltonian (2)?

Effect of different J at fixed $\bar{U}$ for V_2O_3



Simplifications for transition metal oxides



t_{2g} band well separated from other bands (weak hybridization)

Restriction to t_{2g} part ($l = l_d$):

$$G^{\sigma}_{m,m'}(\omega) = \frac{1}{v_{\mathrm{BZ}}} \int d\mathbf{k} \left[\omega + \mu - \left(\tilde{H}^{0}_{\mathrm{LDA}} \right)_{m,m'} (\mathbf{k}) - \Sigma^{\sigma}_{m,m'}(\omega) \right]^{-1}$$

Get $\tilde{H}^{0}_{\mathrm{LDA}}$ e.g. via downfolding with third generation MTO

For orbital degeneracy (without symmetry breaking):

$$\Sigma^{\sigma}_{m,m'}(\omega) = \Sigma(\omega)\delta_{m,m'}; \quad G^{\sigma}_{m,m'}(\omega) = G(\omega)\delta_{m,m'}$$

$$\Longrightarrow \quad G(\omega) = G_{\Sigma=0}(\omega - \Sigma(\omega)) = \int d\varepsilon \, \frac{\rho^{0}(\varepsilon)}{\omega + \mu - \Sigma(\omega) - \varepsilon}$$

$\Rightarrow$ only, t_{2g} DOS needed from LDA calculation!

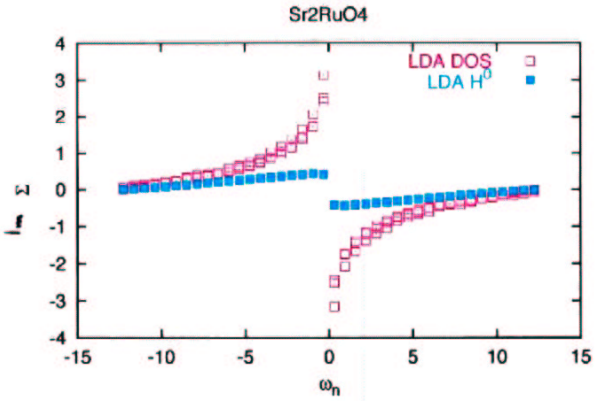
$\Rightarrow$ double counting correction irrelevant (shift of chemical potential)

Without degeneracy of t_{2g} orbitals (e.g. V_2O_3) approximately

$$G_{\nu}(\omega) = \int d\epsilon \, \frac{\rho^{0}_{\nu}(\varepsilon)}{\omega + \mu - \Sigma_{\nu}(\omega) - \varepsilon}$$

"Naive" full Hamiltonioan calculation

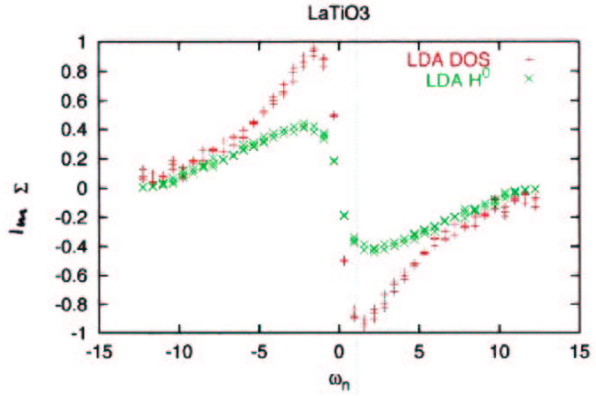
t_{2g} orbitals interacting, oxygen and e_g non-interacting



$n_{t_{2g}}^{DOS} = 4$

$n_{t_{2g}}^{H^0} = 4.52$

Both calculations: $\bar{U} = 2.94$ eV, $J = 0.69$ eV, $T = 0.1$ eV



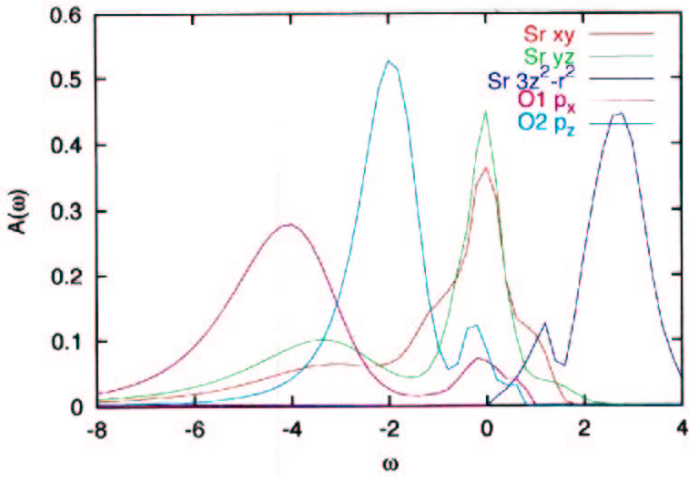
$n_{t_{2g}}^{DOS} = 1$

$n_{t_{2g}}^{H^0} = 1.58$

Both calculations: $\bar{U} = 4$ eV, $J = 0$ eV, $T = 0.1$ eV

⇒ fails (non-integer occupation, no strong electron correlations)

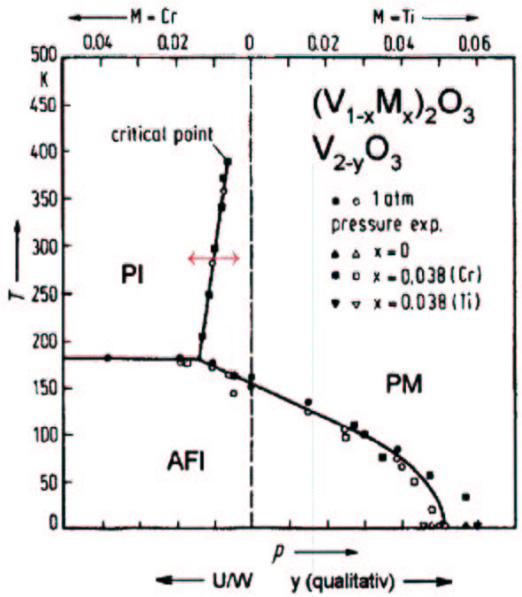
Sr_2RuO_4 spectrum (full Hamiltonian)



Necessary: interaction for all 3d and oxygen orbitals

III Technical details of V_2O_3 calculation

Phase diagram of V_2O_3



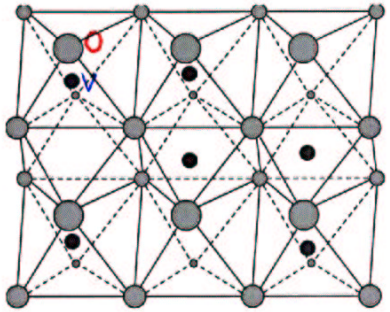
McWahn et al.'73

$\longleftrightarrow$: Mott-Hubbard transition

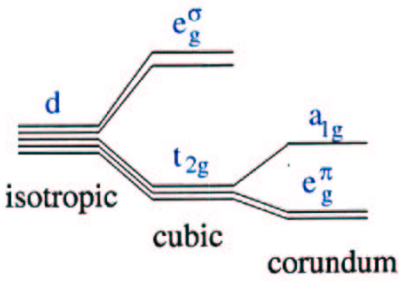
Mott-Hubbard transition in V_2O_3

Basic considerations on electronic structure

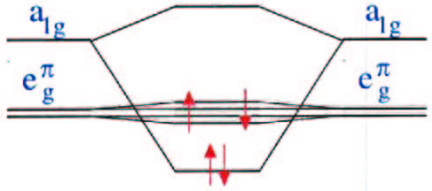
Lattice structure



Electronic structure

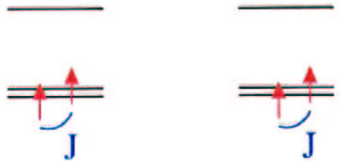


a_{1g}-bond



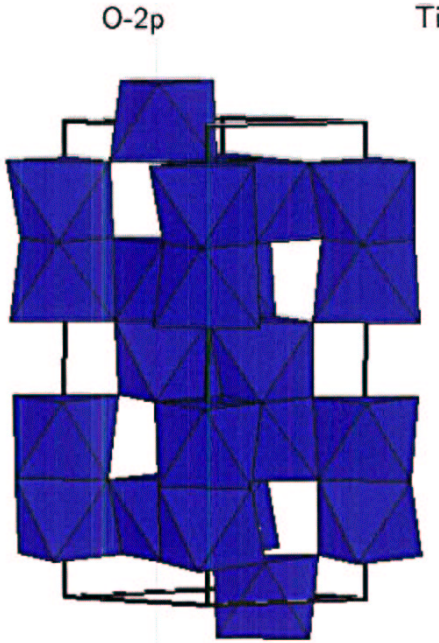
Castellani et al'78

Hund's rule



1. LDA calculation

Corundum crystal structure

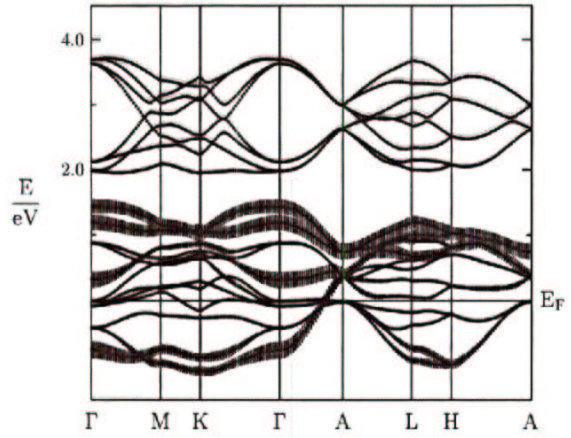


Dernier's (1970) structural data

V_2O_3: $a = 4.9515$Å, $c = 14.003$Å
$z_V = 0.34630$, $x_O = 0.31164$
$(V_{0.962}Cr_{0.038})_2O_3$: $a = 4.9985$Å, $c = 13.912$Å
$z_V = 0.34870$, $x_O = 0.30745$

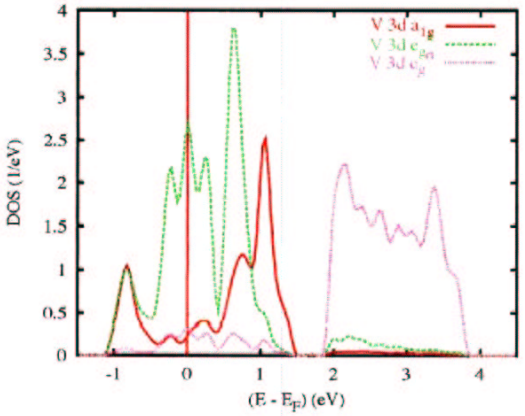
ASW LDA calculation (ver 1.9) (good agreement with Mattheiss '94)

V_2O_3 bandstructure

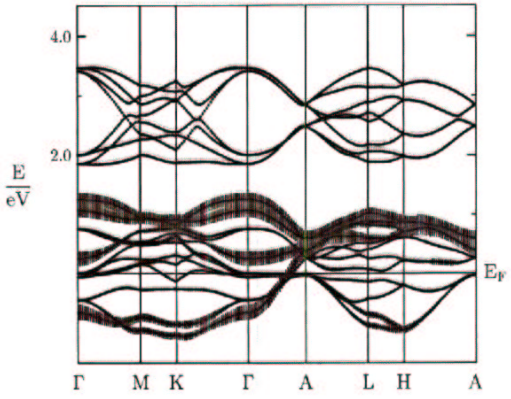


4 atoms per unit cell $\Rightarrow 4 \times 3\ t_{2g}$ bands around E_F
gray bar indicates a_{1g} contribution

V_2O_3 partial DOS

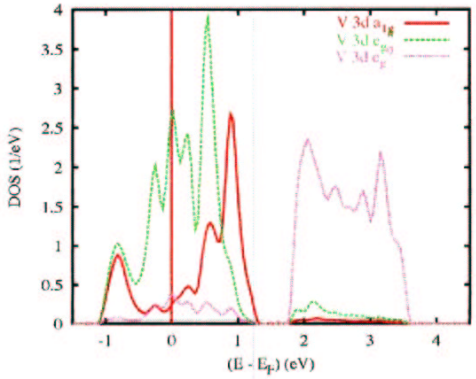


$(V_{0.962}Cr_{0.038})_2O_3$ bandstructure



4 atoms per unit cell $\rightarrow 4 \times 3\ t_{2g}$ bands around E_F
gray bar indicates a_{1g} contribution

$(V_{0.962}Cr_{0.038})_2O_3$ partial DOS



2. Construct LDA+correlation Hamiltonian

Full Hamiltonian with 4 V atoms per unit cell:
76 interacting orbitals (including oxygen) → currently not manageable

Effective Hamiltonian with t_{2g} orbitals only (4 V atoms per unit cell):
24 interacting orbitals

Effective Hamiltonian for V-pair and only t_{2g} orbitals:
12 interacting orbitals

Effective Hamiltonian for one V atom and t_{2g} orbitals:
6 interacting orbitals → done here

Effective Hamiltonian for t_{2g} orbitals + oxygen of same symmetry:
12 interacting orbitals (including oxygen)

2. Construct LDA+correlation Hamiltonian

Take e_g^σ and a_{1g} DOS, cut-off contributions within oxygen bands
renormalize both DOS's to 1

⇒ defines LDA $\hat{H}^0_{\rm LDA}$

Supplement with local Coulomb interaction

$$\hat{H} = \hat{H}^0_{\rm LDA} + U \sum_{i\,m} \hat{n}^i_{m\uparrow}\hat{n}^i_{m\downarrow} + \sum_{i\,m\neq\tilde{m}\,\sigma\tilde{\sigma}} (U' - \delta_{\sigma\tilde{\sigma}} J)\, \hat{n}^i_{m\sigma}\hat{n}^i_{\tilde{m}\tilde{\sigma}}$$

J = 0.93 eV (Solovyev'96); U see below; $U' = U - 2J$

3. DMFT(QMC) calculation

Choose an initial self-energy Σ_m

Calculate G_m from Σ_m via k-integrated Dyson Eq.:

$$G_m(\omega) = \int d\epsilon \, \frac{\rho_m^0(\epsilon)}{\omega + \mu - \Sigma_m(\omega) - \epsilon}$$

$$\mathcal{G}_m = (G_m^{-1} + \Sigma_m)^{-1}$$

Calculate G_m from $\mathcal{G}_m$ via DMFT single-site problem

$$G_m^\sigma = -\frac{1}{\mathcal{Z}} \int \mathcal{D}[\psi]\mathcal{D}[\psi^*] \psi_m^\sigma \, \psi_m^{\sigma *} e^{\mathcal{A}[\psi,\psi^*,\mathcal{G}_m^{-1}]}$$

$$\Sigma_{\mathrm{new}\,m} = \mathcal{G}_m^{-1} - G_m^{-1}$$

Iterate with $\Sigma = \Sigma_{\mathrm{new}}$ until convergence, i.e. $||\Sigma - \Sigma_{\mathrm{new}}|| < \epsilon$

$$\mathcal{A}[\psi, \psi^*, \mathcal{G}_m^{-1}] = \sum_{\nu,\sigma,m} \psi_{\nu m}^{\sigma *} (\mathcal{G}_{\nu m}^\sigma)^{-1} \psi_{\nu m}^\sigma$$

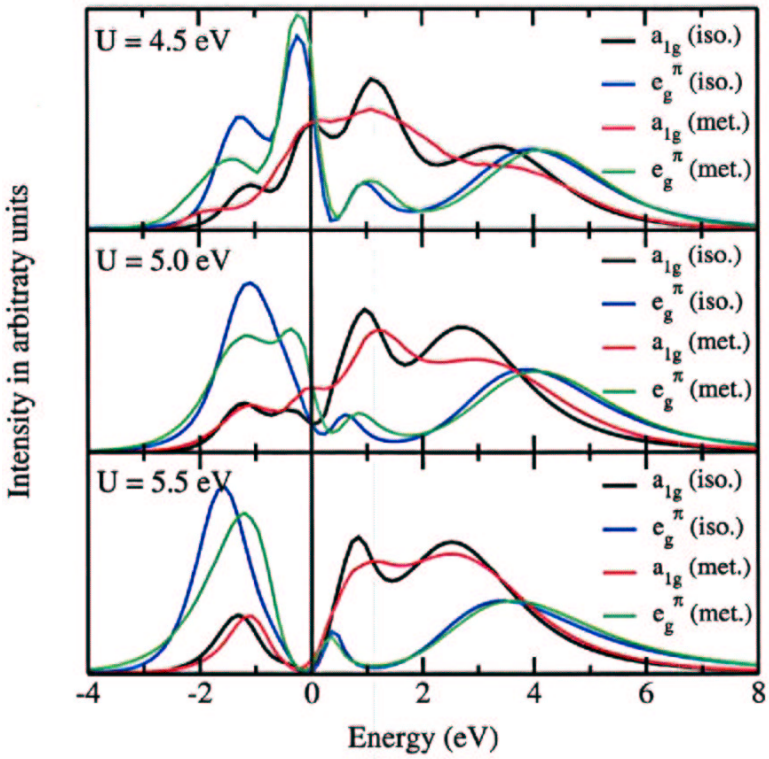
$$-U \sum_m \int_0^\beta d\tau \, \psi_m^{\uparrow *}(\tau)\psi_m^\uparrow(\tau)\psi_m^{\downarrow *}(\tau)\psi_m^\downarrow(\tau)$$

$$- \sum_{m \neq m' \, \sigma\sigma'} (U' - \delta_{\sigma\tilde{\sigma}} J) \int_0^\beta d\tau \, \psi_m^{\sigma *}(\tau)\psi_m^\sigma(\tau)\psi_{m'}^{\sigma' *}(\tau)\psi_{m'}^{\sigma'}(\tau)$$

QMC: $\Delta\tau = 0.25\ \mathrm{eV}^{-1}$

LDA+DMFT(QMC) spectrum for V_2O_3

kh, Keller, Eyert, Vollhardt, Anisimov'01

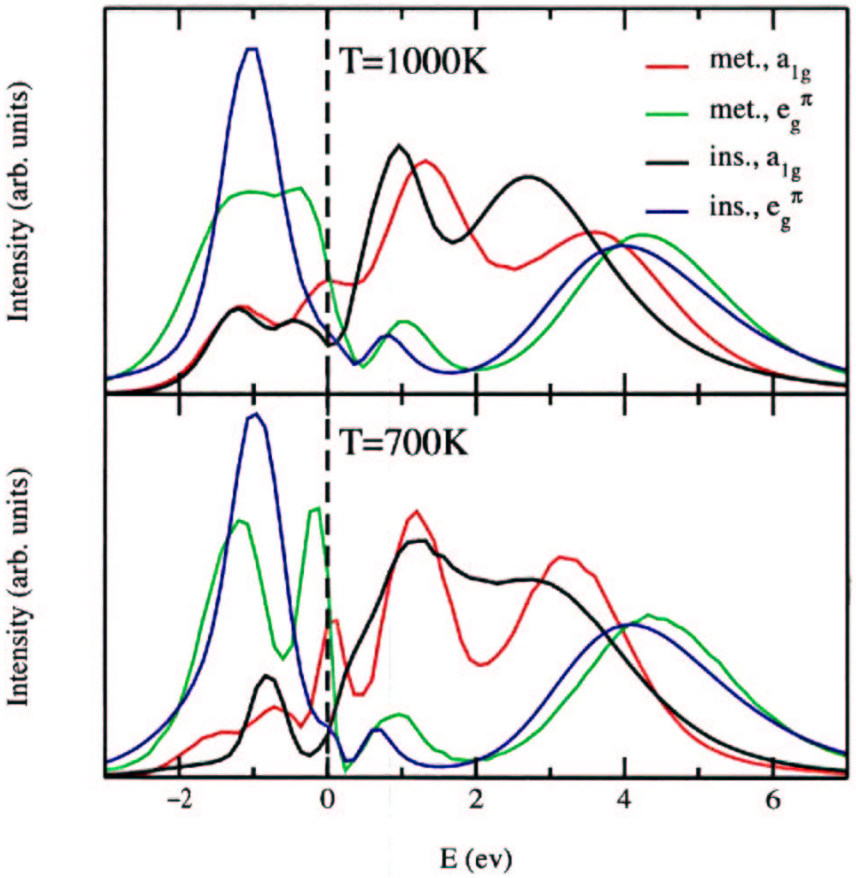


LDA+DMFT(QMC) spectra for paramagnetic $(V_{0.962}Cr_{0.038})_2O_3$ ("iso.") and V_2O_3 ("met.") at $U = 4.5$, 5, 5.5 eV; $T = 1000$ K.

Mott-Hubbard transition at $U \approx 5$ eV.

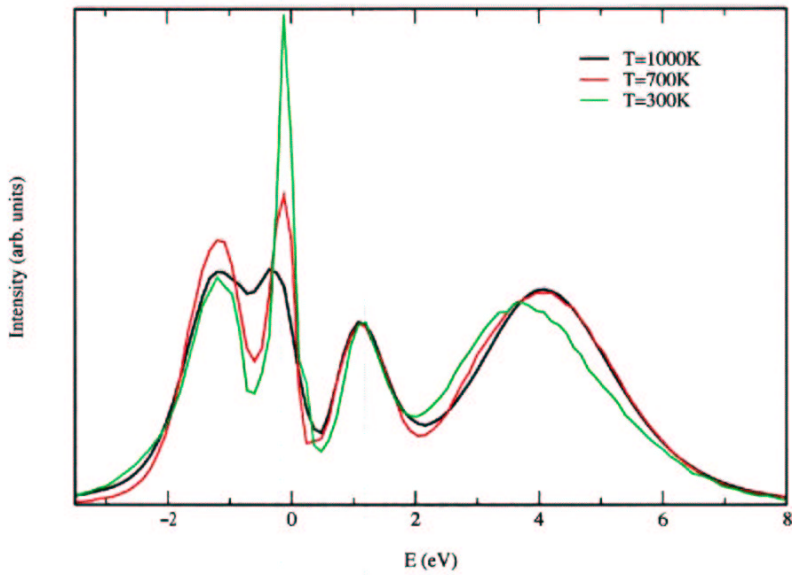
MIT transition at about $U = 5$ eV

Keller, kh, Eyert, Vollhardt, Anisimov '02



DOS of V_2O_3 (metallic paramagnetic phase) and $(V_{0.962}Cr_{0.038})_2O_3$ (insulating paramagnetic phase) at $U = 5$ eV, $J = 0.93$ eV

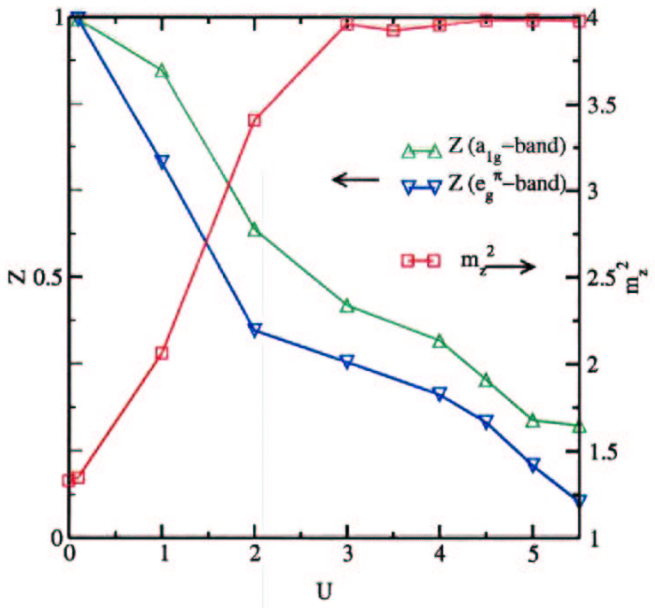
Effect of temperature



t_{2g} DOS for V_2O_3 at $U = 5$ eV, $J = 0.93$ eV

⇒ Sharp QP peak smeared out at surprisingly low T

The Mott-Hubbard transition as a function of U



Quasiparticle weight $Z \propto m/m^*$, local magnetic moment m_z^2 vs. U

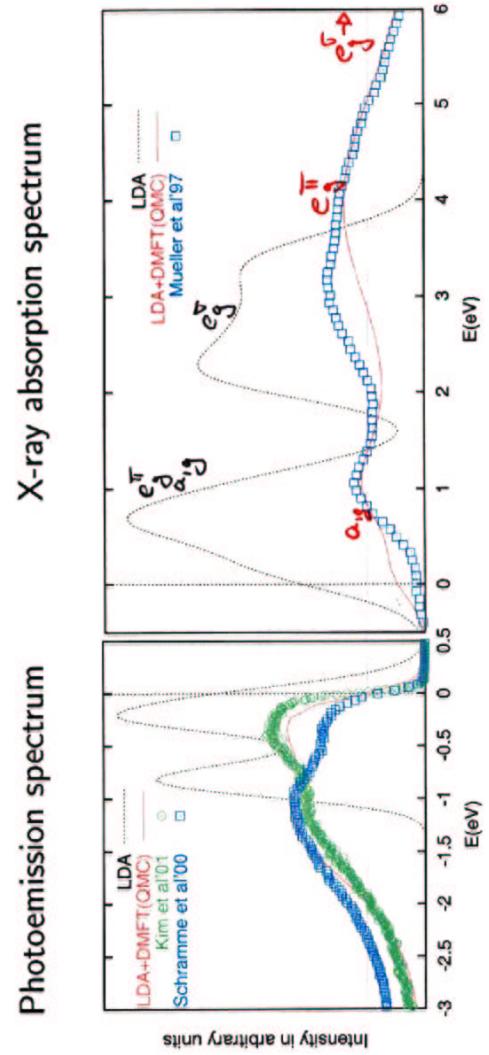
Orbital occupation $(a_{1g}, e_g^\pi, e_g^\pi)$:

	LDA+DMFT(QMC)	X-ray absorption Park *et al.*'00
PI	(0.28,0.86,0.86)	(0.4,0.8,0.8)
PM	(0.37,0.82,0.82)	(0.5,0.75,0.75)

Spin $S=1$

$S=1/2$ Castellani et al'78, one-band Hubbard model

Comparison to experiment

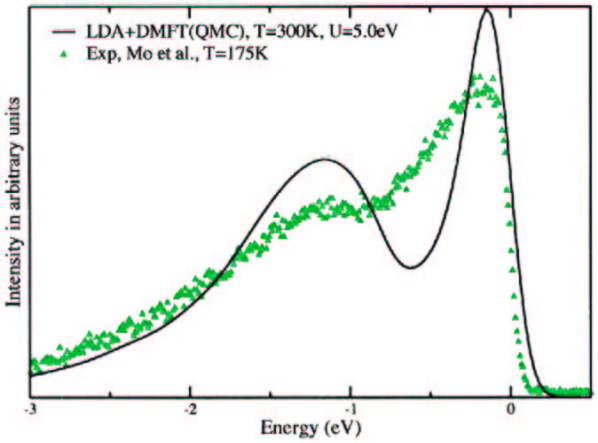


Good agreement with experiment above and below Fermi energy.

Note, one-band Hubbard model (Rozenberg et al'95) is symmetric.

New development in V_2O_3 PES

Mo et al'02



- experiment: improved bulk sensitivity ($h\nu = 300 - 700$ eV)
- experiment: decreased size of PES spot (100 μm)
- theory U=5 eV, J=0.93 eV, T=300 K, broadening 0.09 eV

Conclusion/Questions

- Large uncertainties in Hubbard U in TMO
  better way than to adjust U?
- Use Hund's rule J from atomic line spectra?
  From modified constraint LDA formula?
- Problems with full Hamiltonian approach for TMO
  no strong electron correlations!
  $\Rightarrow$ oxygen-3d interaction necessary?
  $\Rightarrow$ work with effective Hamiltonians at E_F?
- Restriction to t_{2g} bands (2 DOS's) works well for V_2O_3.
  Differences between theory and experiment due to V-pair?
  Why does V_2O_3 PES look not very correlated?
- Origin of 1st order transition in V_2O_3
  due to coexistence of solutions?
  due to concave correlation energy as $Z \to 0$ (van der Waals)?
  or consequence of 1st order lattice transition?

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