Mott Transition in MnO and Valence Transition in Yb under Pressure: Critical Overview of an All-Electron LDA+DMFT Implementation

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Critical Overview of All-Electron LDA+DMFT
Mott transitions, Valence transition: what’s left?

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Mott transition: **spectral** evolution as a function of $\frac{U}{W}$

Mott, Hubbard (and others), 50-60 years ago

On-site Coulomb repulsion $U$ can localize electrons unless the hopping amplitude $W$ is large enough to overcome it.

OK, not so simple. Other energy scales enter the problem:

* Hund's coupling $J_H$
* crystal field splitting $\Delta$
* multiple bands: “orbital selection”

Transition metal monoxides are the “classic case”: unsolved

Can use LDA

Difficult to treat within one-particle theory

Can use LDA+$U$

Georges et al, Rev. Mod. Phys. 1996
(Dynamical Mean-Field Theory)
Mott transition: spectral evolution as a function of $U/W$

Fujimori PRL 69, 1796 (1992)

Georges et al Rev. Mod. Phys.1996
(Dynamical Mean-Field Theory)
LDA+U cannot handle fluctuations induced by strong interaction.

DMFT: Map the lattice to an chosen site embedded in a “bath,” then all sites are made equivalent, self-consistently.

A. Georges et al, Rev. Mod. Phys. 68, 13 (1996)
G. Kotliar and D. Vollhardt, Physics Today (March 2004)
To treat systems with strong on-site correlations: in LDA+DMFT (analogy to LDA+U): original form

\[
H = \sum_{im\sigma} H_{im,i'm'}^{LDA} c^{+}_{im\sigma} c_{i'm'\sigma} \\
+ \frac{1}{2} \sum_{imm'\sigma} \text{correl.} U_{mm'}^{i} n_{im\sigma} n_{im'\sigma} \\
+ \frac{1}{2} \sum_{im\neq m'\sigma} \text{correl.} (U_{mm'}^{i} - J_{mm'}^{i}) n_{im\sigma} n_{im'\sigma} \\
- \sum_{im\sigma} \text{correl.} H_{im,i'm'}^{\text{doublecounting}} c^{+}_{im\sigma} c_{i'm'\sigma}
\]

LDA band structure (K-S Hamiltonian)

U, J from Constrained DFT

Double-counting term

Lichtenstein and Katsnelson, PRB 57, 6884 (1998) (LDA+DMFT)
**LDA** ⇒ Wannier projection: \( \mathcal{H}_{LDA}(k) \)

⇒ constrained LDA: \( U_{ij}, J_{ij} \)

⇒ double counting:

\[
\mathcal{H} = \sum_k \mathcal{H}_0(k) + \sum_R U_{ij} n_{Ri} n_{Rj} - E_{dc} n_d
\]

**DMFT**

Find chem. potential
Compute local propagator

Construct impurity problem
\( \text{FT}: \omega_n \rightarrow \tau \)

\( G_{dd}(i\omega_n) \)

\( G(\tau), U_{ij} \)

solve impurity problem

\( \Sigma(i\omega_n) \)

\( \text{invFT: } \tau \rightarrow \omega_n \)

Compute \( \Sigma \)

One- and two-particle quantities on real axis

**Hirsch-Fye QMC**

**CT-QMC hybridization expansion**

**FPLO & LMTO local orbital basis sets**

9x9x2 (MnO) matrices on 3375 k-points
DMFT Impurity Solvers

- **Hubbard I**
  - ✓ Requires little CPU time
  - ✓ Analytic calculation for all frequencies
  - ✓ All temperatures are accessible
  - ✗ No effects of bath / no Kondo physics

- **FLEX; NCA; ICA; ...**

- **Quantum Monte Carlo (Hirsch-Fye)**
  - ✓ Exact solution, within statistical error + imaginary time discretization
  - ✗ Lots of CPU time required
  - ✗ Ergodicity Issues
  - ✗ Low T requires too much CPU time: CPU time goes as $O(T^{-3})$
  - ✗ Requires analytic continuation for $A(\omega)$ on real axis

- **Continuous Time QMC (Hybridization Expansion)**
  - ✓ “Exact” solution, within statistical error
  - ✓ Faster than Hirsch-Fye
  - ✓ Lower temperatures are accessible
  - ✓ No ergodicity issues?
  - ✗ Requires analytic continuation for $A(\omega)$ on real axis
Theoretical extension:
all-electron + DMFT

**LDA+DMFT** Picture of Moment & Volume collapse in MnO:

- Dynamic treatment of correlations
- Non-zero temperature, above $T_N$  
  $(T=1160 \text{ K is used})$

Collaborators on this part:

- Jan Kunes (Univ Augsburg)
- V. I. Anisimov, A. V. Lukoyanov (Yekaterinberg)
- R. T. Scalettar, W. E. Pickett (UCDavis)
MnO: a prototypical Mott Insulator

- Simple crystal structure (NaCl B1; NiAs B8)
- Half-filled d shell: Mn$^{2+}$ => d$^5$: $S = 5/2$, $L = 0$
- Simple AFM ordered ground state
- 3d mixing with 2p bands =>
  deal explicitly with hybridization
- Intrinsically multiorbital system
- Crystal field (non-spherical environment)

Should be a classic (but real!) Mott transition under pressure

\[
\frac{potential}{kinetic} = \frac{U}{W}
\]

ratio by increasing W with pressure

Insulator->metal transition, loss of moment, volume collapse: simultaneous?

- Complications due to multiorbital aspects; crystal fields?
Experimental Observations

- J.R. Patterson et al., PRB 2004: Mott insulator to metal transition at ~100 GPa
- C.S. Yoo et al., PRL 2005 => B1-B8 transition at 90-100 GPa. Mott transition concurrent with moment, volume collapse at 110 GPa
- Y. Mita et al., PRB 2005 => metallization at 94 GPa
Moment & Isostructural Volume Collapse

Isostructural (NaCl-NiAs)in 90-110 GPa region, 6.6% volume collapse @110 GPa.

XES - Loss of moment @ 103 ± 5 GPa

Pressure-induced Mott transition: I-M; moment, volume collapse. [C. S. Yoo et al., PRL 2005]
Spectral density at ambient pressure: LDA+DMFT

XPS/BIS (van Elp et al. *PRB* 44, 1530 (1991)) vs Mn 3d spectral density: ($U=6.9$ eV, $J=0.86$ eV)

Reproduces exptl data at zero pressure (note: no matrix elements were included).
Pressure induced metallization

Hirsch-Fye QMC “local solver”
Pressure induced metallization

![Graph showing spectral density and energy (eV)](image)

![Inset graphs showing magnetic moment and orbital occupancy](image)
Pressure induced metallization
Pressure induced metallization

![Graph showing spectral density and magnetic moment vs. V/V₀](image)
Pressure induced metallization

![Graph showing spectral density and orbital occupancy vs. energy.](image)

- Black line: $e_g$
- Red line: $t_{2g}$

![Graph showing magnetic moment vs. ratio $V/V_0$.](image)

- LS
- HS
- $M_s$
- $M_{off}$

![Graph showing orbital occupancy vs. ratio $V/V_0$.](image)

- $t_{2g}$
- $e_g$
Pressure induced metallization

Correlation effects weaker in LS state (bold lines: LDA)

Much of the structure is due to the LDA spectrum, correlation effects become milder (still important)
Mott transition in MnO: unconventional mechanism

Increase in $\Delta_{cf}$ under pressure overwhelms $J_H$.
• moment collapse,
• then metallization

Verified by
• varying $J_H$
• varying $U$
Mott transition in MnO: unconventional mechanism

Increase in $\Delta_{cf}$ under pressure overwhelms $J_H$.
• moment collapse,
• then metallization

Verified by
• varying $J_H$
• varying $U$
\[ E_{tot} = E_{LDA} + (E_{DMFT} - E_{HF}) \]

Volume collapse $\sim 120$ GPa

\[ P = -\frac{dE}{dV} \]
Summary: MnO under pressure

- Total energy calculation requires additional ansatz for the energy functional. Outcome:
  - $E - V$ is not convex $\Rightarrow$ volume collapse, due to moment collapse
  - transition pressure $p_c \sim 120$ GPa (expt: $p_c \sim 105$ GPa)

The **Mott transition in MnO** is controlled by competition between Hund’s coupling and crystal-field splitting -- not by band broadening under pressure.
**Theoretical extension:**

*all-electron + DMFT*

**LDA+DMFT Picture of Moment & Volume collapse in FeO**

- Dynamic treatment of correlations
- Non-zero temperature, above $T_N$

No equation of state, however.

**Calculation from:**

Shorikov, Pchelkina, Anisimov, Skornyakov, Korotin, arXiv:1007.4650
Elemental Yb: valence transition under pressure

- Yb Experimental Knowledge
- LDA(+U) Failure
- LMTO-LDA+DMFT
  - Impurity Solvers / QMC and HI
  - DMFT results for Yb
  - Valence / Spectrum
- FPLO+DMFT Implementation
  - Self-energy pole expansion
  - Double counting
  - Charge self-consistency
- Conclusion

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Yb Facts: variable $f^{13}, f^{14}$ character

- Anomalously large volume at $P=0$
- 3x larger thermal expansion than other rare earths

- Gradual valence transition under pressure
  - Begins divalent, but nearly trivalent at 35 GPa
  - Transition robust across crystalline phase boundaries

- Transition appears less robust at lower $T$
- Intermediate state is mixture of $f^{13} + f^{14}$ states.

Syassen et al. PRB 26, 4745 (1982)
LDA (also LDA+U) is unable to describe valence transition

- Failure to produce Hubbard bands
- LDA(+U) can’t give mixture of $f^{13}$ and $f^{14}$ states

- No valence transition
FPLO Code
Koepernik and Eschrig

- Full potential, all-electron
- Local orbital basis set
- Efficient basis set
  - Yb : (5s5p) / 6s6p5d4f + polarization orbitals
- Hamiltonian: 40 x 40, Self-energy: 14 x 14
- Matrix inversion at every Matsubara frequency
Yb Valence Transition: LDA+DMFT describes it successfully

- HI and QMC agree quantitatively at large V
  - HI gives qualitative behavior
- Imaginary time discretization error ≈ charge self-consistent error
- L=80 points 9100 CPU-hours each
- Temp dependence follows experimental data (YbAgCu₄ and YbAl₃)


Convergence behavior
Temperature dependence
Yb Spectrum

- Many body state
  \[ \alpha f^{14} + \beta f^{13} \]
  is apparent

- Lower/upper Hubbard bands gradually gain/lose weight

- Non-integral weights
  \[ f^{14} \] spectral weights


Yb: charge fluctuations in the 4f shell

Equal-time charge fluctuations

$$\langle \delta n_f^2 \rangle = \langle n_f^2 \rangle - \langle n_f \rangle^2$$

Correlated charge fluctuations (susceptibility)

Local susceptibility $$\chi^{(1)} = \partial \langle n_f \rangle / \partial V_i$$

![Graphs showing charge fluctuations](image)
Yb: charge fluctuations in the 4f shell

\[ \langle \delta n_f^2 \rangle = \langle n_f^2 \rangle - \langle n_f \rangle^2 \]

Local susceptibility \( \chi^{(1)} = \partial \langle n_f \rangle / \partial V_i \)
Yb: charge fluctuations in the 4f shell

\[ \langle \delta n_f^2 \rangle = \langle n_f^2 \rangle - \langle n_f \rangle^2 \]

Local susceptibility \( \chi^{(1)} = \partial \langle n_f \rangle / \partial V_i \)
Summary: MnO & FeO MIT; Yb valence transition

- Inclusion of local dynamic correlations can lead to qualitatively different physics compared to static methods.
- DMFT can capture spectral weight transfers without band shifts.
- Real systems with multiple bands provide many different possibilities to realize Mott insulator and metal-insulator transition (MnO, FeO, …).
- Two-particle response functions in DMFT are not simple convolutions of single-particle ones, e.g. different spin and charge gaps, crystal-field excitations in Mott insulators, fluctuating valence states.
NiO: Phonons in LSDA vs. LDA+DMFT

Solid circles – theory, open circles – exp. *(Roy et.al, 1976)*

*(Savrasov, Kotliar, PRL 2003)*
Phonons in δ-Pu

<table>
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<th>$C_{11}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C'$ (GPa)</th>
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<td>Theory</td>
<td>34.56</td>
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<td>26.81</td>
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<td>Experiment</td>
<td>36.28</td>
<td>33.59</td>
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(Dai, Savrasov, Kotliar, Ledbetter, Migliori, Abrahams, Science, 9 May 2003)
(experiments from Wong et.al, Science, 22 August 2003)
Limitations: challenges for the future

“LDA+DMFT” calculates;
- one-electron spectrum, gap: insulating vs. metallic
- orbital occupation, including (rms) spin moment
- fluctuations; local susceptibility

“LDA+DMFT” doesn’t calculate much more (yet)

Challenges are:
- free energies: EOS, phase diagrams
- forces: phonons, atomic dynamics
- linear response: susceptibilities, correlations
- LRO: order parameters, phase transitions
- all the other things DFT-based methods are doing
A well formulated functional forms the basis of DFT and its extensions.

Challenge #1: thermodynamic grand potential
I.e. a robust free energy functional:
- formulation: approximate, then minimize
- double counting issues (an LDA++ issue)
- entropy: electronic, magnetic, lattice
- numerous details: U & J; full $U_{ijkl}$?
- specific choice of the local orbitals

Formalism:
Electronic structure calculations with DMFT.
Kotliar, Savrasov, Haule, Oudovenko, Parcollet, Marianetti, RMP 2006
...many other papers, rarely starting at the free energy functional level
Energy Functional #1: McMahan et al.
strongly correlated $U_f$ + moderately correlated $LDA$

DMFT functional: McMahan, KH, RTS: PRB 72, 115125 (2005)

$$E_{McM} = E_{LDA} + [E_{DMFT} - E_{mLDA}] = E_{LDA} + \Delta E_{McM}$$

$$\Delta E_{McM} = Tr[H_k\{G(\Sigma_{DMFT}) - G(\Sigma_{mLDA})\}] \quad \text{K.E.}$$

$$+ \frac{1}{2} Tr[\Sigma \tilde{G}(\Sigma_{DMFT}) - \frac{1}{2} Tr[\Sigma_{mLDA}G(\Sigma_{mLDA})] \quad \text{P.E.}$$

$$\rightarrow Tr[H_k\{G(\Sigma_{DMFT}) - G(\Sigma_{mLDA})\}]$$

$$+ \frac{1}{2} \sum_{ms \neq m's'} U^f_{mm'}[\langle n_m s n_{m'} s' \rangle - \langle n_m s \rangle \langle n_{m'} s' \rangle]$$

$$\Sigma_{mLDA} = U_f(n_f - \frac{1}{2}) \quad \{mLDA \equiv \text{model LDA}\}$$

For reference: the density-functional functional is

$$E_{LDA}[\rho] = (T_0[\rho] + Tr[v_{ext\rho}]) + E_{hxc}[\rho]$$

$$= (Tr[\epsilon_k f_k] - Tr[v_{hxc\rho}]) + E_{hxc}[\rho]$$
Challenge #2

charge self-consistency
Ground-state density, Kohn-Sham Hamiltonian and DFT total energy.

Yes

Converged?

No

Calculation Bath function $G_0(T)$ from $H$ and $\Sigma(\omega)$

Impurity Solver
Calculates new self-energy

Converged?

No

Calculate new density, compare with old

Yes

DFT-LDA Loop

Converged?

Guess initial Density $n(r)$

Potential $v(r)$

Construct KS Hamiltonian

Calculate New Density

Solve for Wavefunctions

Done with DFT. Ground-state density, Kohn-Sham Hamiltonian and DFT total energy.

Charge Self-Consistency

DMFT Loop

Current self-energy $\Sigma(\omega)$
(Lack of) charge self-consistency

MnO EOS seems impressive:
Mn$^{2+}$, O$^{2-}$ ions independent of volume.
Change of density with pressure was minor.

Yb EOS (not shown) was poor:
valence transition $\rightarrow$
change in occupation of s-d bonding electrons
Challenge #3
restore k-dependence to $\Sigma(k,\omega)$: essential

Challenge #4
calculate ordered phases, phase transitions, ...

..................

Challenge #N
dynamical linear response functions; forces, AIMD for correlated materials; etc etc etc
LDA+DMFT is not the holy grail.

It is a promising path toward a full treatment of dynamical interactions and strong correlations in materials with open d- and f-shells. Check back in 2021.