The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2220-15

15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

13 - 15 January 2011

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

Warren Pickett
University of California, Davis
USA

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

Critical Overview of All-Electron LDA+DMFT

Mott transitions, Valence transition: what's left?

Warren Pickett, UCDavis

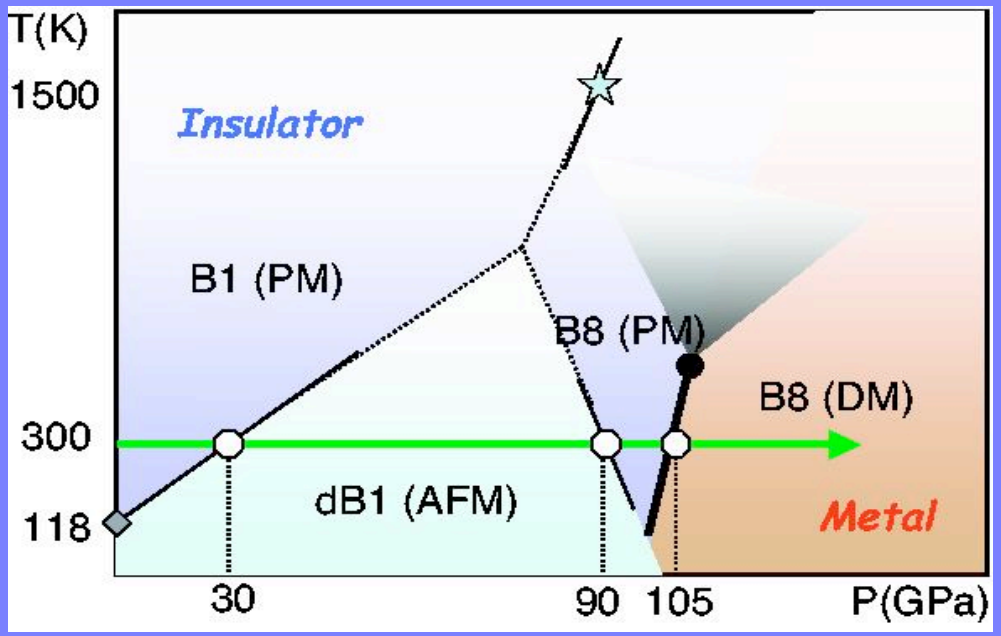
Acknowledgments

Jan Kunes
UCDavis
University of Augsburg
Czech Academy of Sciences

Erik Ylvisaker

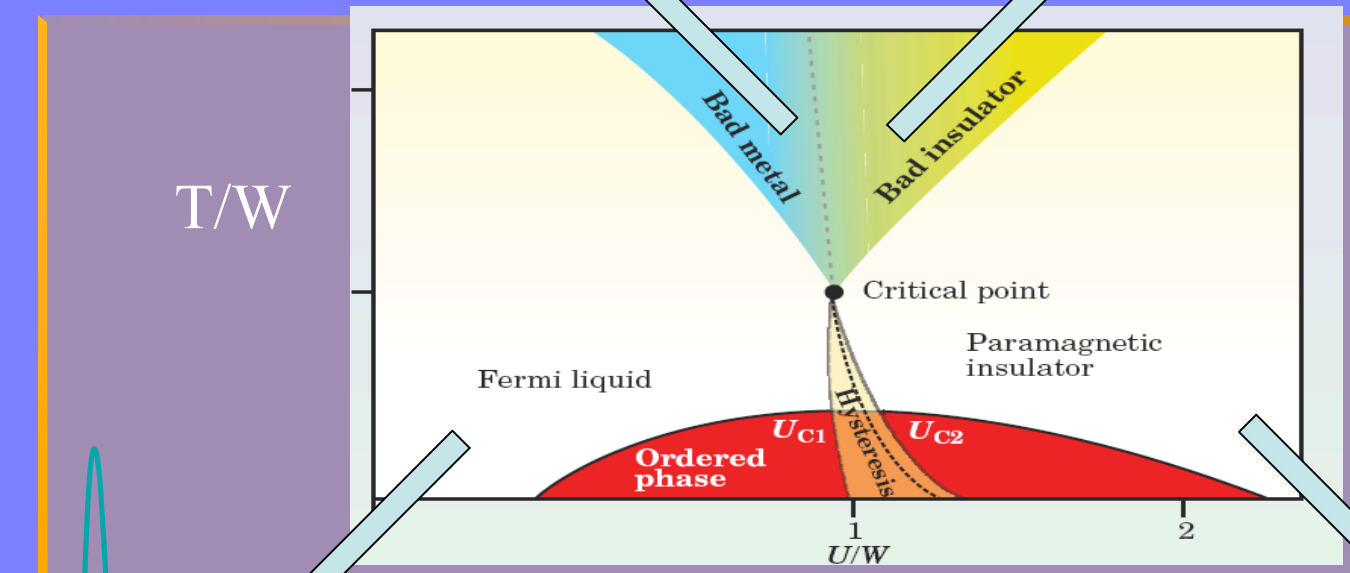
Richard Scaletter
UC Davis

Andrew McMahan
LLNL



Acknowledgement:
DOE BES support
DOE's SciDAC program

COHERENCE-INCOHERENCE CROSSOVER



Phase diagram of a Hubbard model with partial frustration at integer filling. *M. Rozenberg et.al.*, Phys. Rev. Lett. 75, 105-108 (1995).

Mott transition: spectral evolution as a function of U/W

metal

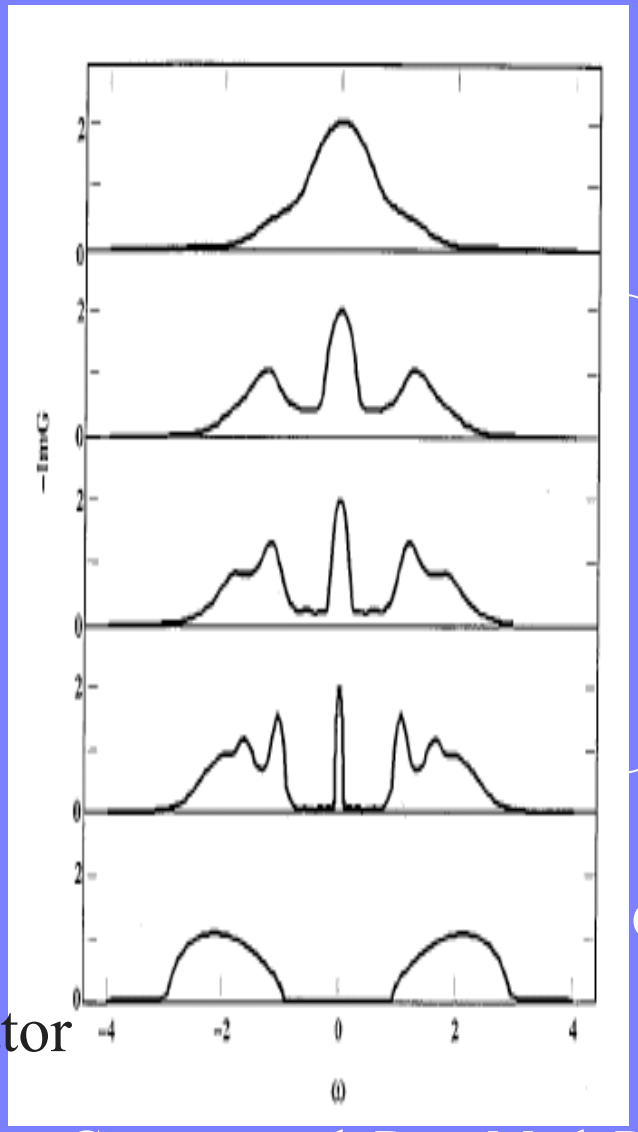
Mott, Hubbard (and others), 50-60 years ago

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

OK, not so simple. Other energy scales enter the problem:
* Hunds coupling J_H
* crystal field splitting Δ
* multiple bands: "orbital selection"

Transition metal monoxides are the "classic case": unsolved

insulator



Can use LDA

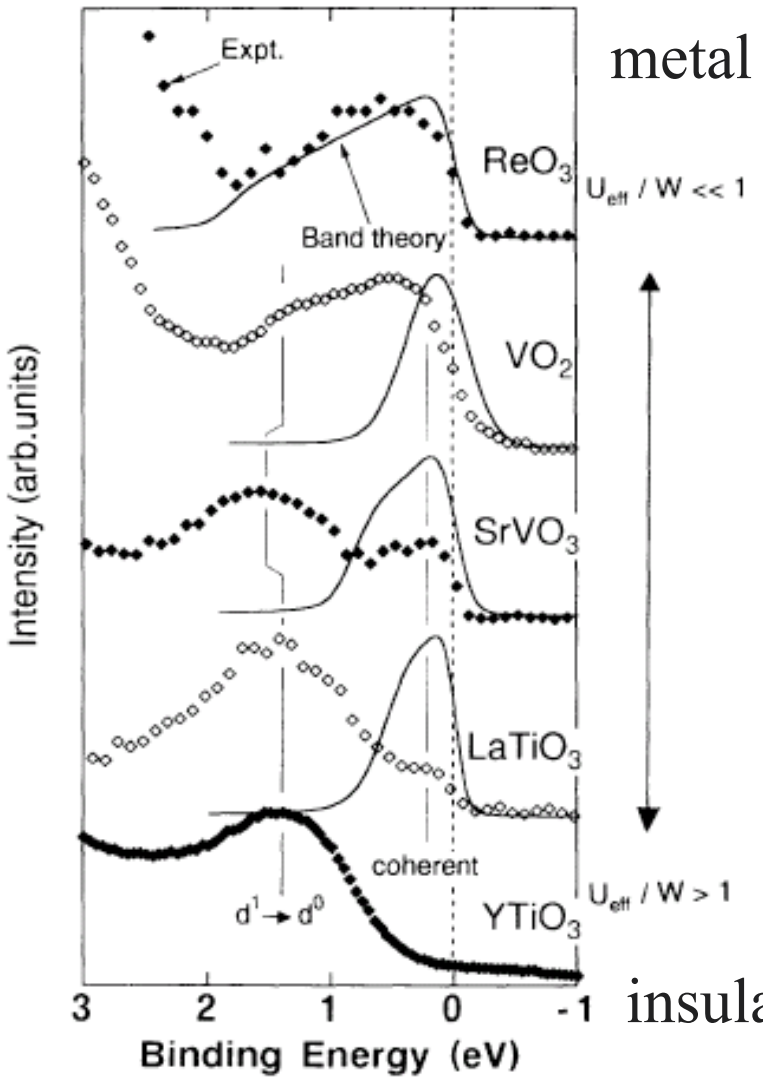
Difficult to treat within one-particle theory

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



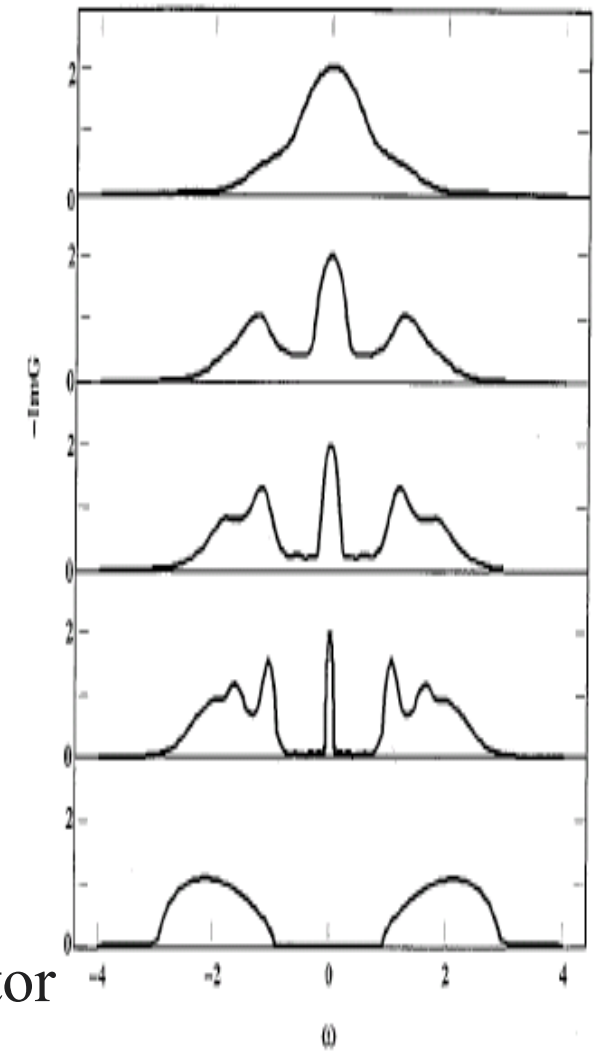
metal

U_{eff} / W << 1

U_{eff} / W > 1

insulator

Fujimori PRL 69, 1796 (1992)



Can use LDA

Difficult to treat within one-particle theory

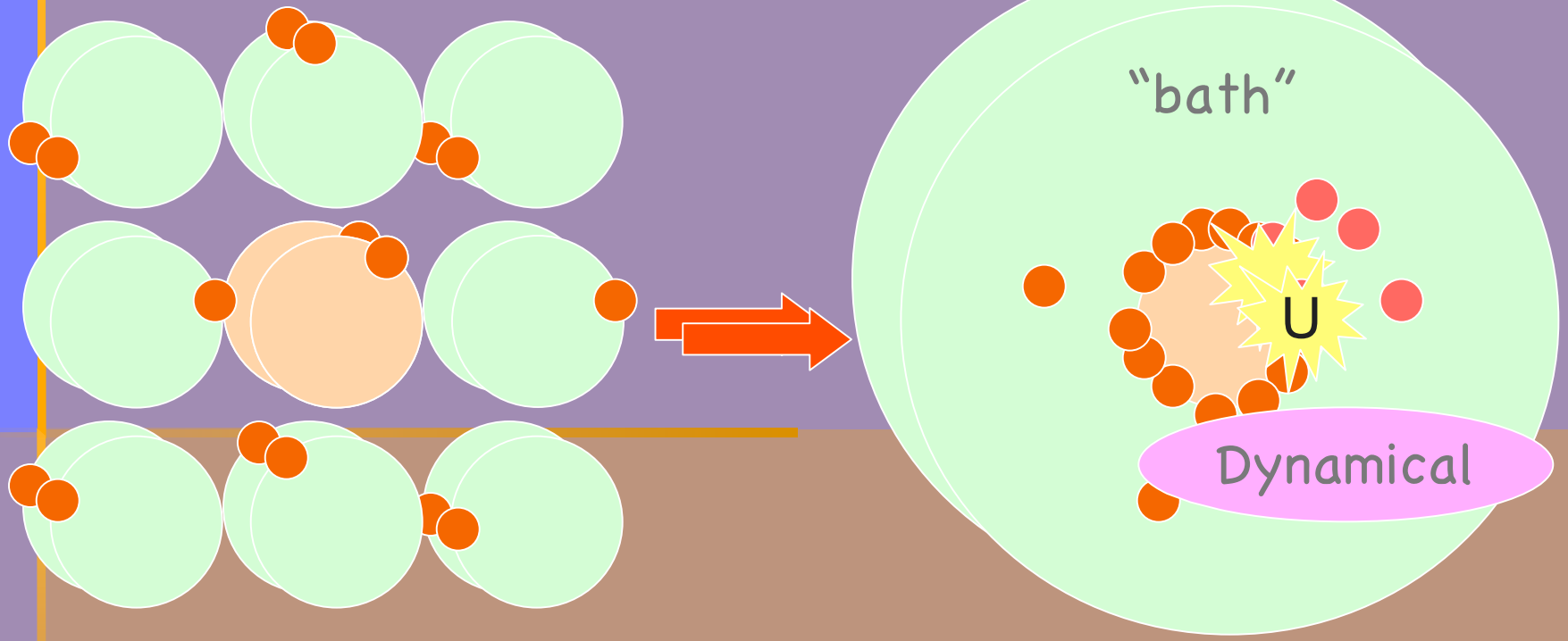
Can use LDA+U

Georges et al Rev. Mod. Phys.1996

(Dynamical Mean-Field Theory)

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))

$\longrightarrow \quad \Sigma_{jj'}(\omega)$

To treat systems with strong on-site correlations: in LDA+DMFT (analogy to LDA+U): original form

$$H = \sum_{im\sigma}^{all} H^{LDA}_{im,i'm'} c^{+}_{im\sigma} c_{i'm'\sigma}$$

$$+ \frac{1}{2} \sum_{imm'\sigma}^{correl.} U^{i}_{mm'} n_{im\sigma} n_{im'-\sigma}$$

$$+ \frac{1}{2} \sum_{im\neq m'\sigma}^{correl.} (U^{i}_{mm'} - J^{i}_{mm'}) n_{im\sigma} n_{im'\sigma}$$

$$- \sum_{im\sigma}^{correl.} H^{doublecounting}_{im,i'm'} c^{+}_{im\sigma} c_{i'm'\sigma}$$

LDA band structure (K-S Hamiltonian)

U, J from Constrained DFT

Double-counting term

Anisimov *et al,* J. Phys. Condens. Matter 9, 7359 (1997) (LDA+U, LDA+DMFT)
Lichtenstein and Katsnelson, PRB 57, 6884 (1998) (LDA+DMFT)

LDA $\Rightarrow$ Wannier projection: $\mathcal{H}_{\mathrm{LDA}}(\boldsymbol{k})$

$\Rightarrow$ constrained LDA: $\boldsymbol{U}_{ij}, \boldsymbol{J}_{ij}$

$\Rightarrow$ double counting : $\mathcal{H}_0(\boldsymbol{k}) = \mathcal{H}_{\mathrm{LDA}}(\boldsymbol{k}) - E_{dc} n_{\mathrm{d}}$

$\mathcal{H} = \Sigma_{\boldsymbol{k}} \mathcal{H}_0(\boldsymbol{k}) + \Sigma_{\boldsymbol{R}} \boldsymbol{U}_{ij} n_{\boldsymbol{R}i} n_{\boldsymbol{R}\mathrm{j}}$

FPLO & LMTO
local orbital basis sets

9x9x2 (MnO) matrices on 3375 k-points

DMFT

Find chem. potential
Compute local propagator

$G_{dd}(i\omega_n)$

$\Sigma(i\omega_n)$

Construct impurity problem
FT: $\omega_n \rightarrow \tau$

invFT: $\tau \rightarrow \omega_n$
Compute Σ

$\mathcal{G}(\tau)$, $\mathbf{U}_{ij}$

solve impurity problem

$G_{dd}(\tau)$

Hirsch-Fye QMC
CT-QMC hybridization expansion

MaxEnt

One- and two-particle
quantities on real axis

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; 1CA; …**
- **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(ω) 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(ω) on real axis

Theoretical extension:
all-electron + DMFT

DMFT: Metzner & Vollhardt, 1898 for Hubbard model
Reviews: Georges et al., RMP 1994
Kotliar, Savrasov, et al., papers in 2005-2007
……

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

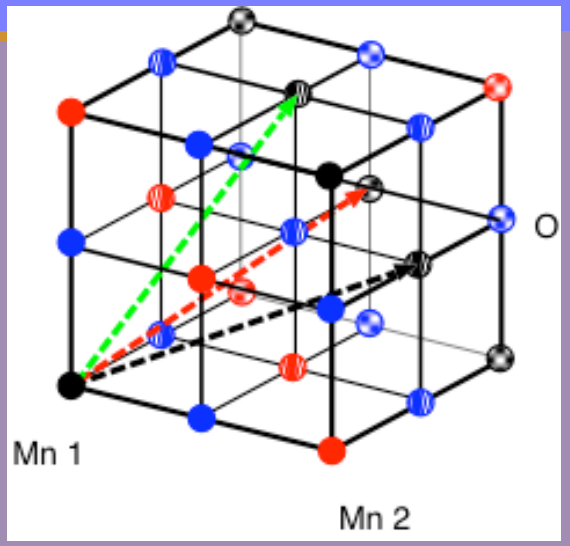
- **Dynamic treatment of correlations**
- **Non-zero temperature, above T_N** **(T=1160 K is used)**

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

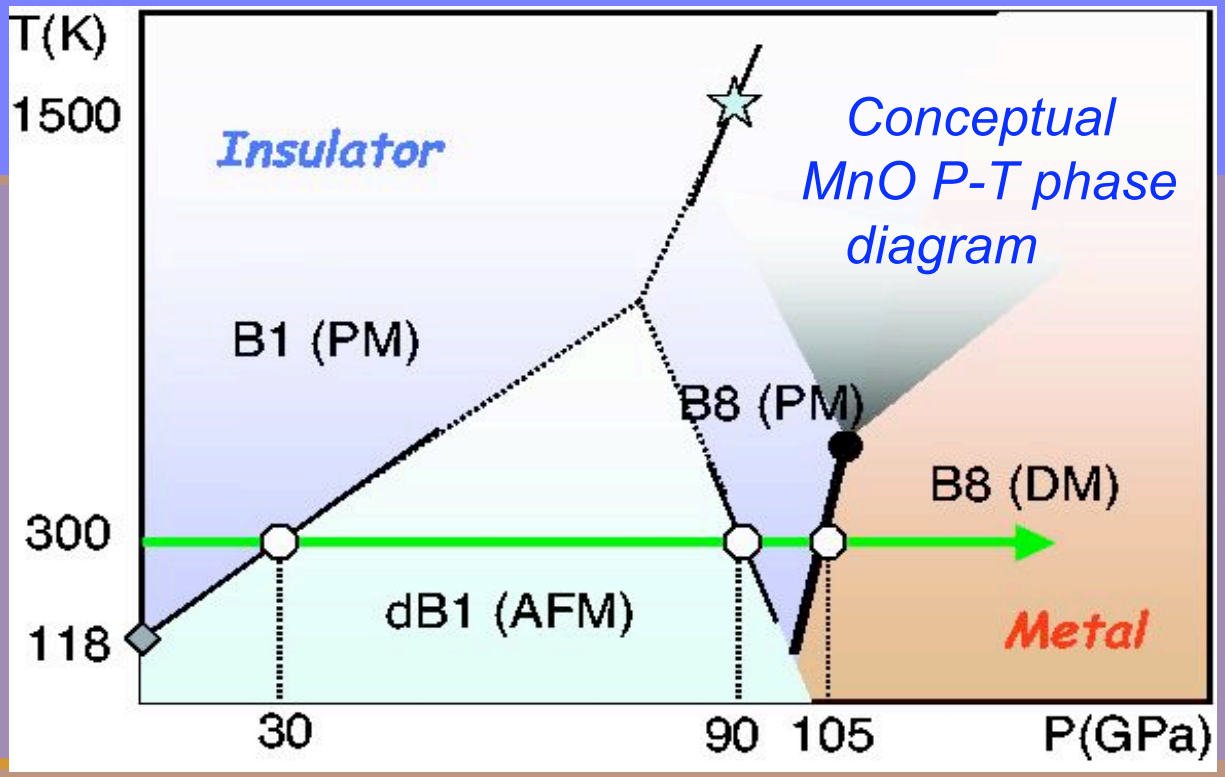
Vary $\frac{potential}{kinetic} = \frac{U}{W}$ ratio by increasing W with pressure

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

- Complications due to multiorbital aspects; crystal fields?

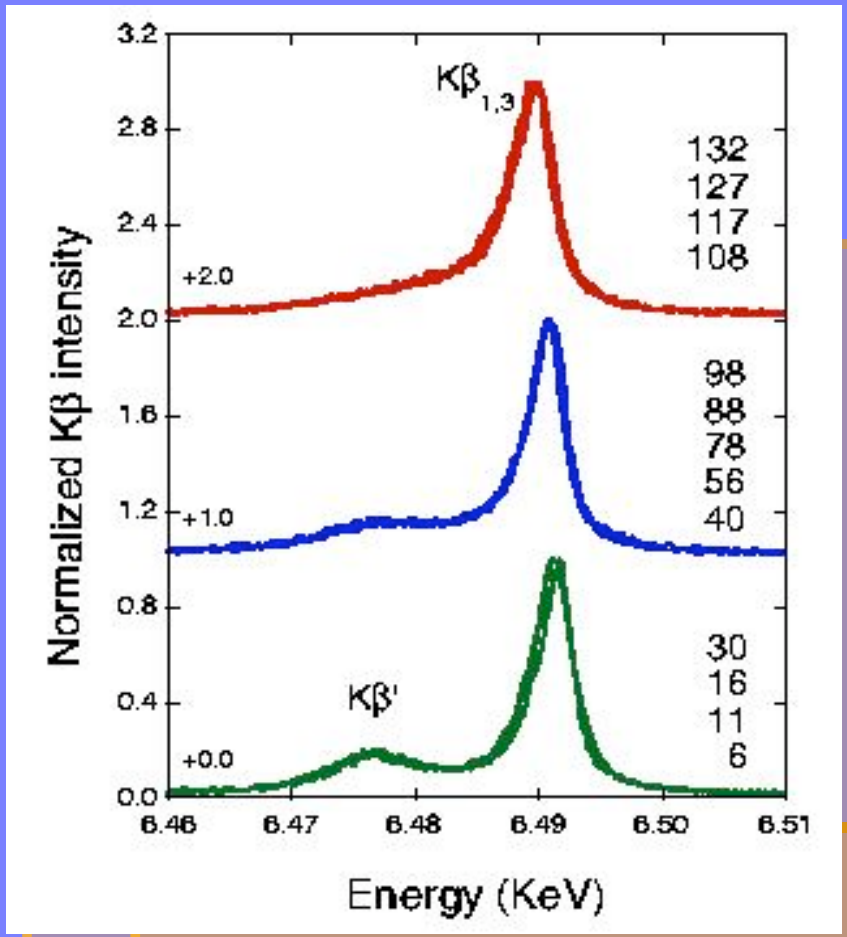
Experimental Observations

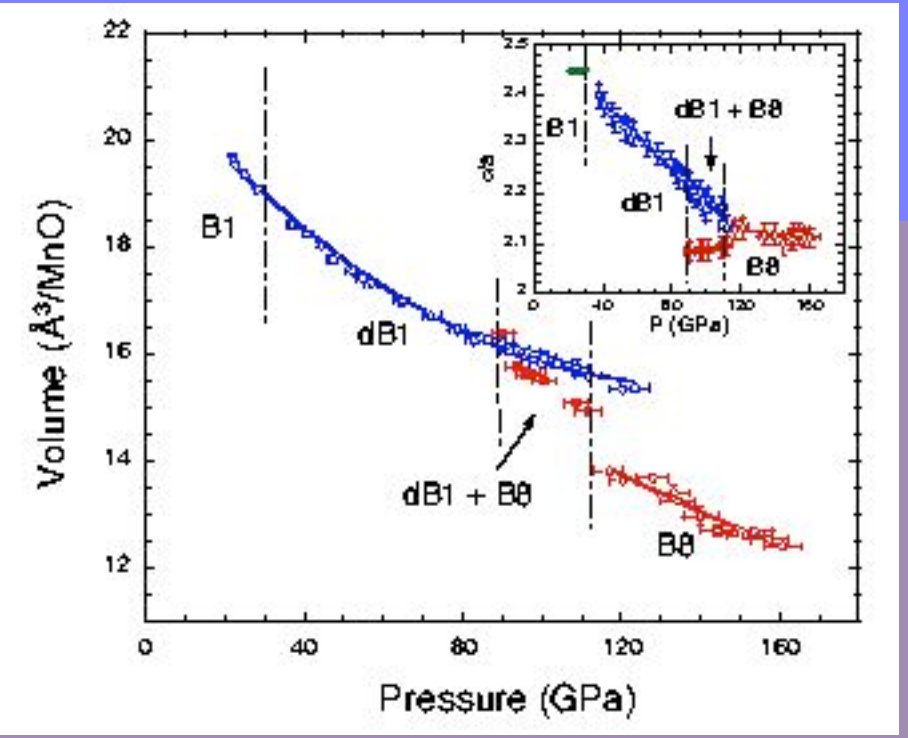
Mott transition under pressure has been observed in MnO!



- 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]

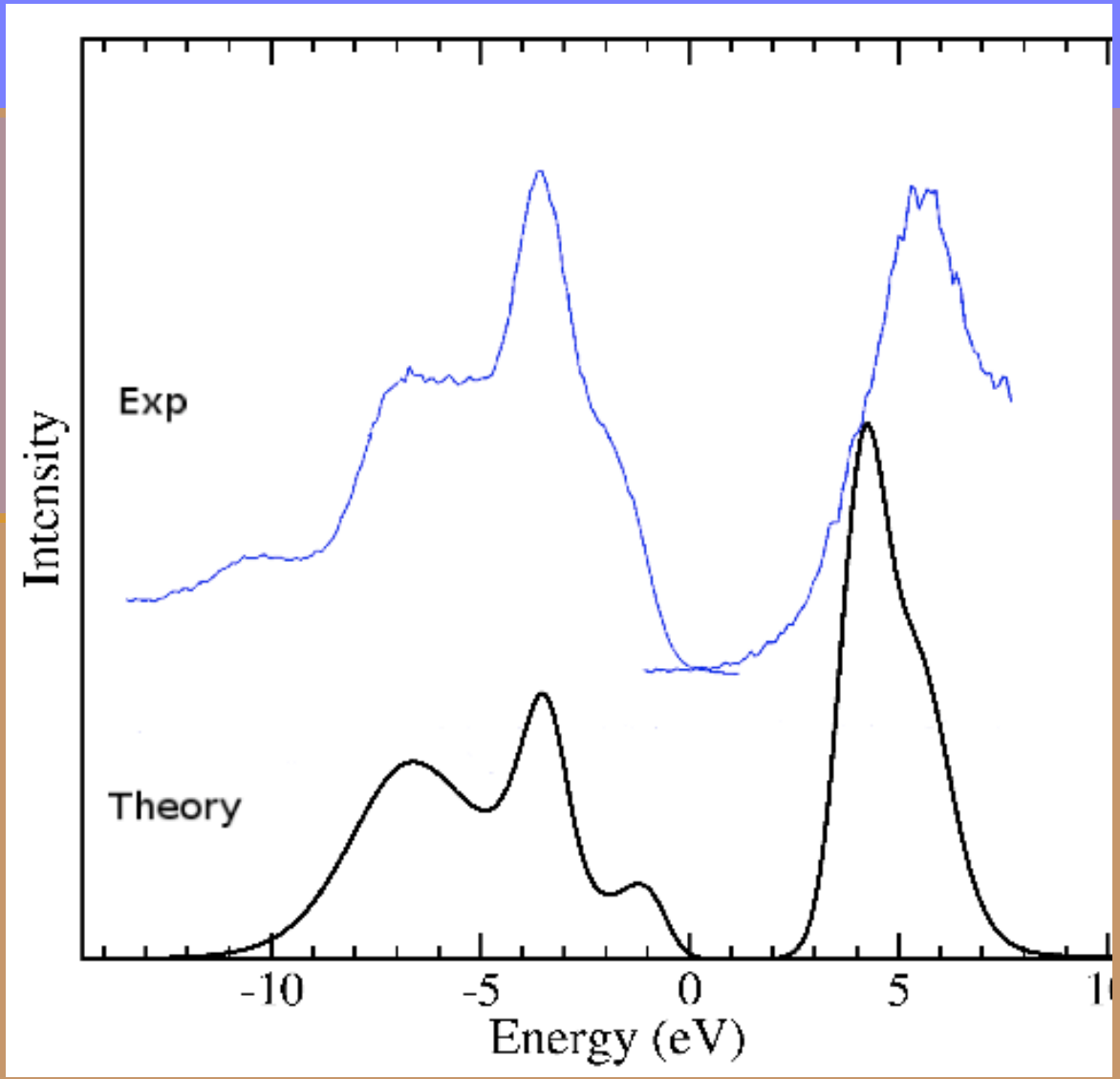
Spectral density at ambient pressure: LDA+DMFT

XPS/BIS (*van Elp et al. PRB* ***44****, 1530 (1991)*)

vs

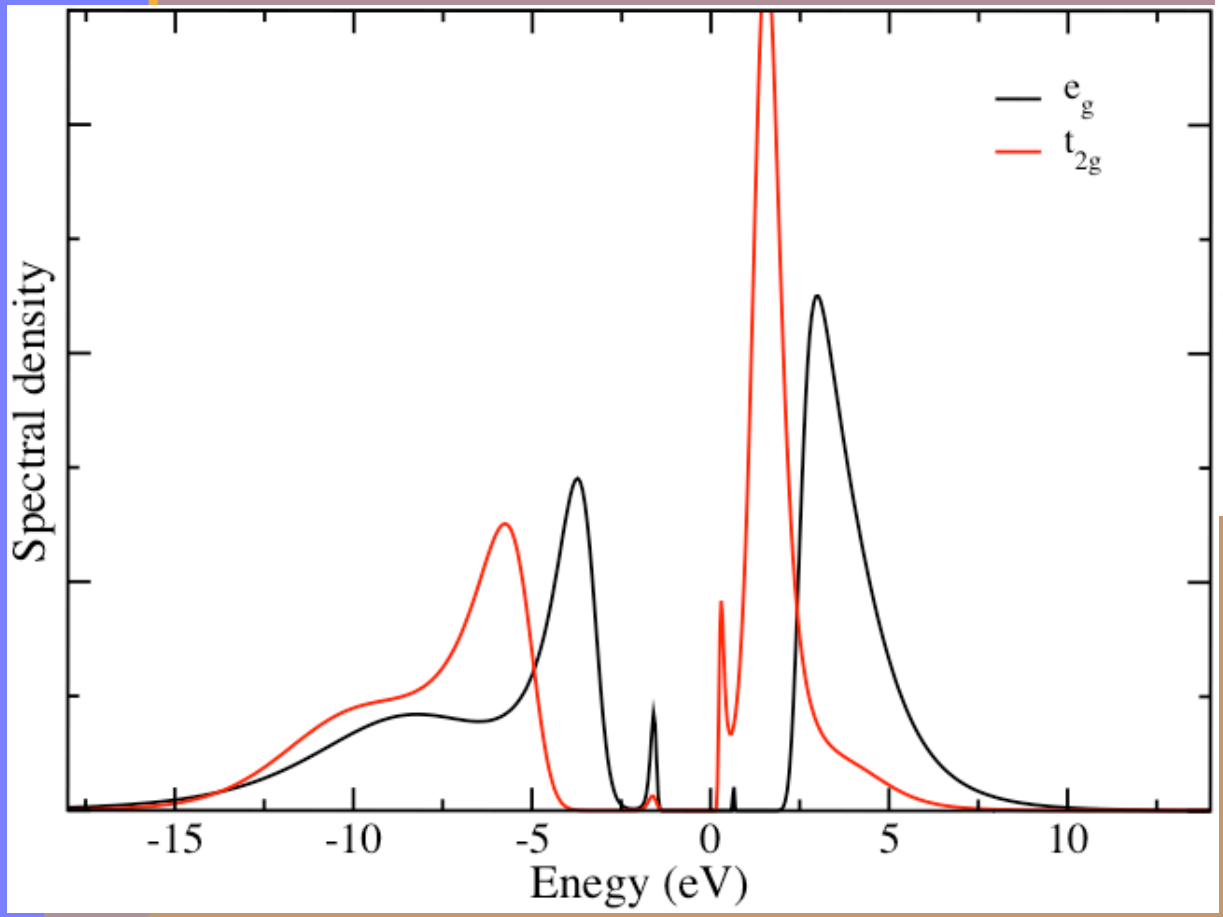
Mn *3d* spectral density:
(*U*=6.9 eV, *J*=0.86 eV)

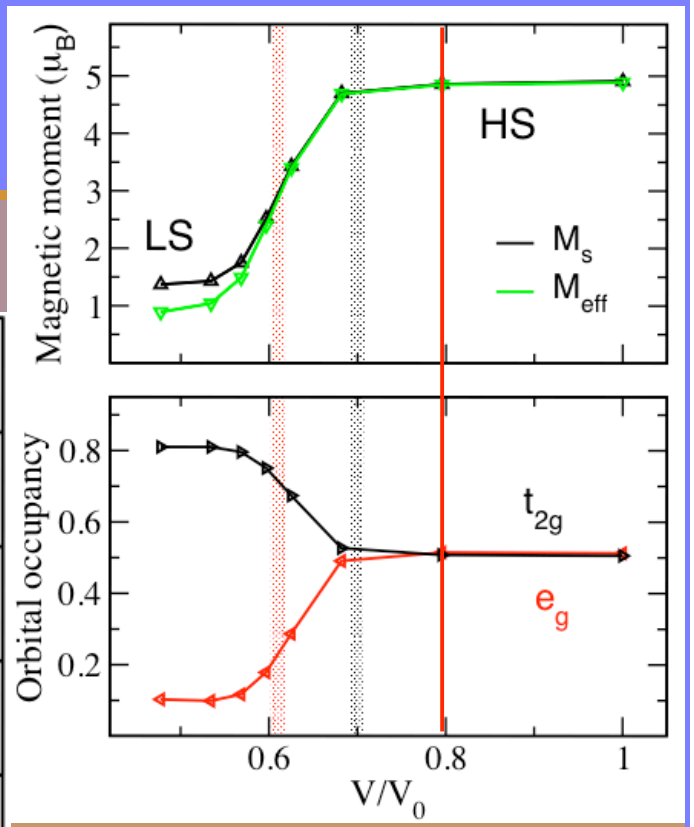
Reproduces exptl data at zero pressure (note: no matrix elements were included).



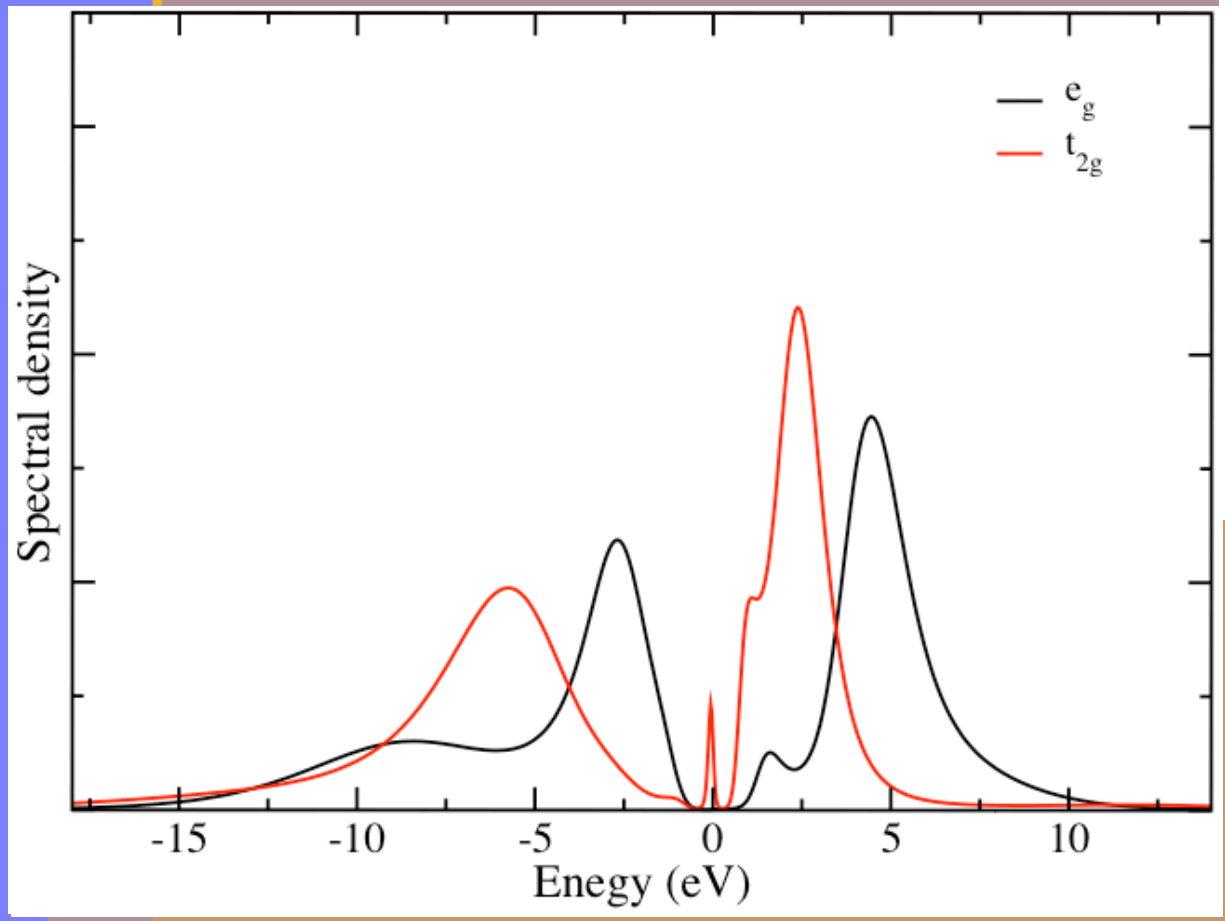
Pressure induced metallization

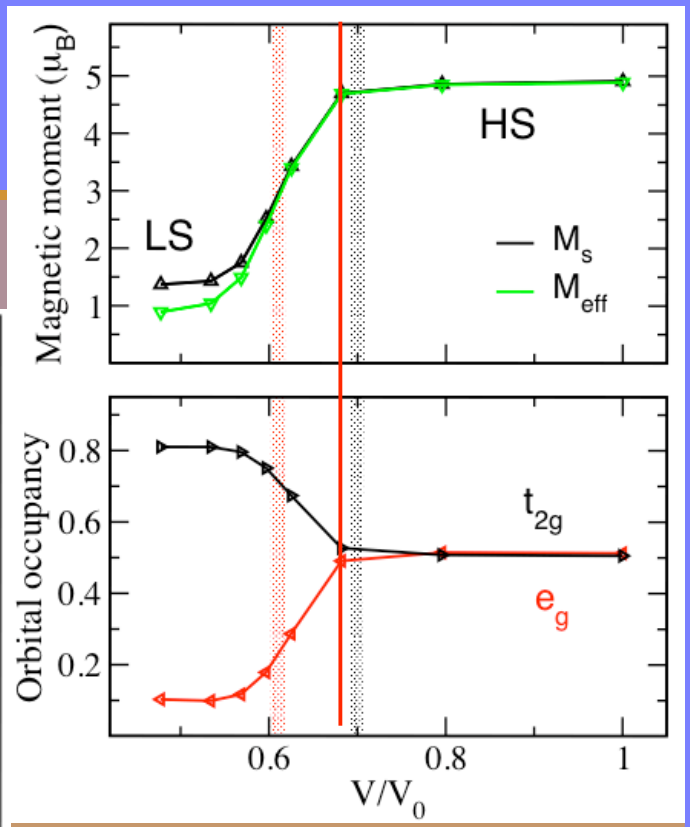
Hirsch-Fye QMC "local solver"



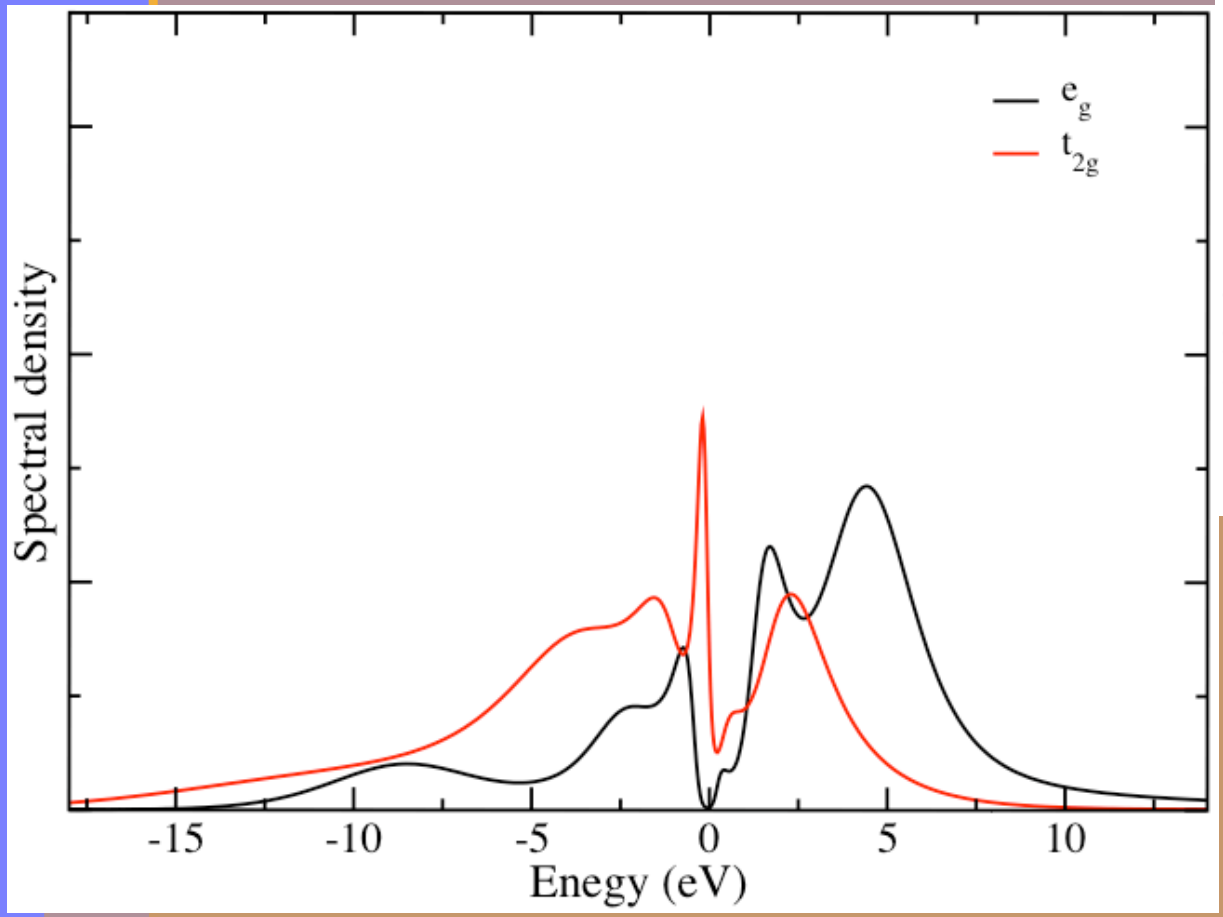


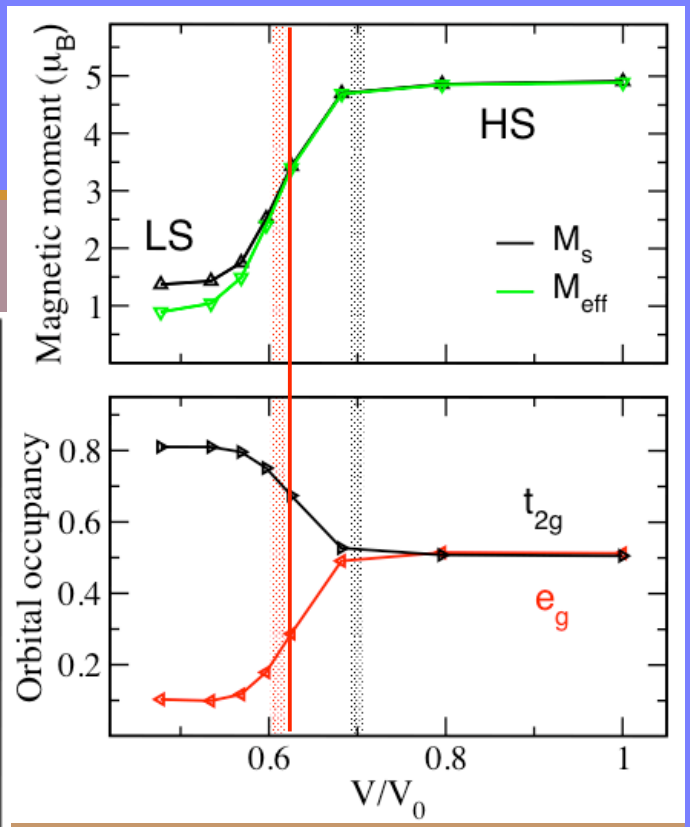
Pressure induced metallization



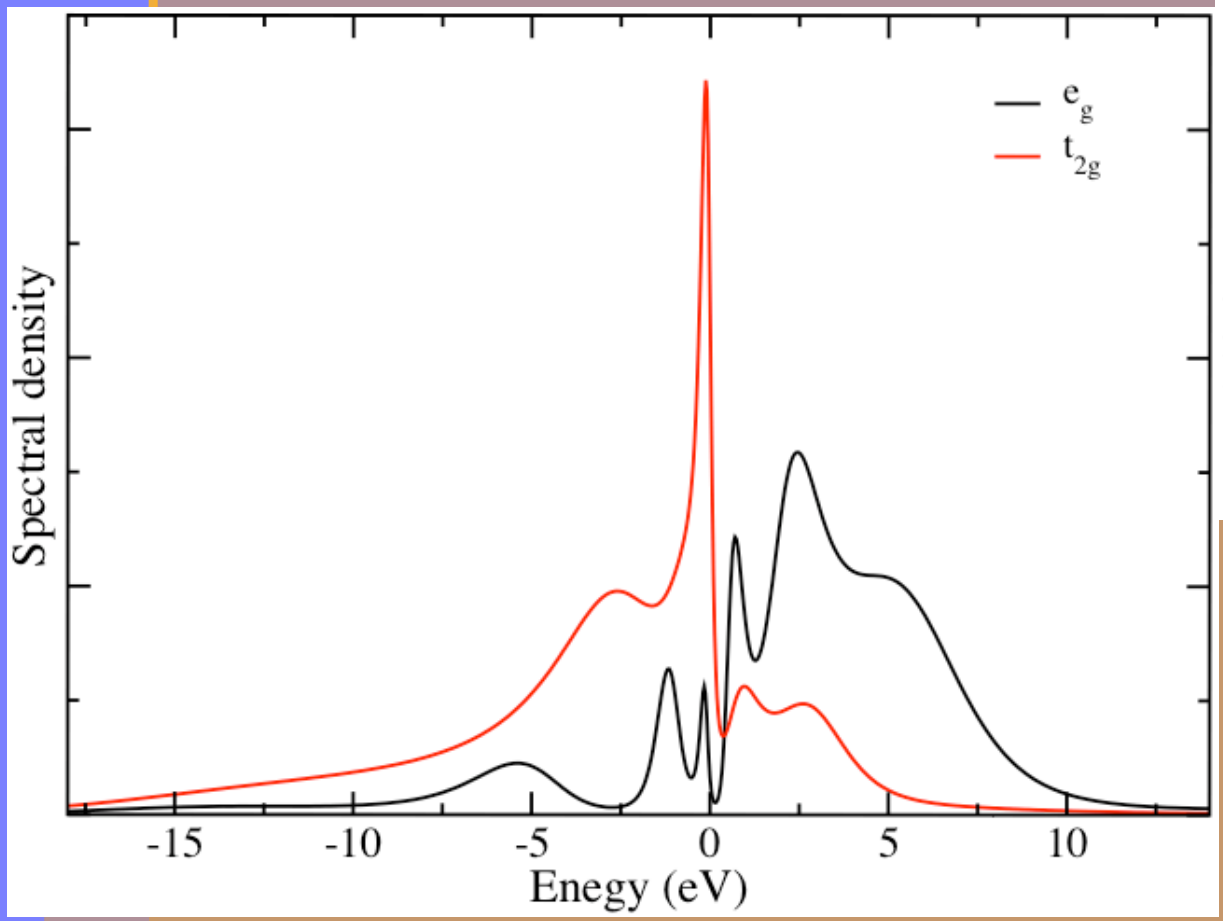


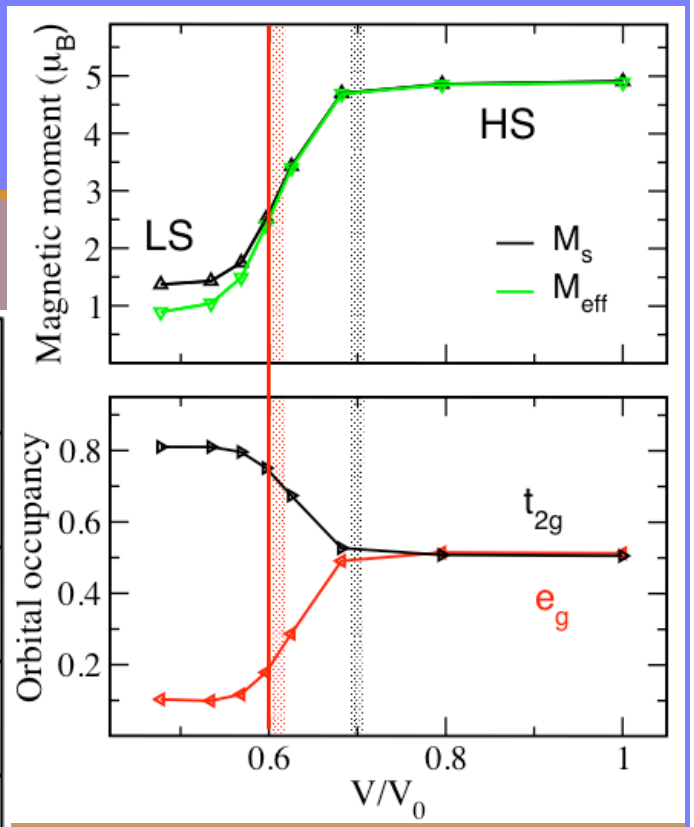
Pressure induced metallization



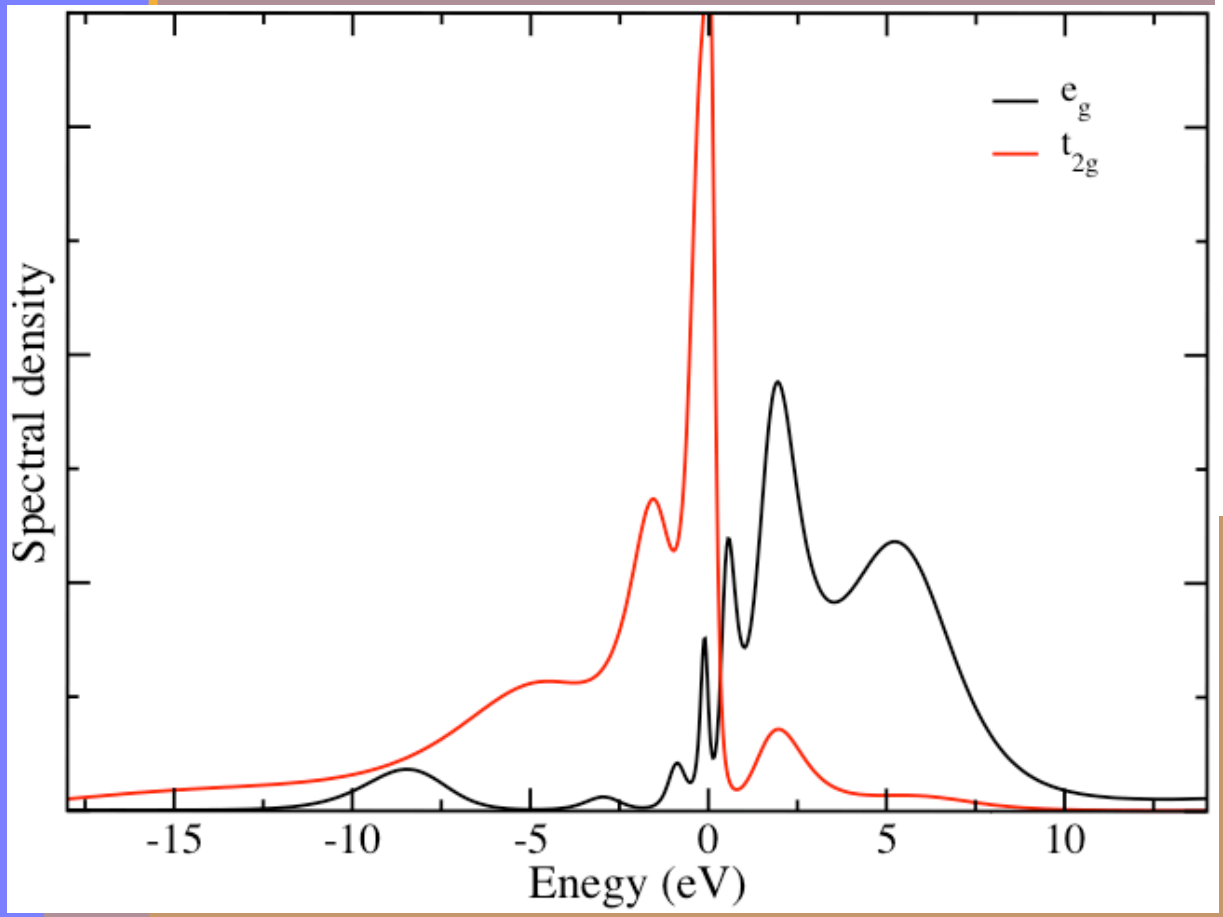


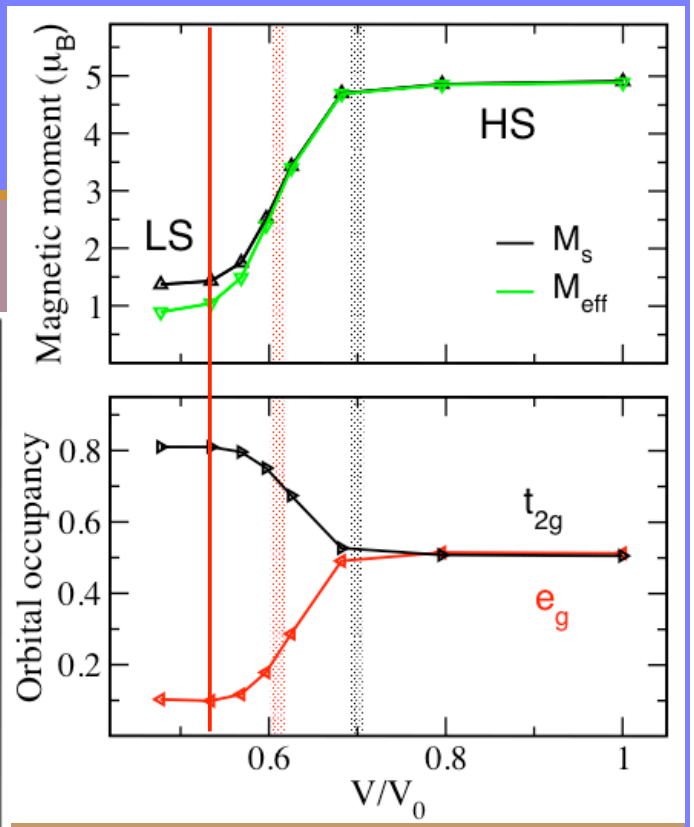
Pressure induced metallization





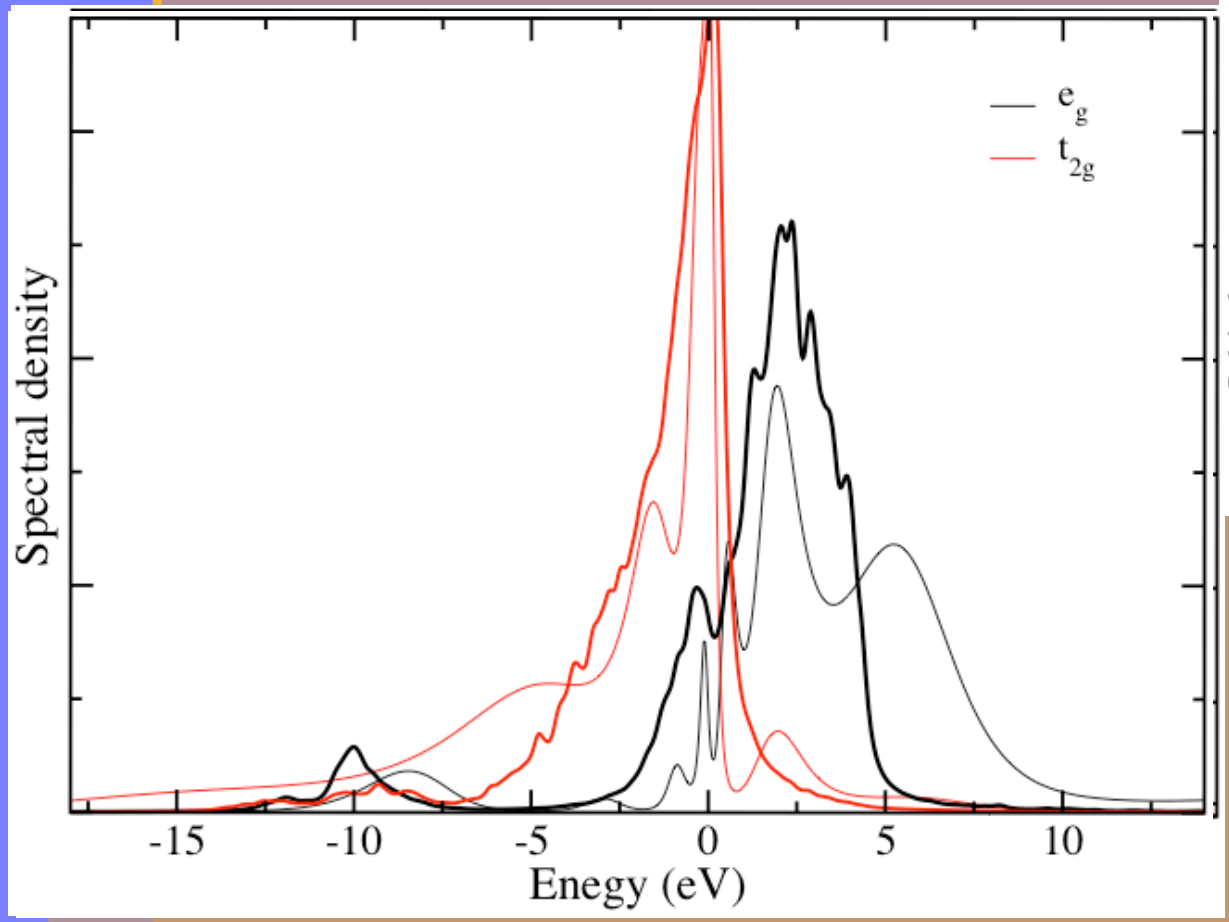
Pressure induced metallization

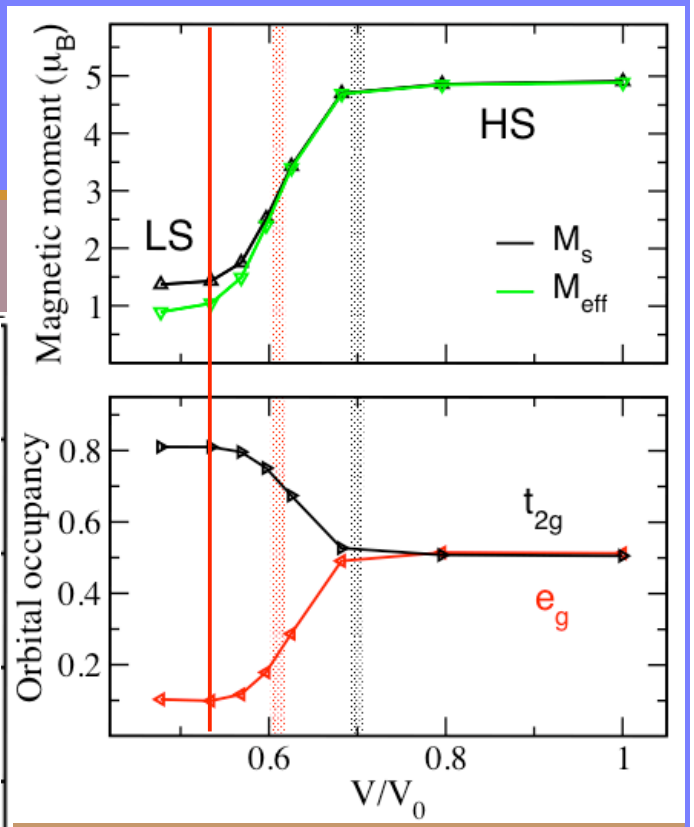




Pressure induced metallization

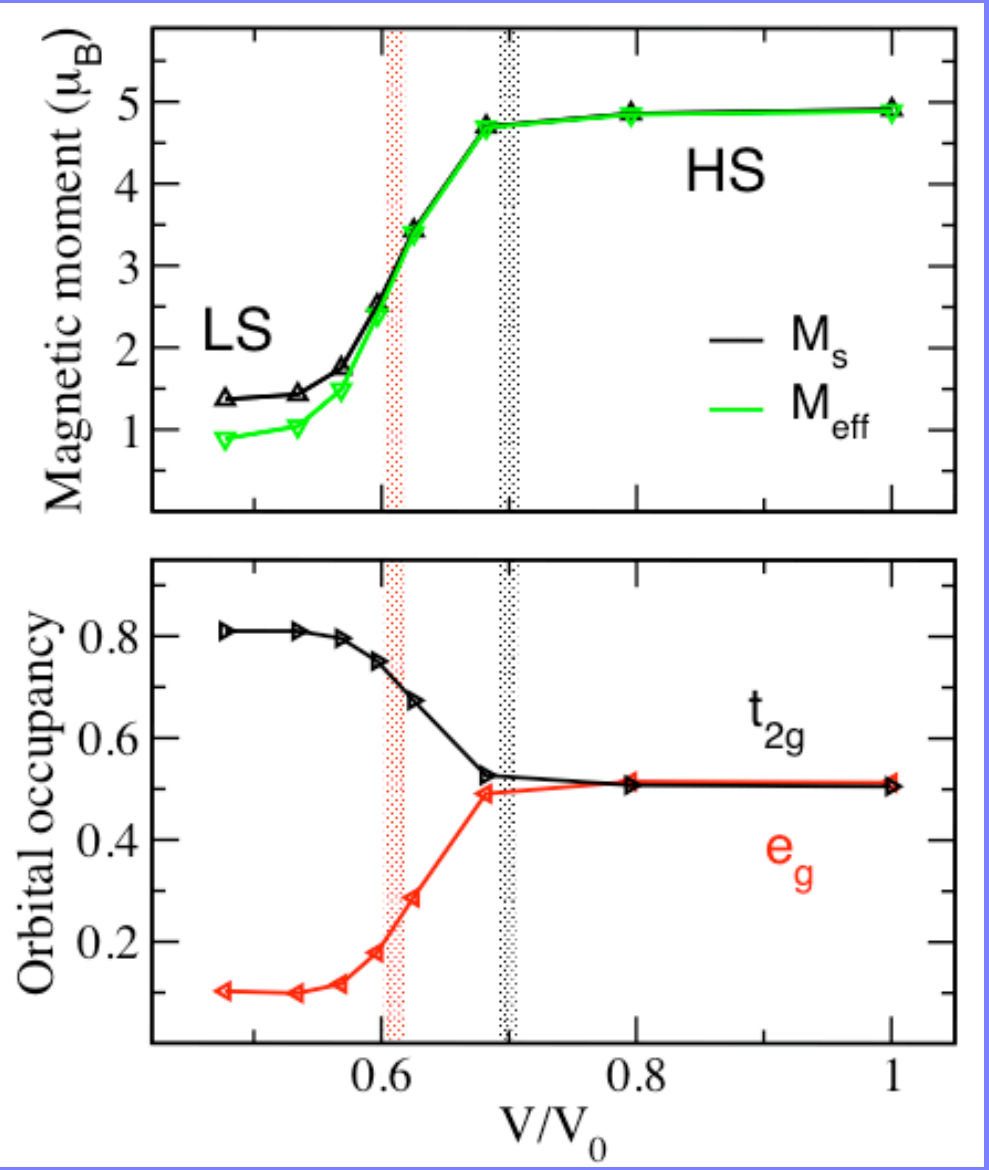
Correlation effects weaker in LS state (bold lines: LDA)





Much of the structure is due to the LDA spectrum, correlation effects become milder (still important)

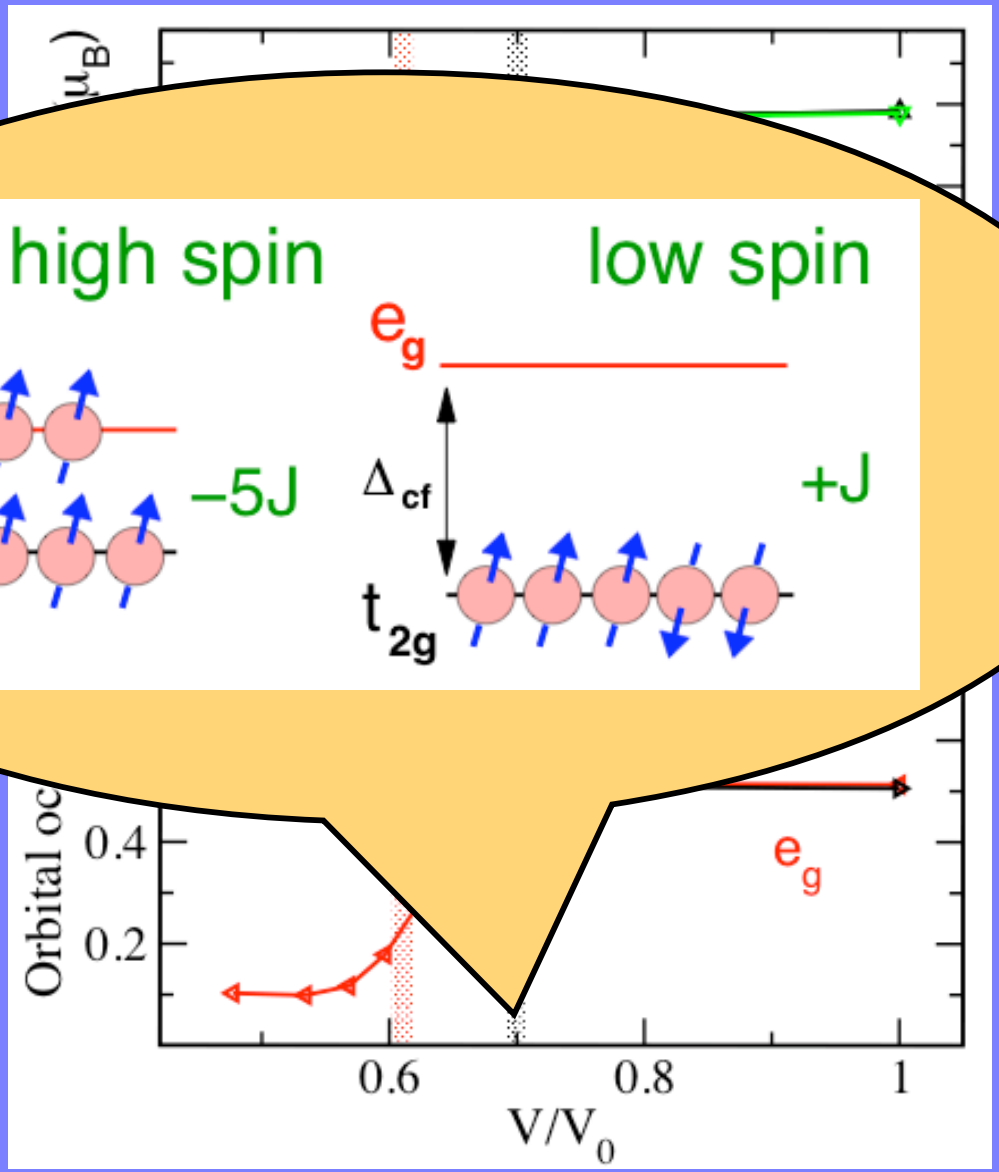
Mott transition in MnO: unconventional mechanism



Increase in Δ_{cf} under pressure overwhelms J_H.
- moment collapse,
- then metallization

Verified by
- varying J_H
- varying U

Mott transition in MnO: unconventional mechanism



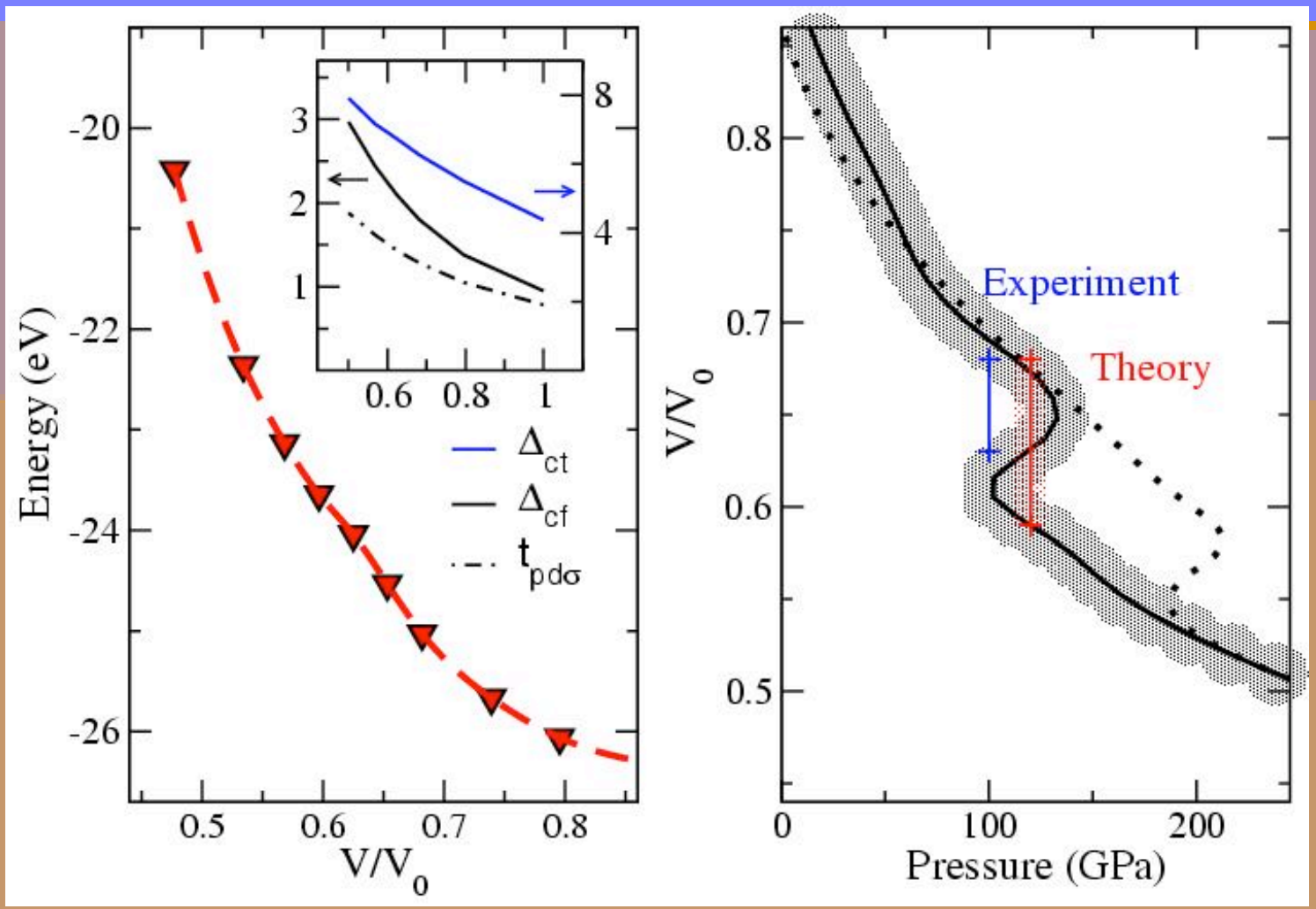
Increase in Δ_{cf} under pressure overwhelms J_H.
- moment collapse,
- then metallization

Verified by
- varying J_H
- varying U

$$E_{tot}=E_{LDA}+(E_{DMFT}-E_{HF})$$

$$P=-dE/dV$$

Volume collapse ~ 120 GPa



Summary: MnO under pressure

- Total energy calculation requires additional ansatz for the energy functional. Outcome:

✓ E - V is not convex => 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

DMFT: Metzner & Vollhardt, 1898 for Hubbard model
Reviews: Georges et al., RMP 1994
Kotliar, Savrasov, et al., papers in 2005-2007
……

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

Erik Ylvisaker
UC Davis

Jan Kunes
UCDavis
University of Augsburg
Czech Academy of Sciences

Warren Pickett
UC Davis

Andrew McMahan
LLNL

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

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

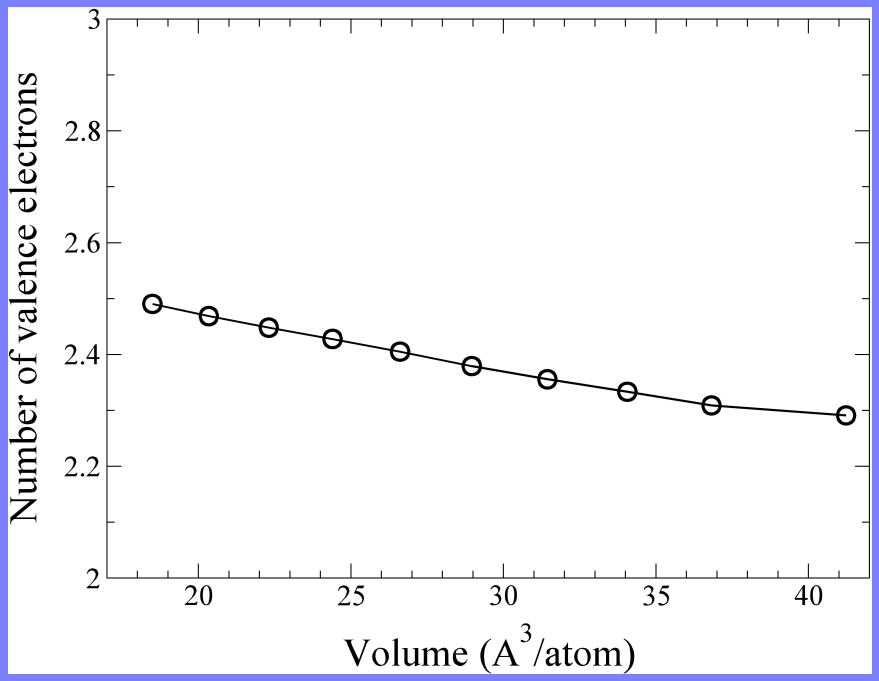
  - **Gradual valence transition under pressure**
  - **Begins divalent, but nearly trivalent at 35 GPa**
  - **Transition robust across crystalline phase boundaries**

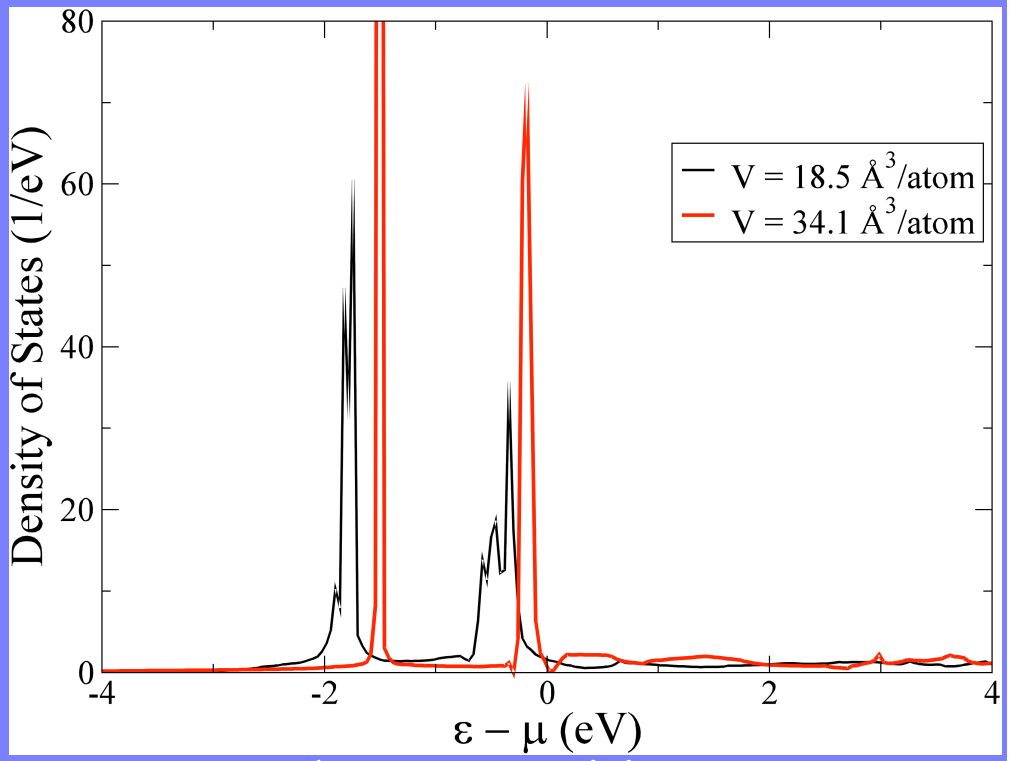
    - Transition appears less robust at lower T
    - Intermediate state is mixture of f^{13} + f^{14} states.

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

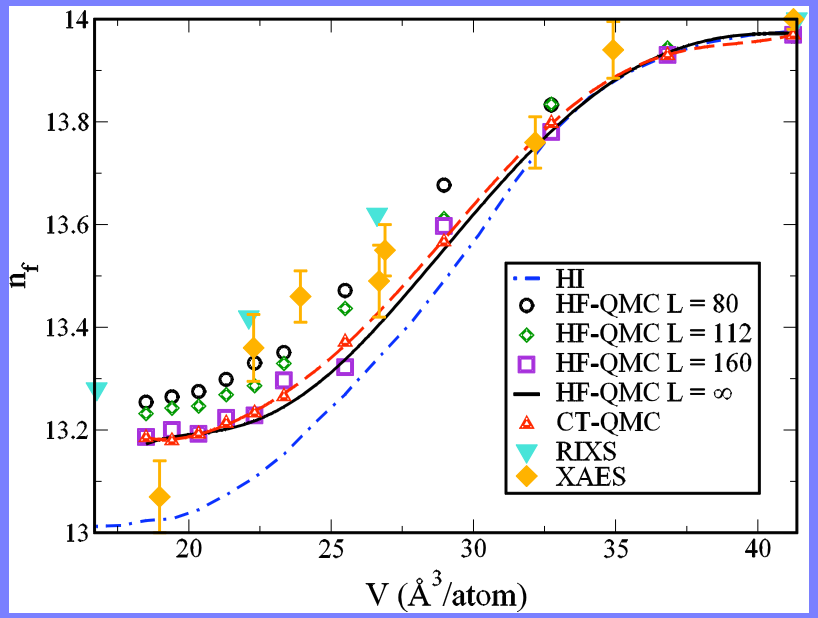
FPLO Code
Koepernik and Eschrig

- 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

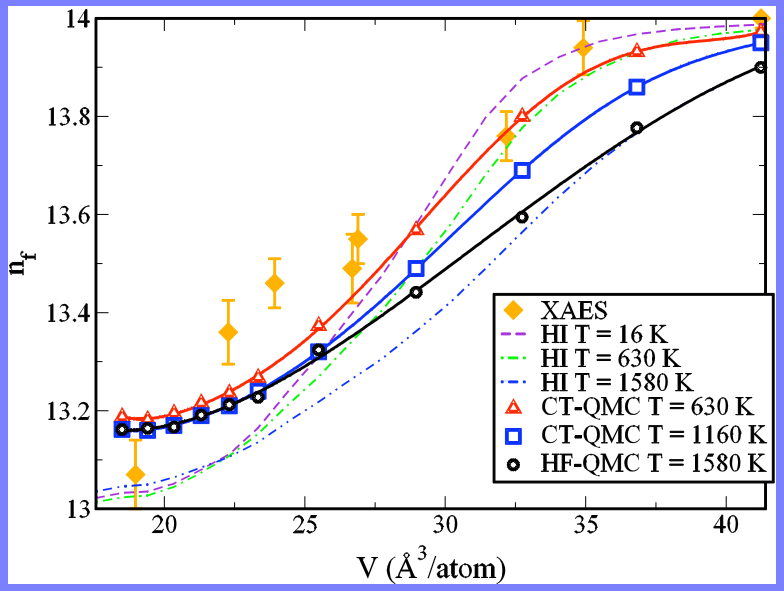
Yb Valence Transition: LDA+DMFT describes it successfully

- HI and QMC agree quantitatively at large V
  HI gives qualitative behavior
- Imaginary time discritization error ≈ charge self-consistent error
- L=80 points 9100 CPU-hours each
- Temp dependence follows experimental data ($YbAgCu_4$ and $YbAl_3$)



Convergence behavior

Temperature dependence



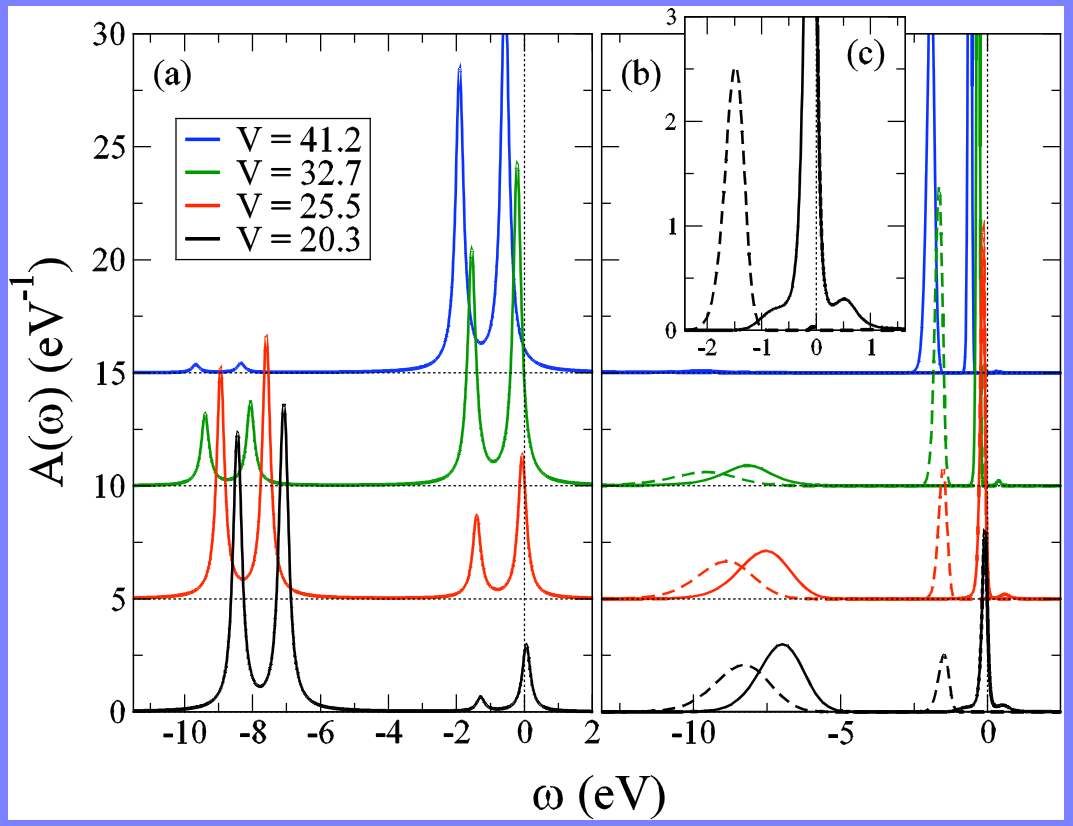
XAES: Phys. Rev. B, 26:4745, 1982
RIXS: Phys. Rev. B, 75:081101(R), 2006

Yb Spectrum

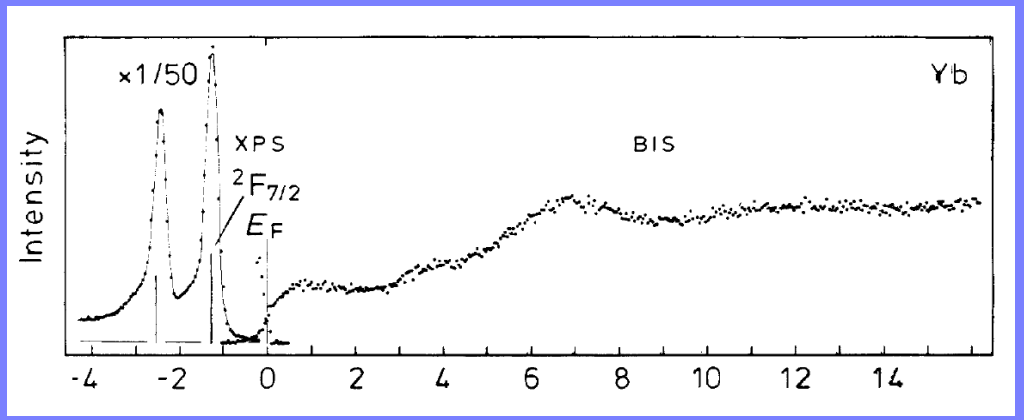
- Many body state
- $\alpha f^{14} + \beta f^{13}$
- is apparent

- Lower/upper Hubbard bands gradually gain/lose weight

- Non-integral weights



Hubbard I CT-QMC



f^{14} spectral weights

J. Phys. F **11**, 121 (1981)

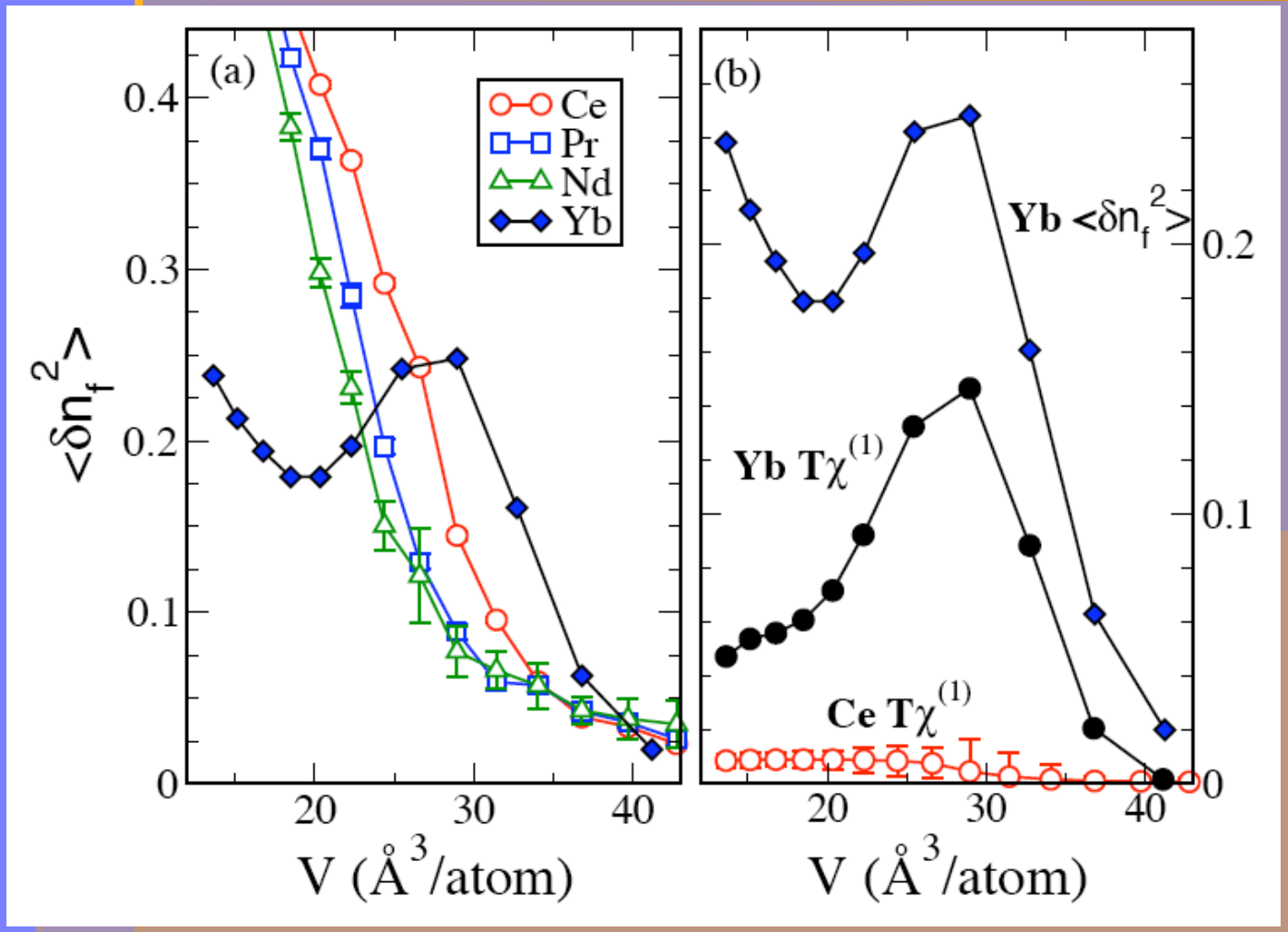
Yb: charge fluctuations in the *4f* shell

Equal-time charge fluctuations

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

Correlated charge fluctuations (susceptibility)

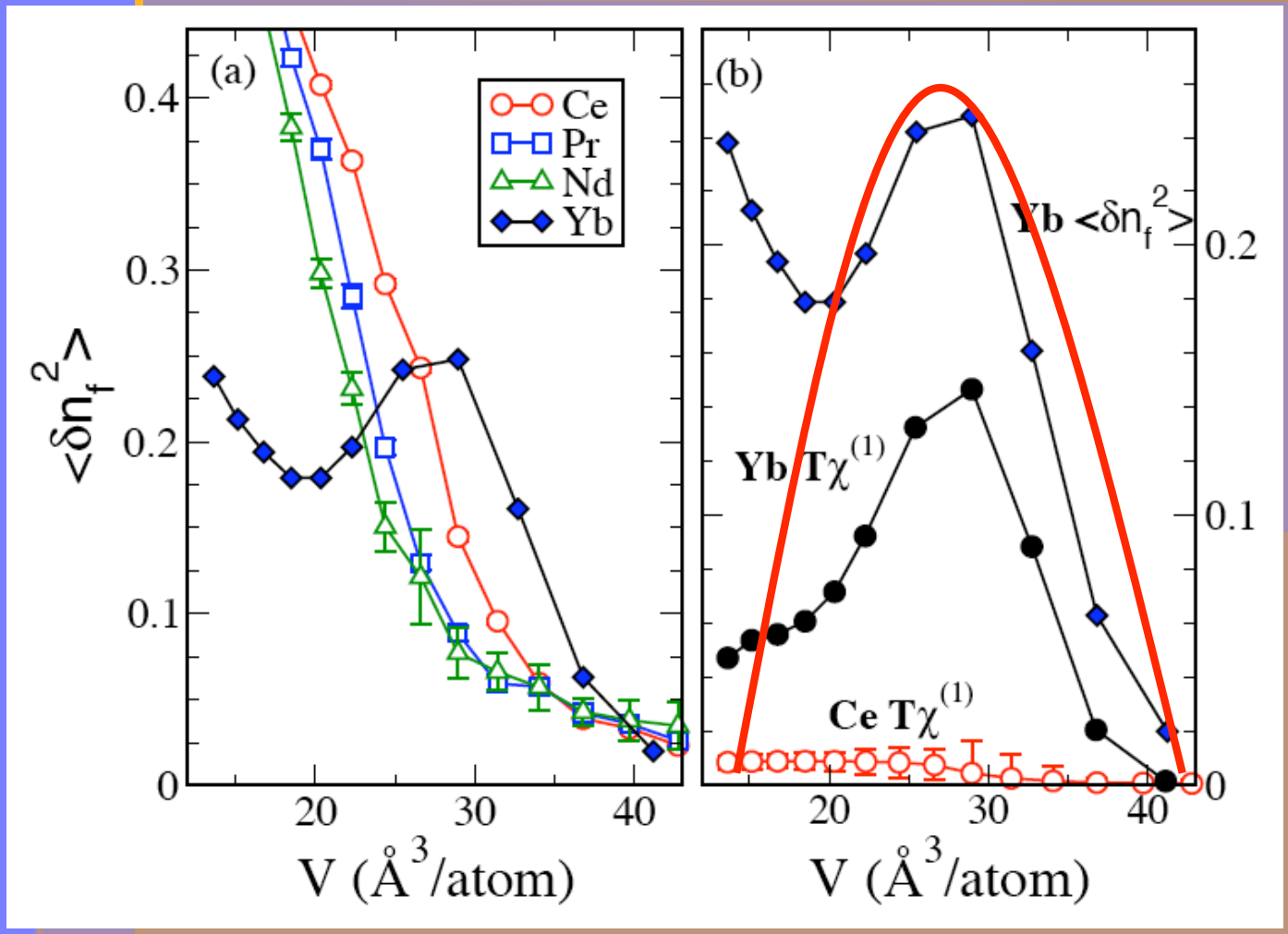
Local susceptibility $\chi^{(1)} = \partial \langle\langle n_f \rangle\rangle / \partial V_i$



Yb: charge fluctuations in the *4f* shell

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

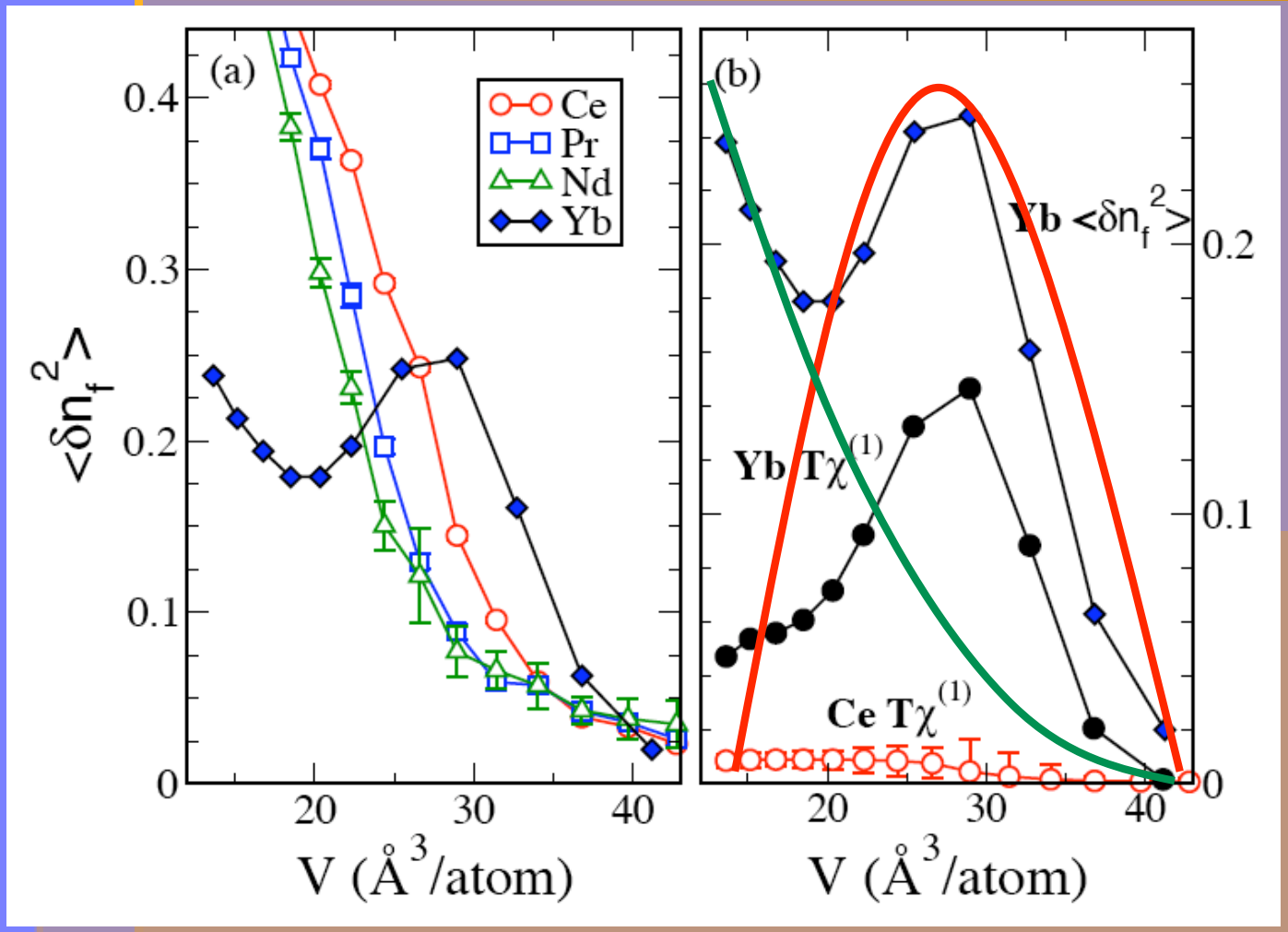
Local susceptibility $\chi^{(1)} = \partial \langle\langle n_f \rangle\rangle / \partial V_i$



Yb: charge fluctuations in the *4f* shell

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

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



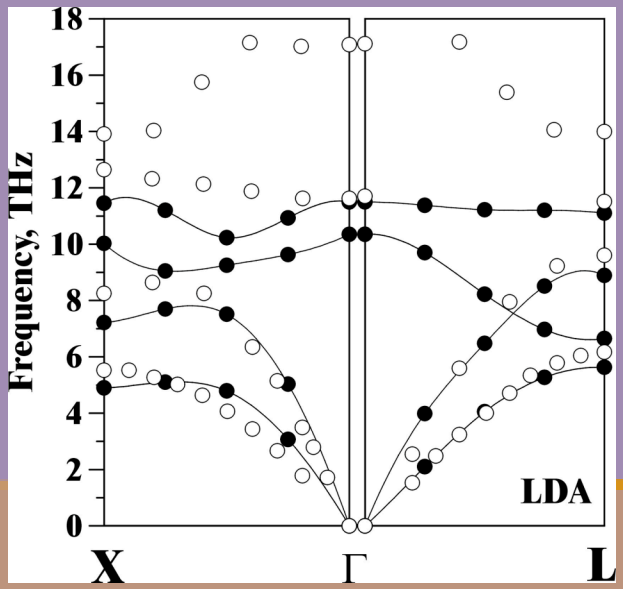
Summary: MnO & FeO MIT; Yb valence transition

- 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

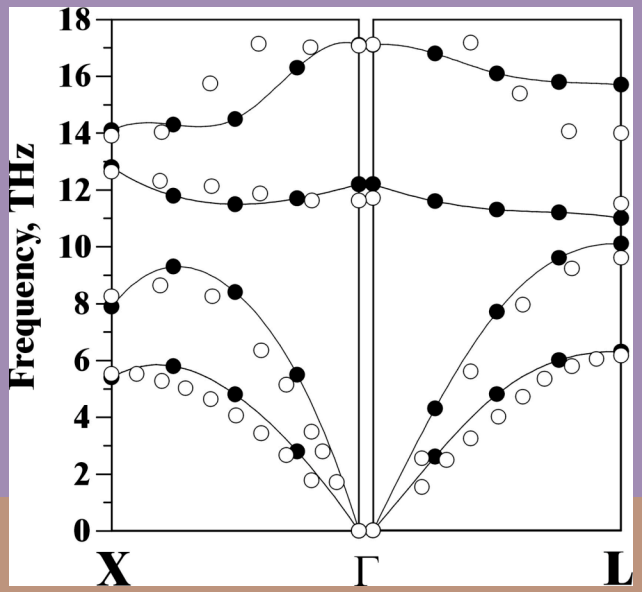
NiO: Phonons in LSDA vs. LDA+DMFT

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

LSDA, AFM phase

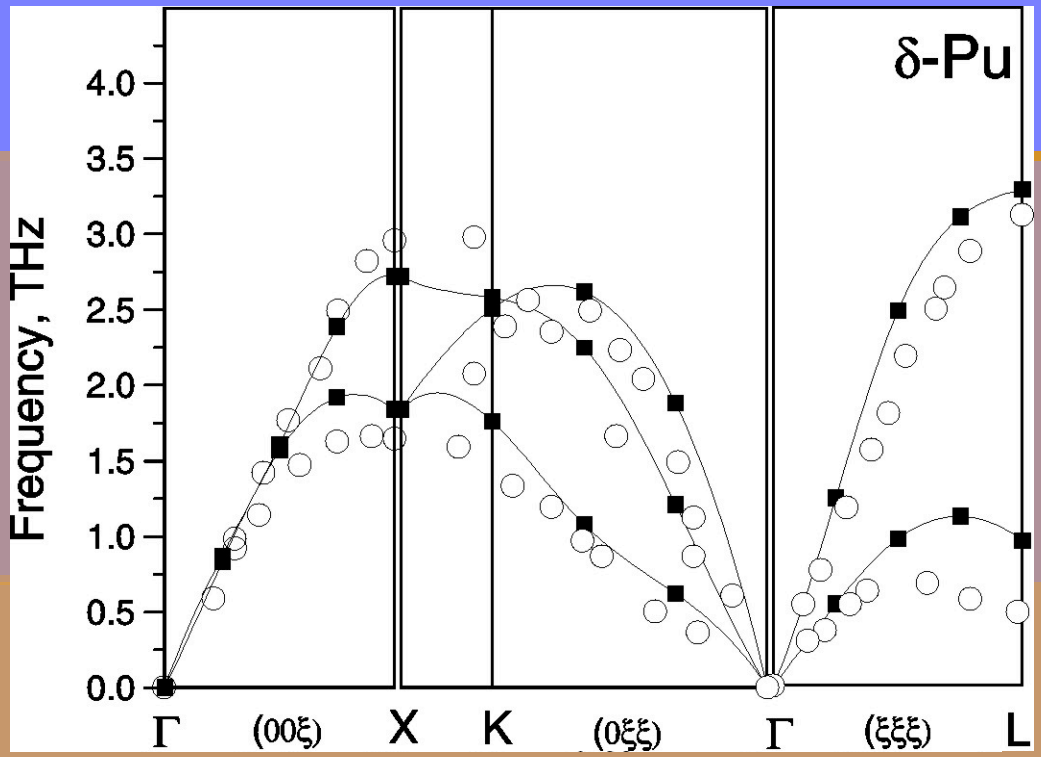


LDA+DMFT, PM phase



(Savrasov, Kotliar, PRL 2003)

Phonons in δ-Pu



	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	C'(GPa)
Theory	34.56	33.03	26.81	3.88
Experiment	36.28	33.59	26.73	4.78

(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:

Spectral density functionals for el. str. calcs. Savrasov & Kotliar, PRB (2004)
Electronic structure calculations with DMFT.
Kotliar, Savrasov, Haule, Oudovenko, Parcollet, Marianetti, RMP 2006
…many other papers, rarely starting at the free energy functioal level

Energy Functional #1: McMahan *et al.*

strongly correlated U_f + moderately correlated *LDA*

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

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

$$\begin{aligned}
\Delta E_{McM} &= Tr[H_k\{G(\Sigma_{DMFT}) - G(\Sigma_{mLDA})\}] && \text{K.E.} \\
&+ \frac{1}{2}Tr[\Sigma\bar{G}(\Sigma_{DMFT}] - \frac{1}{2}Tr[\Sigma_{mLDA}G(\Sigma_{mLDA}] && \text{P.E.} \\
&\rightarrow Tr[H_k\{G(\Sigma_{DMFT}) - G(\Sigma_{mLDA})\}] \\
&+ \frac{1}{2}\sum_{ms\neq m's'} U^f_{mm'}[\langle n_{ms}n_{m's'}\rangle - \langle n_{ms}\rangle\langle n_{m's'}\rangle] \\
\Sigma_{mLDA} &= U_f(n_f - \frac{1}{2}) \quad \{mLDA \equiv \text{model LDA}\}
\end{aligned}$$

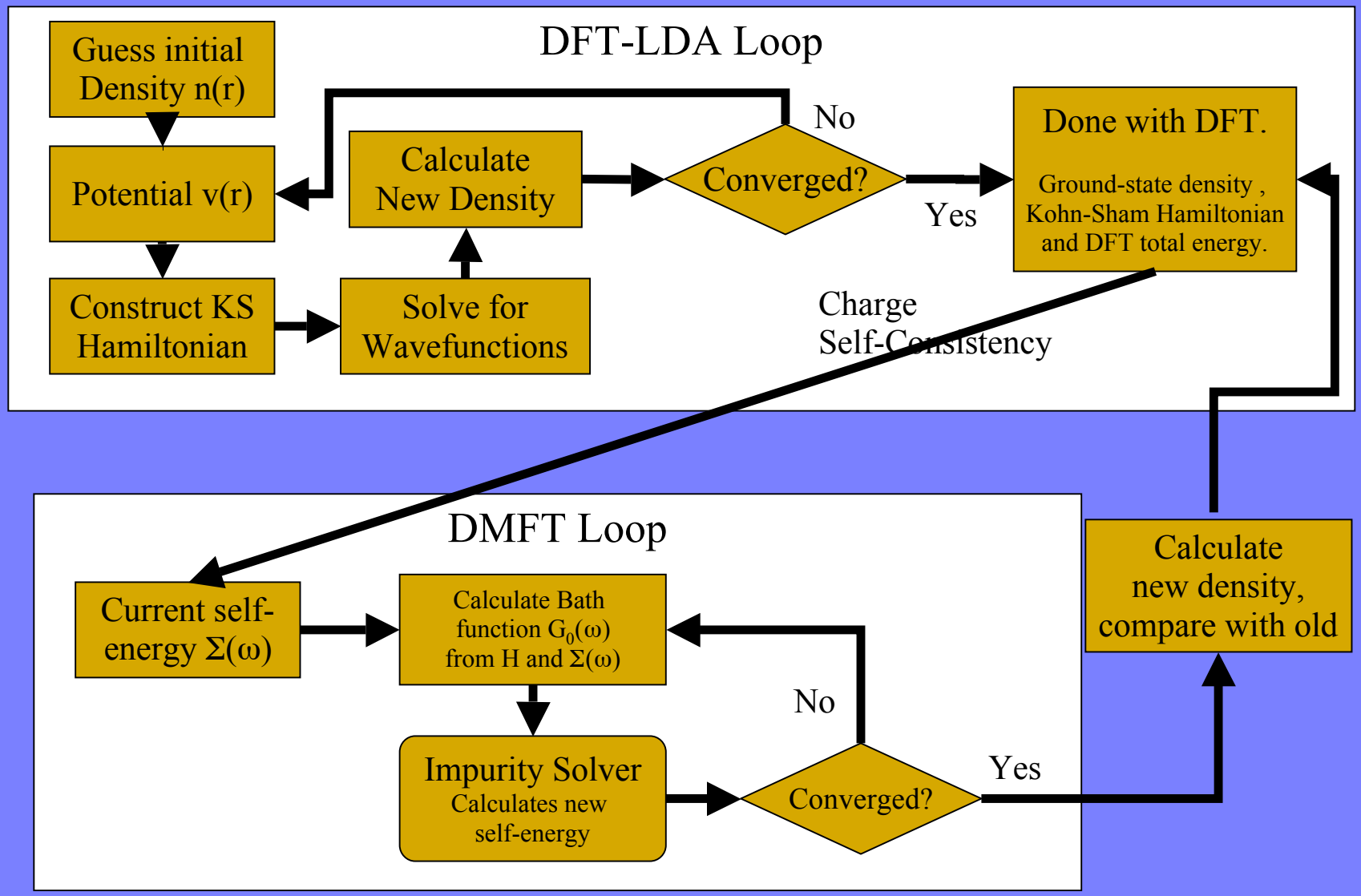
For reference: the density-functional functional is

$$\begin{aligned}
E_{LDA}[\rho] &= (T_o[\rho] + Tr[v_{ext}\rho]) + E_{hxc}[\rho] \\
&= (Tr[\epsilon_k f_k] - Tr[v_{hxc}\rho]) + E_{hxc}[\rho]
\end{aligned}$$

Challenge #2

charge self-consistency

Self-consistency in ae LDA+DMFT



(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 -->
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.