Quantitative Calculations: Bringing together different computational approaches

Using Basic Principles and idealized models for guidance and interpretation

Richard M. Martin

Department of Physics
University of Illinois at Urbana-Champaign
Department of Applied Physics
Stanford University

Grateful acknowledgements to
Lucia Reining and David Ceperley

Overview

Not necessarily in this order

Quantum Materials:

Does a quantum phenomenon actually occur in some material?

Experiments are on an actual material

"Strongly Correlated" materials

Not easy to interpret experiments

Not easy to do calculations

Quantitative Calculations:

Different theoretical and computational approaches

What should one be able to describe (or not) with an approach

Basic Principles:

Mathematical knowledge – topology, …..

Physical arguments – Luttinger Theorem, ….

Occam's razor – Continuity Prionciple, ….

When do they apply?

Idealized models:

Identify classes of behaviors

Clarify the consequences of Basic Principles

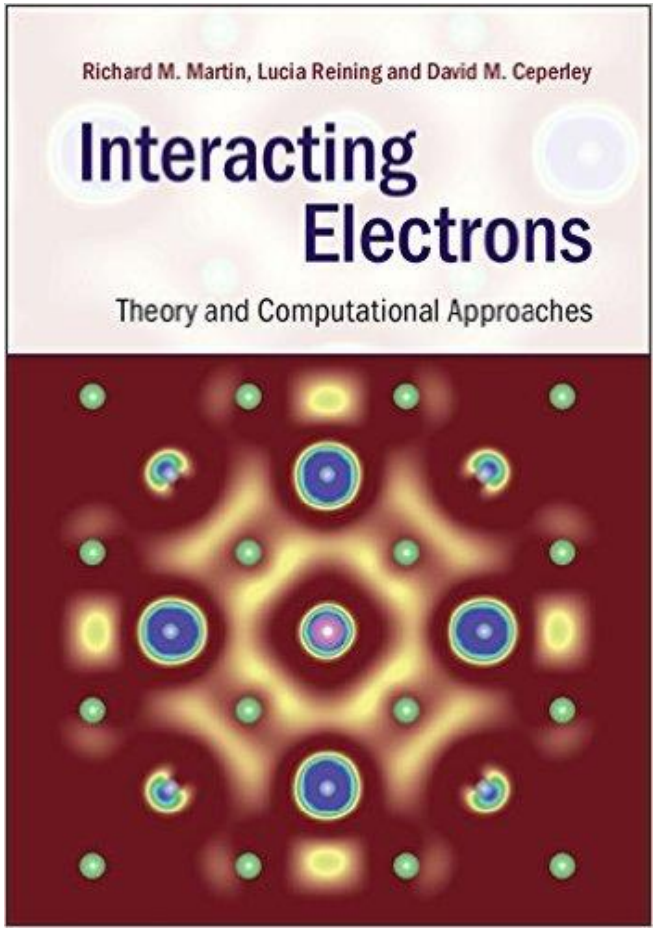
Especially important for Quantum Materials

Understanding many problems using basic principles:

Topological Insulators

Materials at the center of the earth – high P and T

……



…. a unified exposition of the most-used tools:
many-body perturbation theory,
dynamical mean field theory and
quantum Monte Carlo simulations.
Each topic is introduced with a less technical overview for a broad readership, followed by in-depth descriptions …….

To be published in May –
available in the Americas in July

Quantitative Calculations

Complementary theoretical methods

- **DFT - Kohn-Sham – treats the ground state of interacting systems**
  - Very successful for ground state structures, phonons, static screening, …
  - Often the starting point for other methods

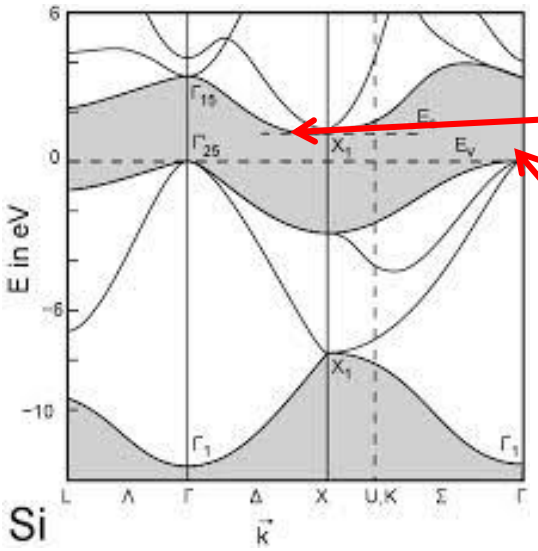
- **GW – example of many-body perturbation theory**
  - Designed to calculate excitations
  - Dynamic Green's function $G(r,r',\omega)$, screening $W(\omega)$

- **DMFT – treats interacting electrons on an embedded site**
  - Approximates correlation between sites
  - Dynamic Green's function $G_{ij}(\omega)$
  - Excitations and temperature dependence
  - Set of methods – requires inputs of parameters in some way

- **QMC – treats interacting electrons by stochastic sampling**
  - Best method known to calculate energies and static correlations for solids
  - Difficult to get excitations

How do we know Si is an insulator?

Textbook independent particle bands



The gap is NOT an ind. part. concept

Lowest energy for an added electron

Lowest energy for removing an electron

For some range of energies starting at the band edge the energy vs k is precisely defined including interactions

How do we know Si is an insulator?

We tell ourselves that we can start from in particles treat interactions in perturbation theory.

Indep. part. Si  **real interacting part. Si**

Similarly for a metal states at the Fermi energy a well-defined

Indep. part. Na  **real interacting part. Na**

Very reasonable – but never rigorously proven!

How do we know Si is an insulator?

What we really do is to invoke the continuity principle, "adiabatic continuity"

Indep. part. Si → **real interacting part. Si**

Indep. part. Na → **real interacting part. Na**

The principle is that this is valid so long as there is no phase transition as interactions are turned on.

Does NOT depend upon perturbation theory

Applying the continuity principle

1. Choose which properties are well-defined in the interacting system – gap in a insulator, Fermi surface in metal

2. Continuity for those properties

Some indep. part. System → real interacting part. system

3. Valid so long as there is no phase transition

This is the key point that is from experiment!

In a real material we never have a rigorous proof that there is no transition.

4. Does NOT apply to other properties, e.g., bands away from the Fermi energy, satellites, high energy multiplets, ….

5. We understand this and we not let this get in our way for getting at the properties we can address!

More difficult cases

Materials where interactions play a crucial role

Mott Insulator - What does the term mean?

NiO, MnO, Vanadium oxides

- **Magnetism, Order vs disorder**
- **High-Low Spin transition**
- **Metal-insulator transition**

Luttinger Theorem

Cerium

- **Phase transition with large volume change, Kondo-like effects**
- **$CeRuIn_5$ – Heavy fermions at low temperature**

Topological insulators

SmB_6

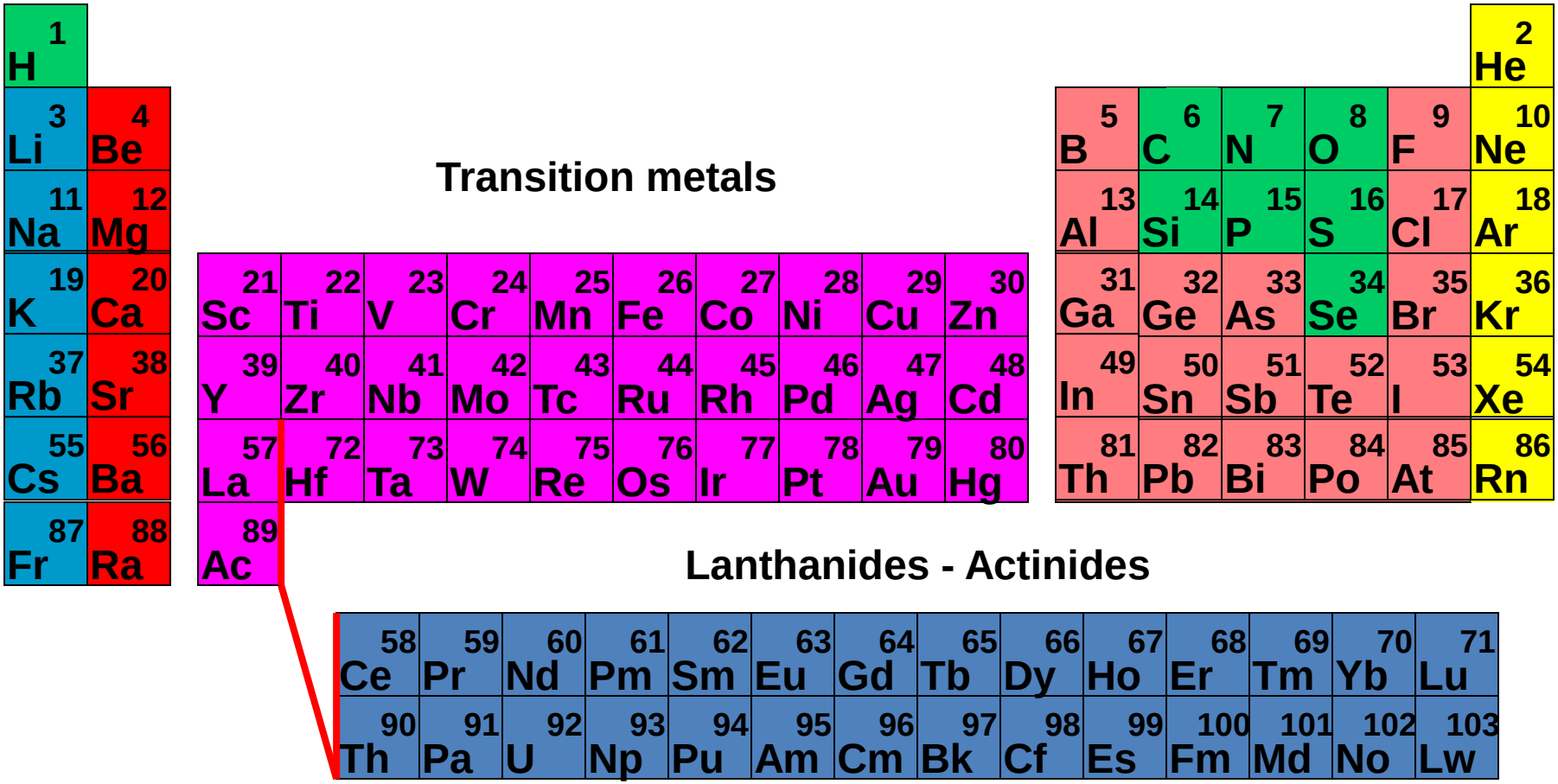
- **How could possibly claim to understand calculation of a gap of meV with complex bands and interactions of many eV**

Common features

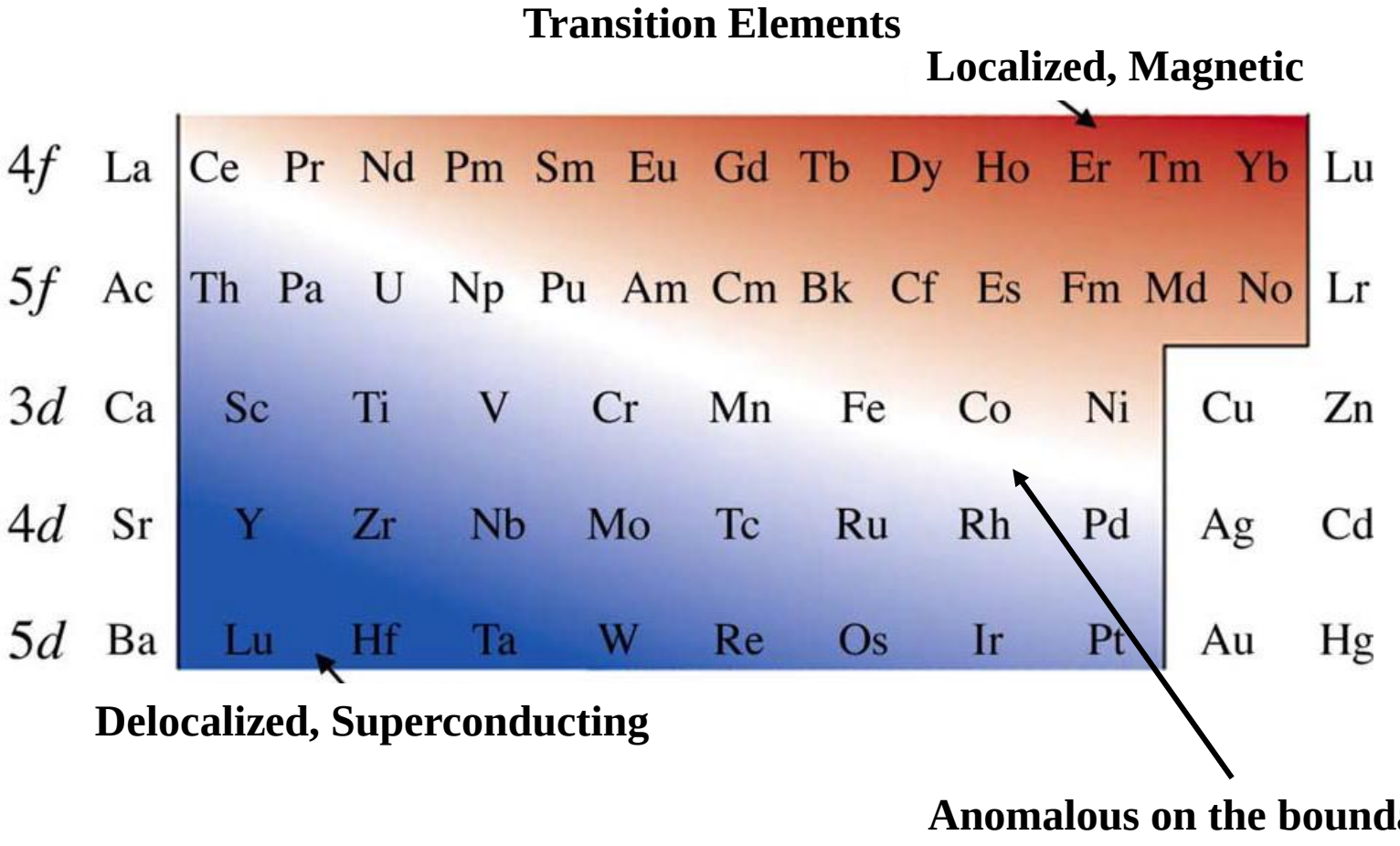
- **-- Local moments**
- **-- Temperature**
- **-- symmetry**

Background

Periodic Table



Periodic Table of transition elements (arranged delocalized ---- localized)

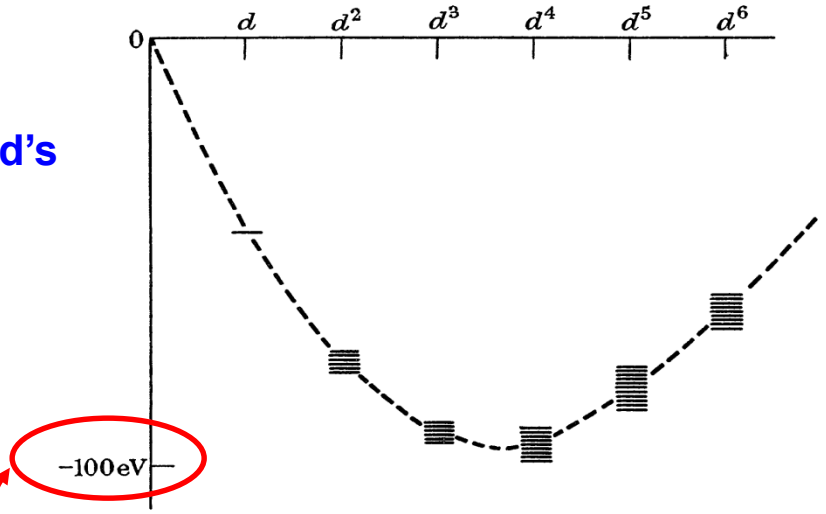


Original due to J. L. Smith

Interaction U in 3d atoms

$$E(N) = (\varepsilon_0 - \mu)N + \frac{1}{2}UN(N-1)$$

Copied from Hubbard's paper



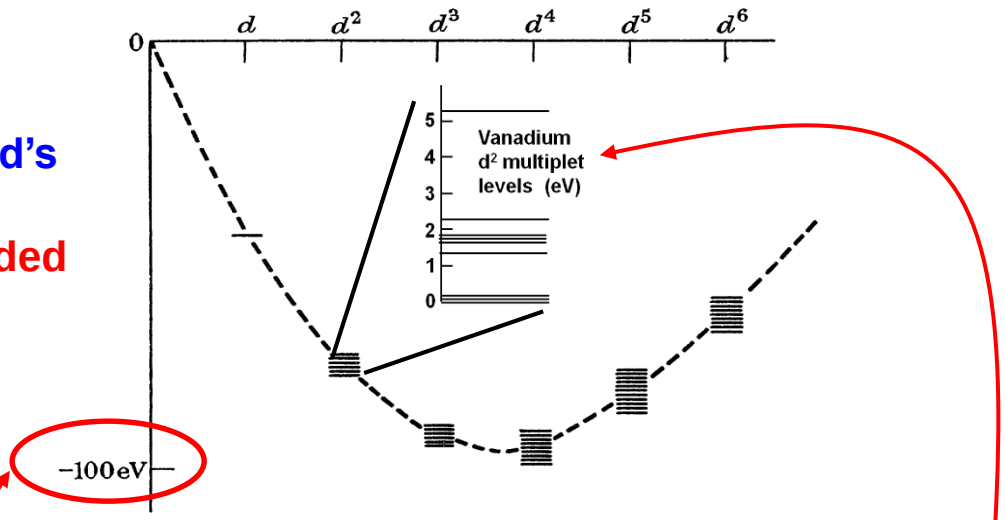
Note the energy scale. In an atom U ~ 15 eV

In a solid the effective U is reduced to 2-8 eV

Interaction U and J in 3d atoms

$$E(N) = (\varepsilon_0 - \mu)N + \frac{1}{2}UN(N-1)$$ + J .....

Copied from Hubbard's paper with V multiplets added



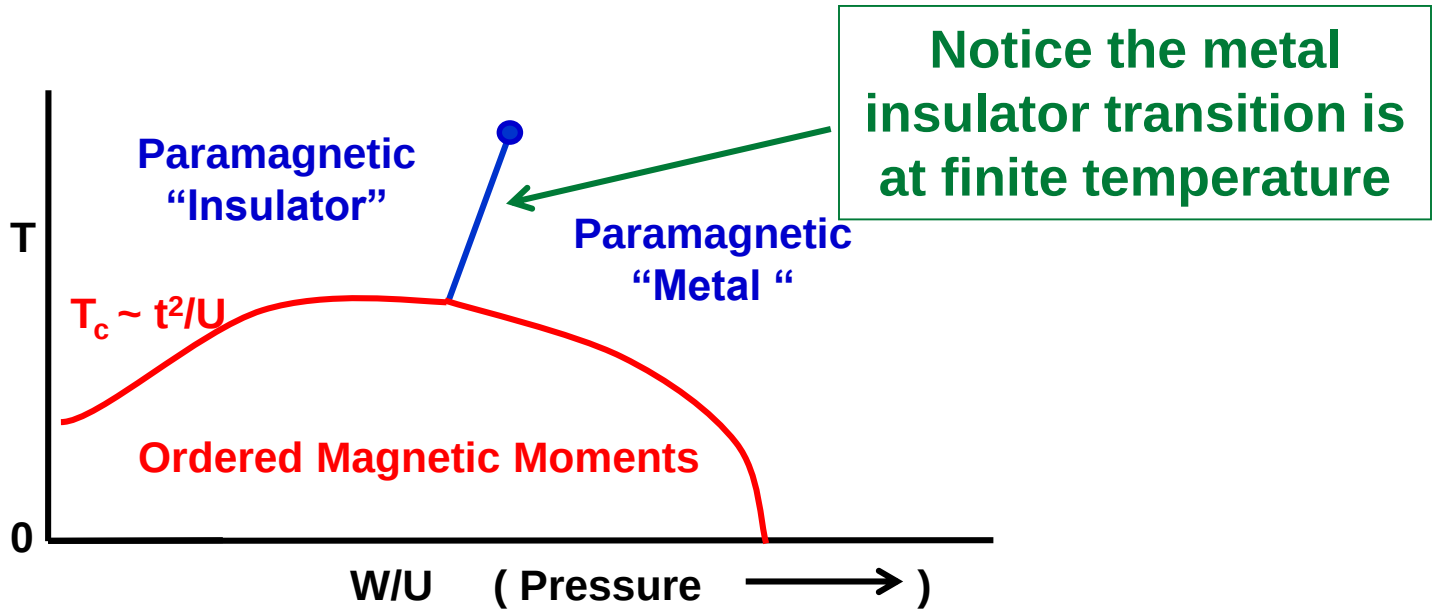
Note the energy scale. In an atom U ~ 15 eV

In a solid the effective U is reduced to 2-8 eV

In an atom with N>1 electrons there are different states called multiplets
Simplest example: 2 electrons that can be ↑↑ or ↑↓– energy difference is J
In an atom J ~ 1 eV - NOT reduced in the solid

Hund's rule – the ground state is usually the high spin state
Such a state has a magnetic moment – local moment in a solid
that can form magnetically ordered states

Characteristic Phase Diagram For correlated electron system



Universal form isomorphic to transitions in many systems:
water – steam – ice
V_2O_3 – cerium and its compounds – NiO - MnO

……..

Mott Insulator

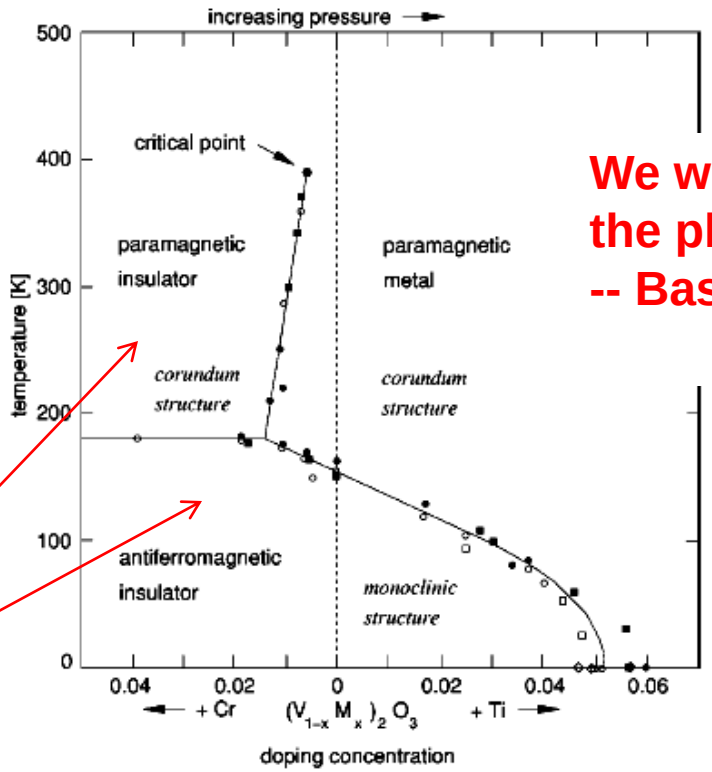
What does the term mean?

Any material that should be a metal if electrons were independent, but turns into an insulator?

The above but only if the material acts like an insulator with no order?

The above but only if the material acts like an insulator with no order at T=0?

Metal-insulator transition – V_2O_3



We wish to explain the phase transitions -- Basic questions

It would be nice to get the gap about right

Note: Pure V_2O_3 is what is often called a "Slater insulator". Paramagnetic "Mott insulator" occurs with alloying

Continuity: No sharp distinction of Slater and Mott at finite T

NiO
Often called the prototype "Mott insulator"

Face-centered cubic – NaCl structure

Antiferromagnetic for $T < T_{Neel} = 525$ K

Magnetic moment ~ 2 Bohr magnetons – expected for Ni d^8

Momentum remain but are disordered for $T > T_{Neel}$

Energy gap 4eV – does not change for $T > T_{Neel}$

Often called a "Mott Insulator" because it is still acts like an Insulator in the disordered state for $T > T_{Neel}$ – does not depend on the order

Calculations

Density functional calculations

Very successful for ground state properties of many classes of materials

Structures, phonons, ….
in semiconductors, transition metals, oxides, …..

For example: NiO

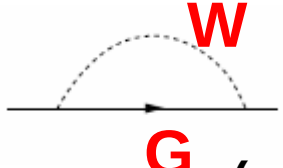
Antiferromagnetic state stable
Magnetic moment ~ experiment in the ordered state at T=0

Energy gap very small for traditional functionals
(DFT was not designed for excitations)
More later

Point we will come back to:
If the solution is restricted to be non-magnetic, the result is a metal with no gap.
Easy to show using only information about the symmetry of the states.
Is this a failure?
Basic principles are needed.

Perturbation expansions in the interaction

"GW" Approximation $\Sigma =$



Screened interaction W (not bare $V_{Coulomb}$)

(not bare G_0)

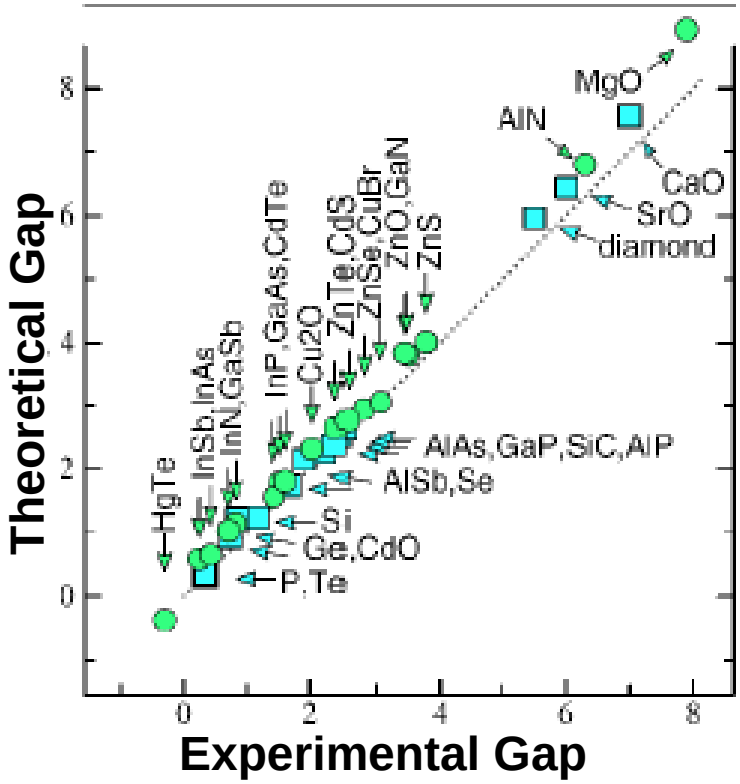
Widely used

Only a few years ago the field was saddled with arguments and arbitrariness in the approximations in actual GW calculations G_0W_0 ? Self-consistent? ….

More recently methods been established where the same approach is applied to many materials -- G_0W_0 with well-chosen input – usually NOT LDA or GGA

Perturbation expansions in the interaction

GW with "quasiparticle self-consistency"
NOT depend upon DFT input



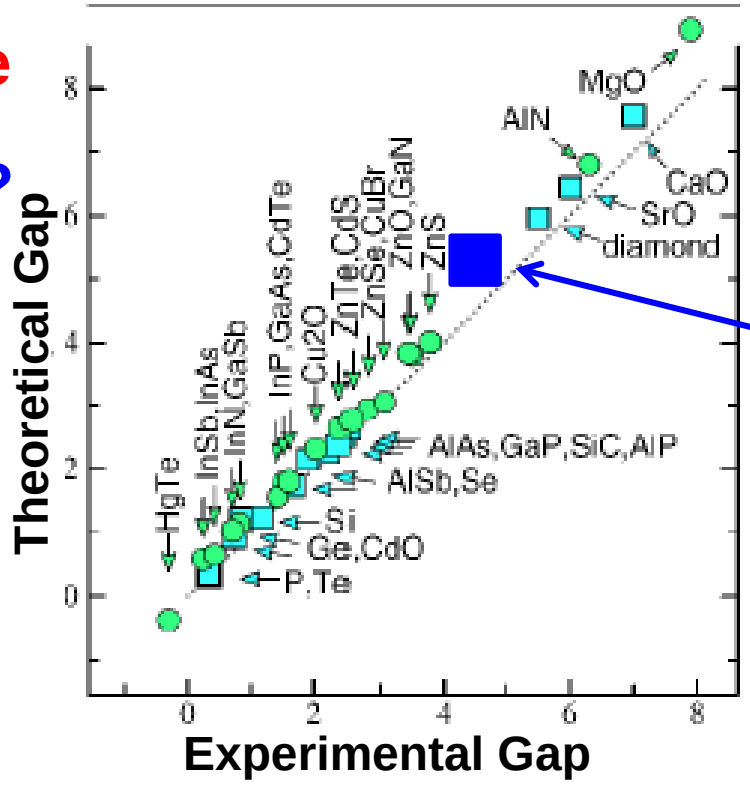
"QPSCF" method
Van Schilfgaarde

Semiconductors and "band insulators"

Perturbation expansions in the interaction

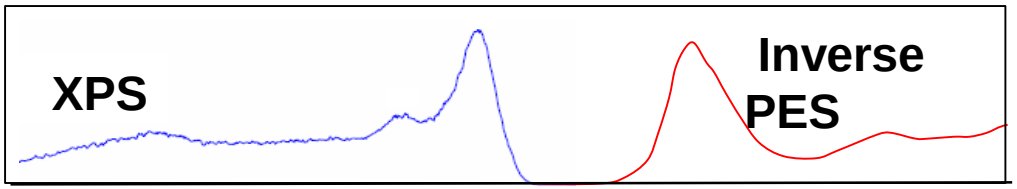
GW with "quasiparticle self-consistency"
NOT depend upon DFT input

Can GW describe a Mott insulator?



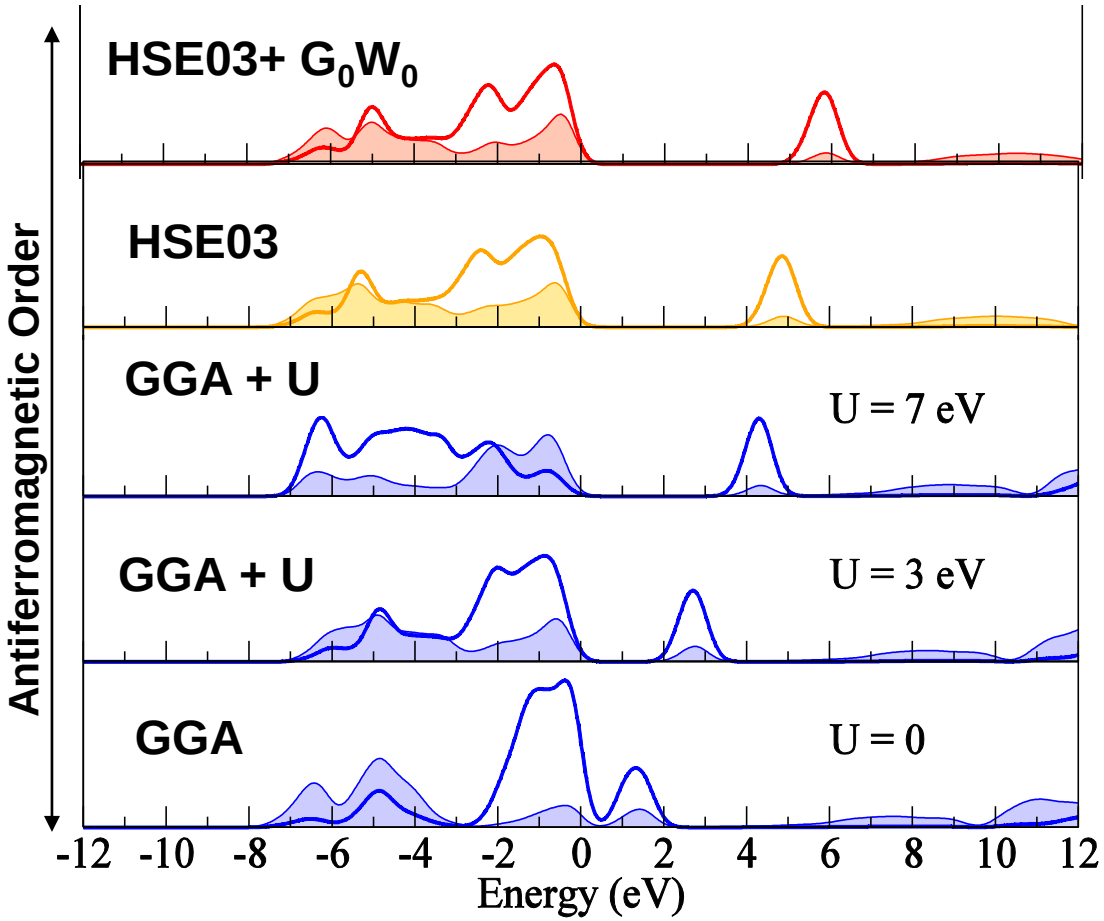
NiO
(Antiferromagnetic)

NiO



Experiment
L. H. Tjeng

Paramagnetic state for T > Tc
filled in later

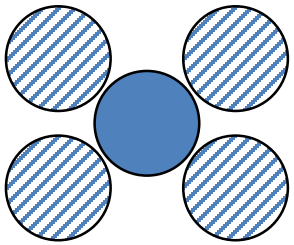


DFT+U , HSE, GW
Provided by C. Roedl
(similar to others)

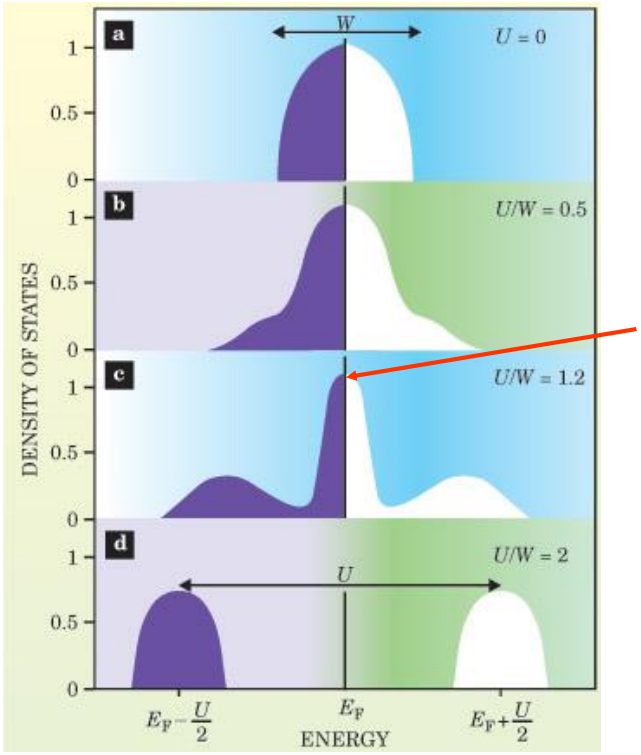
DMFT

Naturally applicable to high temperature

Solve for atom embedded in average field due to neighbors



Example for a one-band Hubbard model



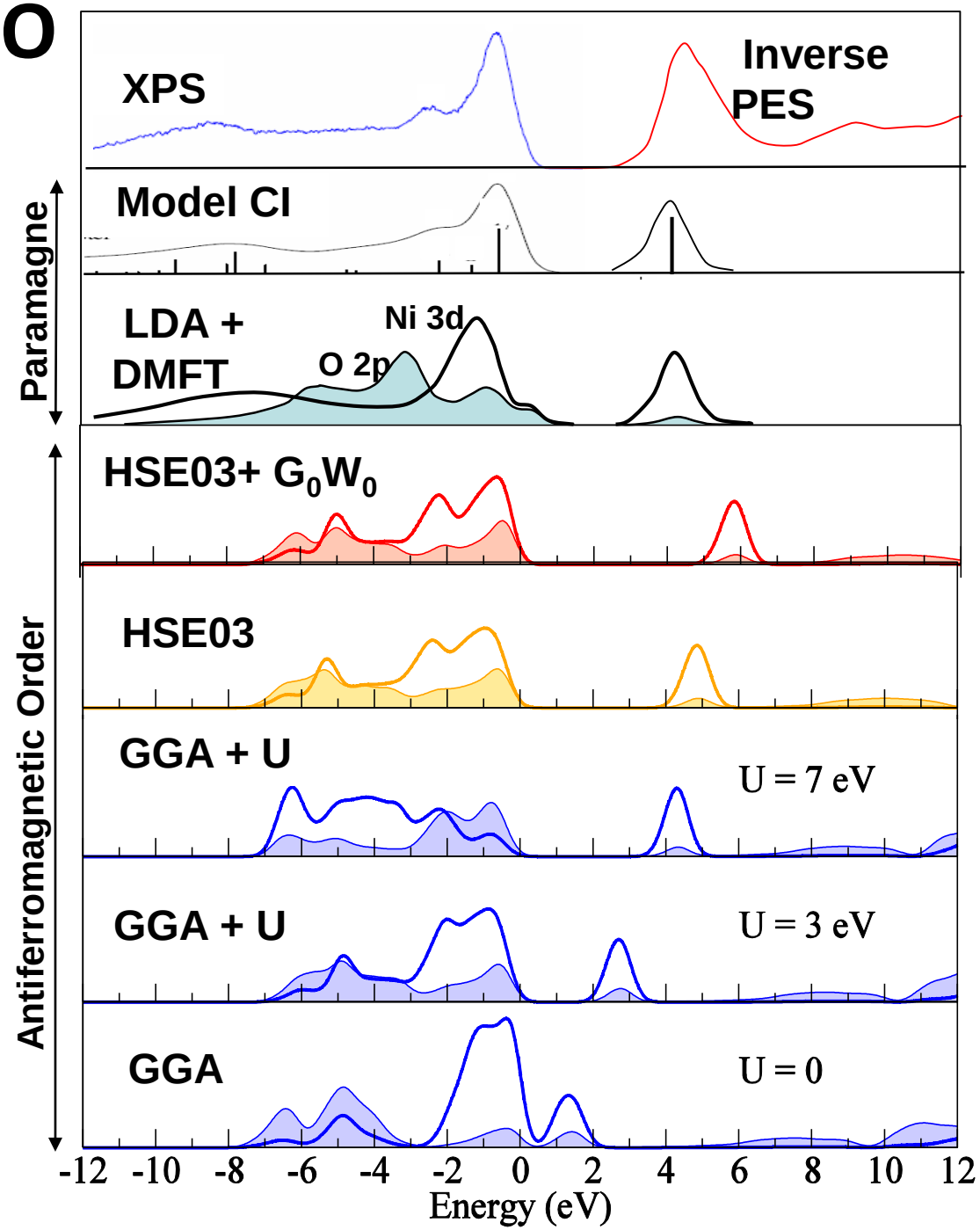
New energy scale

- **Spectrum of Green's function on central site**
  $G(E) = [\, E - H_0 - \Sigma(E) \pm i\delta]^{-1}$
  consistent with neighbors

- **Solve by Monte Carlo, exact diagonalization, ….**

Kotliar and Vollardt, Physics Today 2004

NiO



Experiment
L. H. Tjeng

Fujimori

Kunes 2001, 2003
LDA input to DMFT
U ~ 8 eV, AFMC (Hirsch-Fye)
Maxent transform to real ω

DFT+U , HSE, GW
Provided by C. Roedl
(similar to others)

What can we conclude?

NiO as an example of a Mott insulator

The ordered state at low temperature is described rather well

Methods like DMFT can capture the features that the moments and the insulating character can persist above the transition temperature

What can we conclude?

Concerning a Mott insulator

What about the qualitative question:

Is it a fundamental "failure" that DFT (and GW) do not find NiO to be an insulator if it is not ordered antiferromagnetically?

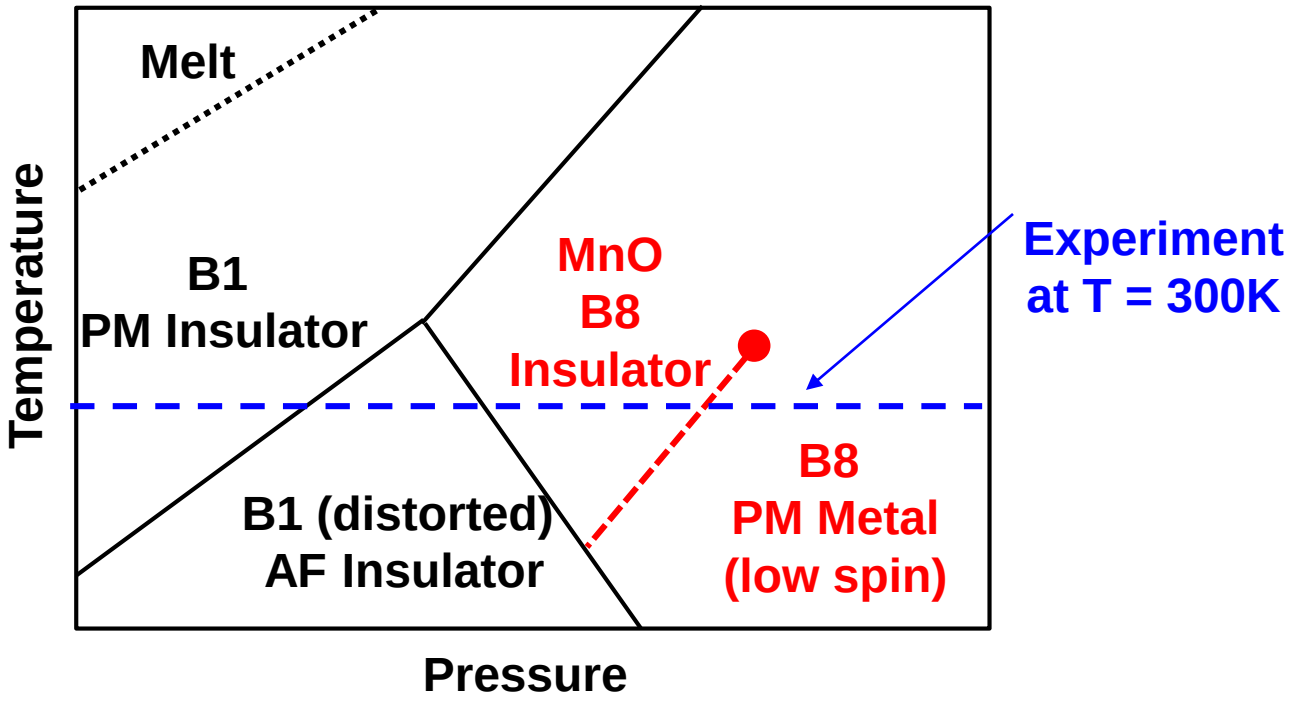
No

The actual state is at $T > T_{Neel}$ and this is a T=0 method.

It is much more profound to ask the question the other way.
Can the insulating state with no long range order occur at T=0?

This has been a central question in condensed matter physics for many years. In recent years the answer as emerged:
If such an insulator exists it must have topological order.

Phase transition in MnO at high pressure



Is there a spin transition simultaneous with a volume transition?
Important for geophysics

Vanadium Oxides

VO_2 **one d electron per vanadium**

Generally agreed (GW and DMFT calculations) that metal-insulator transition is due to pairing of atoms (Peierls transition) with correlation playing an important role

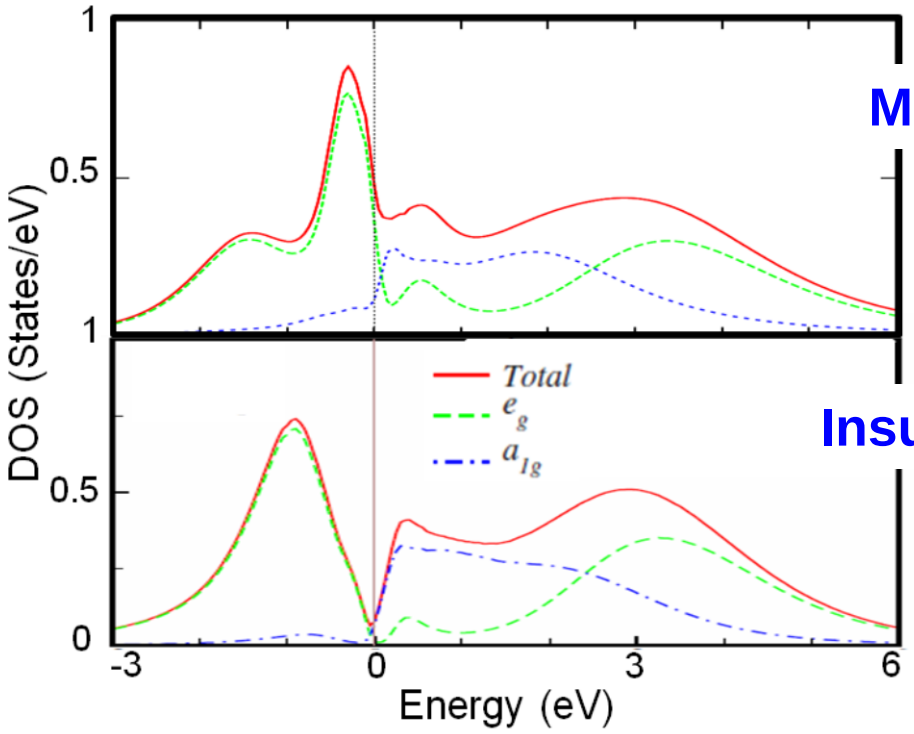
V_2O_3 - two d electrons per vanadium

Question debated many years:
Is it best to first consider the atomic effects – Hunds rule high spin state – and consider the solid state effects as a perturbation?
Or
Is it best to first consider the interatomic bonding -- a low spin state – and consider the atomic exchange interaction as a perturbation?

(S. Yu. Ezhov,et al. *Phys. Rev. Lett. 83:4136*– 4139, 1999.)

Metal-insulator transition – V_2O_3

DMFT Spectra



Bottom: Insulator - two electrons in the e_g states – high-spin local moment with a gap to the higher states.

Top: metal due to overlap with the a_{1g} bands - in agreement with experimental results for the occupation of the a_{1g} states.

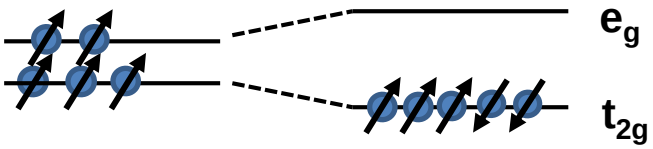
A. I. Poteryaev, et al., Phys. Rev. B 76:085127, 2007

MnO

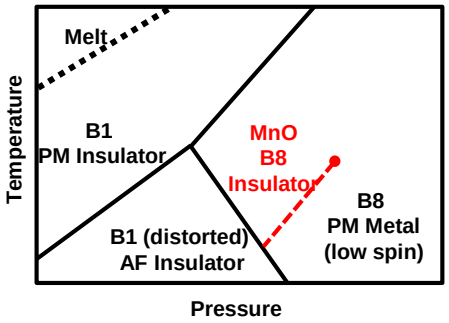
Δ (Crystal fields) vs W (band widths) vs J (exchange)

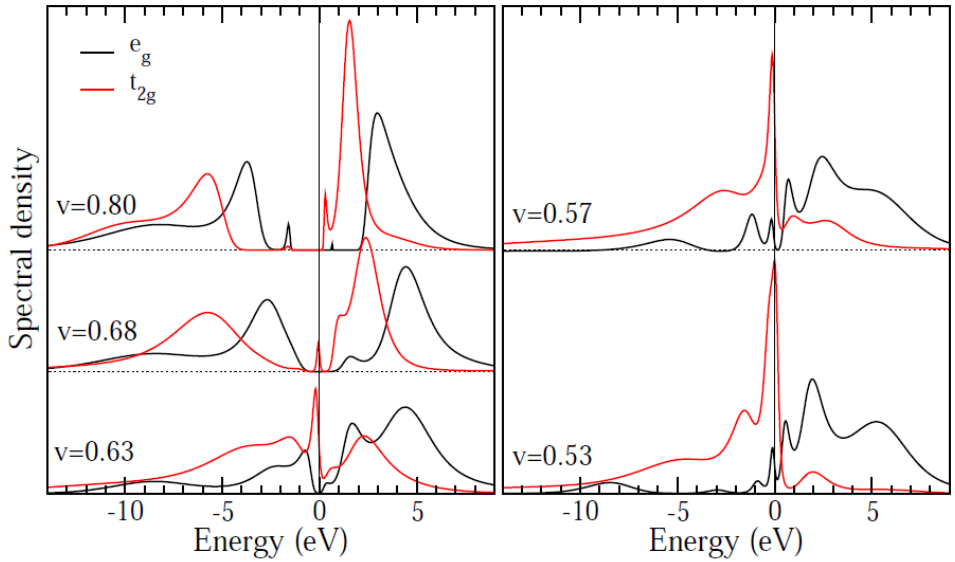
(ranges relevant for lower mantel in the earth)

"High Spin"



"Low Spin"





Kunes, et al.
Natutre Mat. 2008

Conclusion: M-I transition with no change of order

Simultaneous with the low-high spin transition

Crystal field states crucial – not like the simplest version of a Mott transition

Luttinger Theorem

Statement:

The volume enclosed by the Fermi surface in an interacting system is the same as a non-interacting system.

Odd # of electrons – metal

Even # electron – insulator or semimetal of multiple partially filled bands

Defined ONLY at T=0. At finite T the surface is not sharply defined and there cannot be such a theorem.

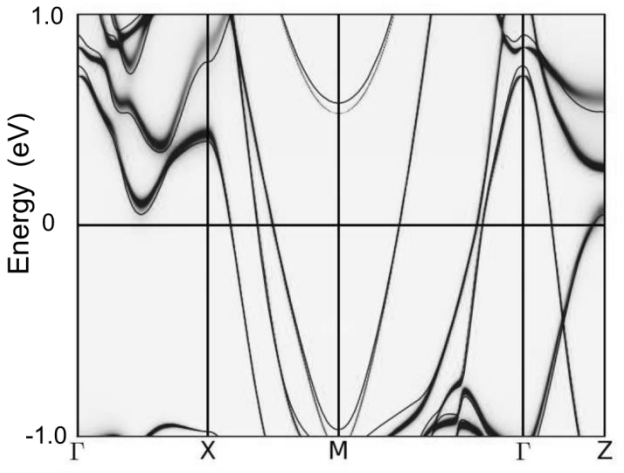
Derived by Luttinger and Ward using Green's function methods and assuming diagram sums converge

More powerful – consider it as a continuity principle that occurs so long as there is an adiabatic connection

DMFT calculation -- CeIrIn5

Heavy Fermion Material

T = 300 K



Acts as if the f states were decoupled
Almost the same as DFT
with 4f-states removed

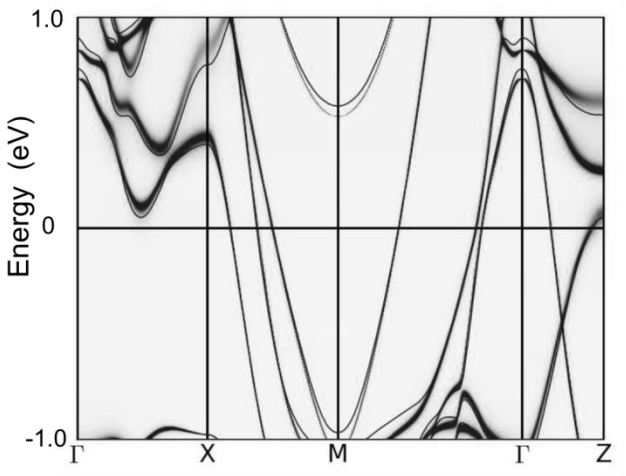
LDA+DMFT, single-site approximation

Choi, H. C., Min, B. I., Shim, J. H., Haule, K. and Kotliar, G.
Temperature-dependent fermi surface evolution in heavy fermion ceirin5.
PRL 108, 016402 (2012)

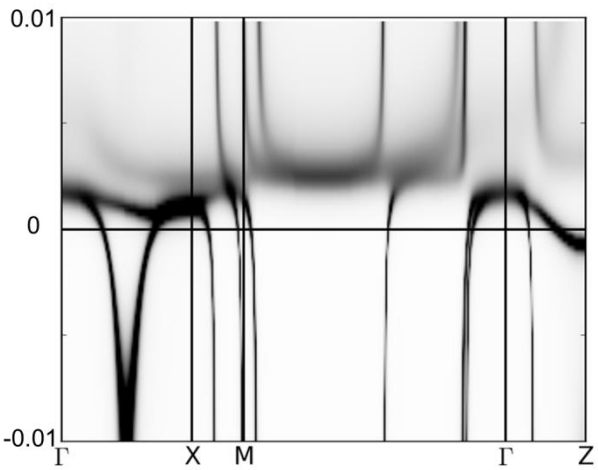
DMFT calculation -- CeIrIn5

Heavy Fermion Material

T = 300 K



T = 10 K



Note: scale is 100 times smaller!

Acts as if the f states were decoupled
Almost the same as DFT
with 4f-states removed

f states strongly coupled to form narrow band at low T

LDA+DMFT, single-site approximation

Choi, H. C., Min, B. I., Shim, J. H., Haule, K. and Kotliar, G.
Temperature-dependent fermi surface evolution in heavy fermion ceirin5.
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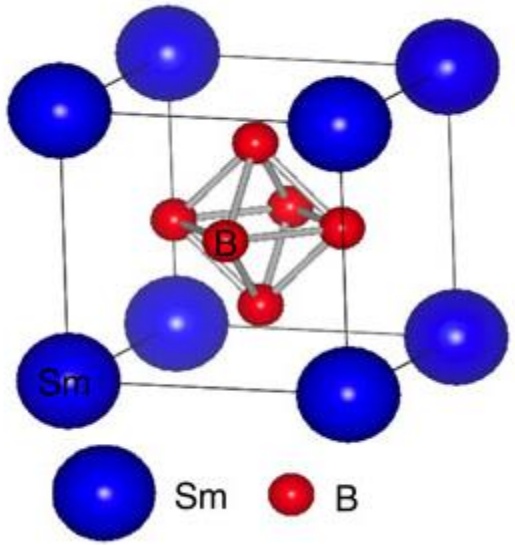
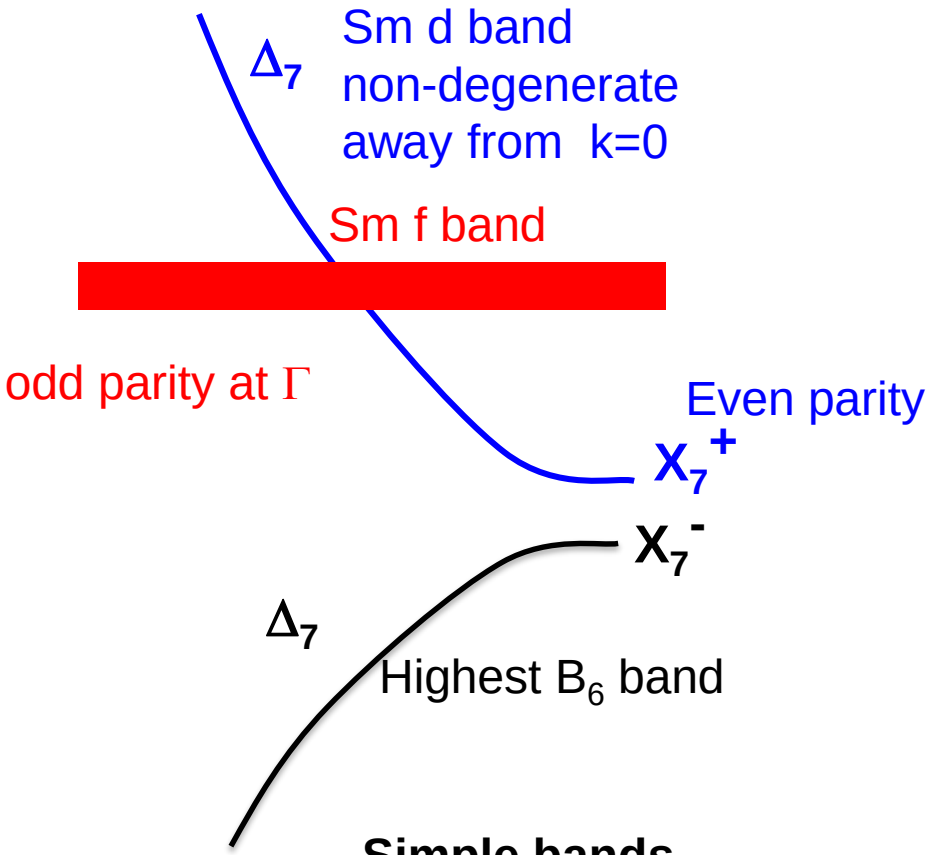
Topological Insulators

SmB_6 – Topological "Kondo Insulator"



Simplest possible structure
Simple cubic



Simple bands
Well known from LaB_6

Until we put in the f states

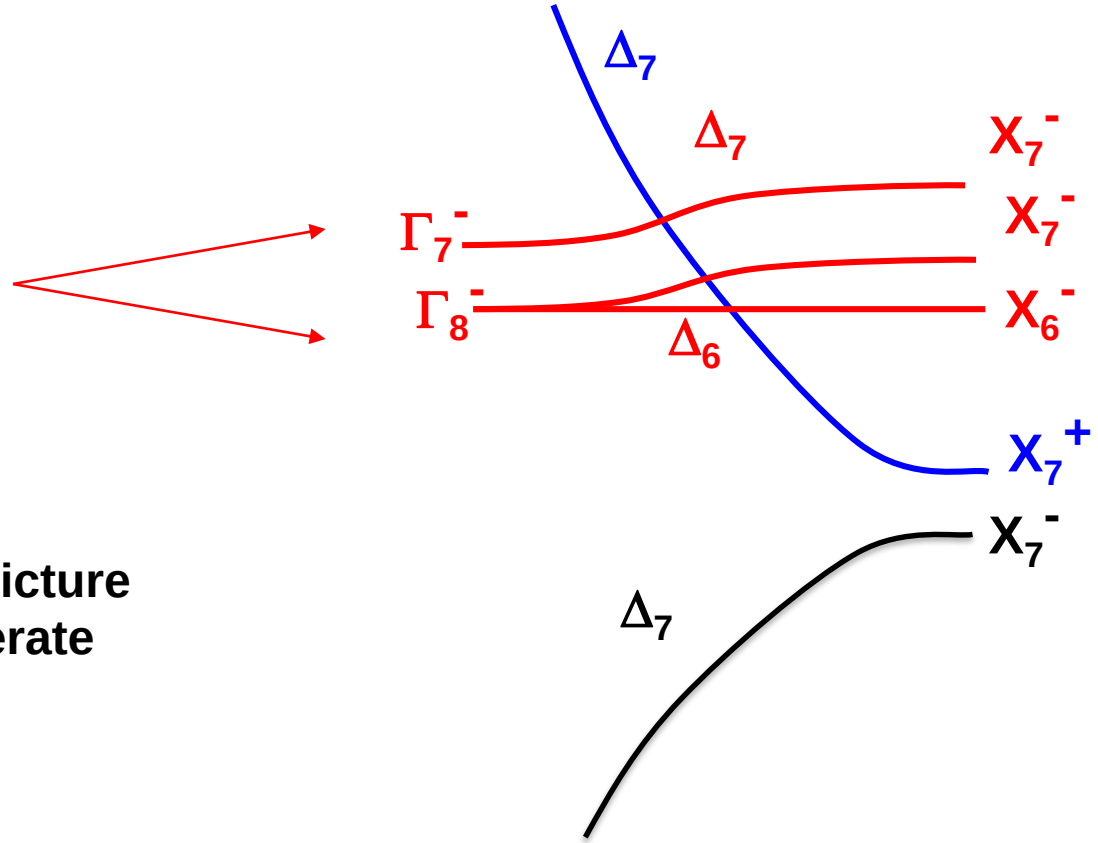
What is required for a topological insulator?
Bands cross – change parity
Spin-orbit coupling

SmB_6 – Topological "Kondo Insulator"

Including the f states – independent particle picture

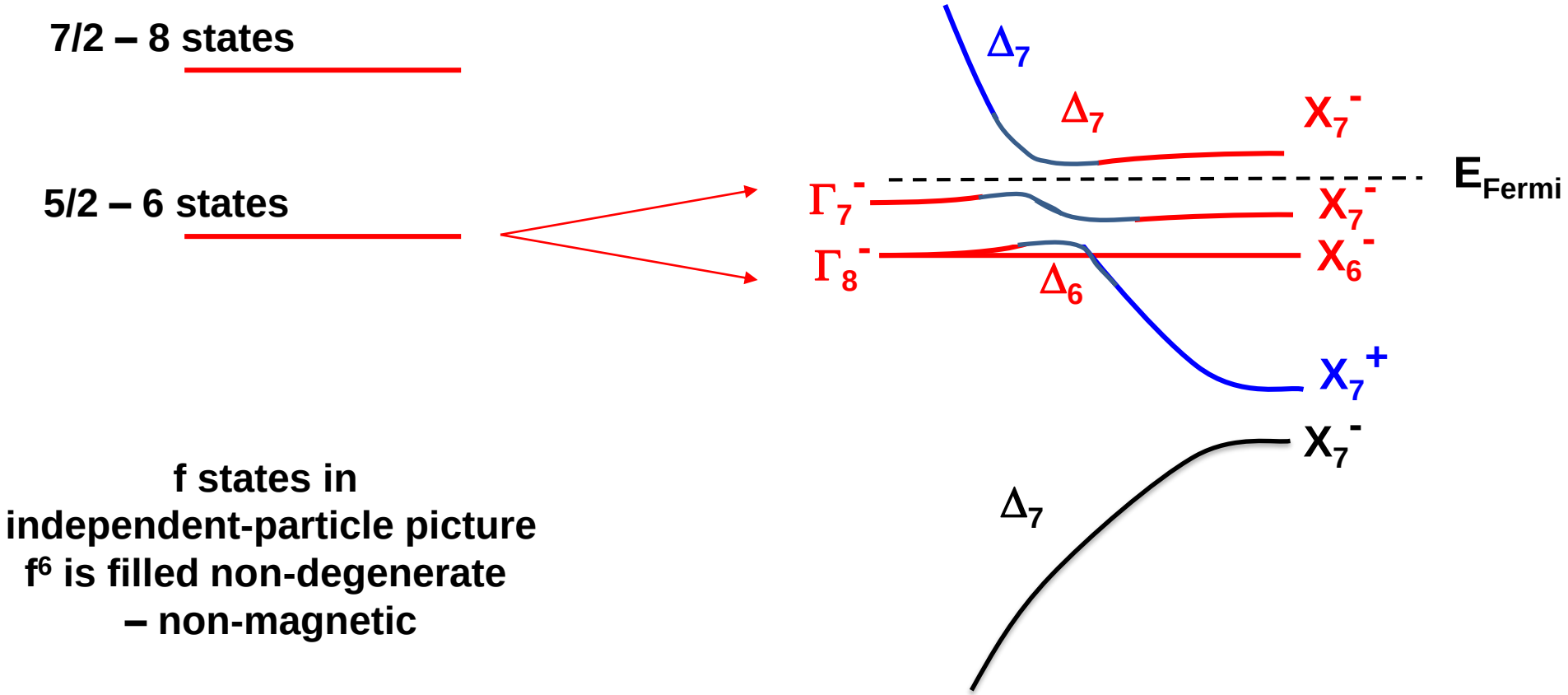
7/2 – 8 states

5/2 – 6 states



f states in independent-particle picture
f^6 is filled non-degenerate
– non-magnetic

SmB_6 – Topological "Kondo Insulator"

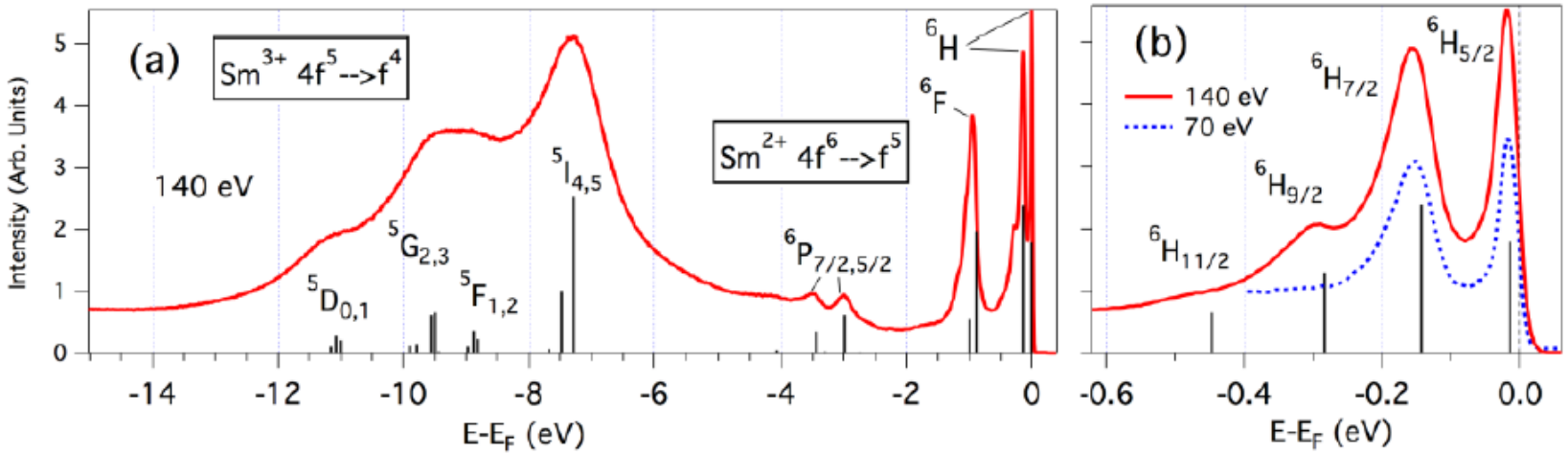


f states in independent-particle picture
f^6 is filled non-degenerate – non-magnetic

Hybridization opens a gap
Properties needed for topological insulator

Actual spectrum of f states in SmB_6?

Photoemission measures the spectrum for removing an electron



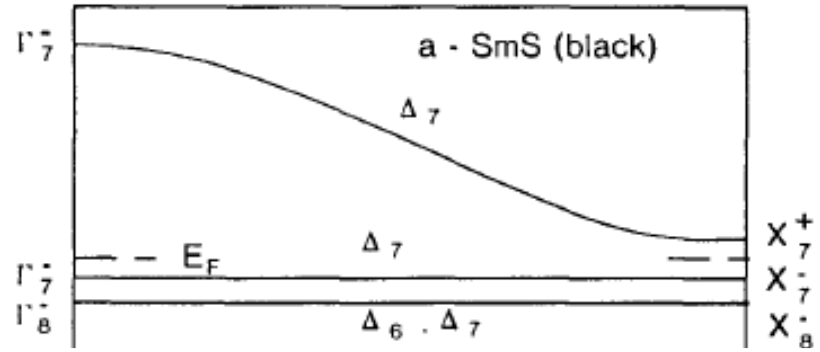
Interactions of many eV, multiplets, ….

How can we hope to understand a gap of meV?

How can we hope to show it is a topological insulator or not?

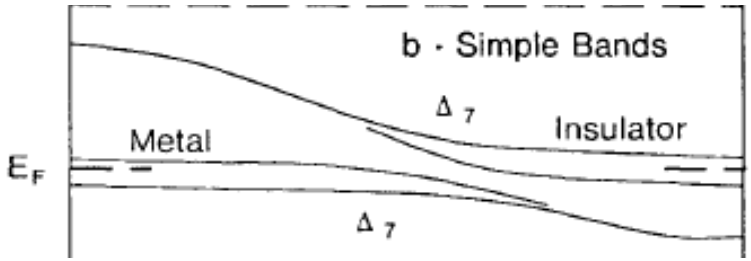
"Real" properties of f^6 and f^5

First consider SmS



Black SmS Neutron scattering had already shown this is correct order

Lowest energy to remove electrons is Γ_7



Gold SmS

Bands meant to describe ONLY the lowest state (closest to E_F)
Could not answer – is f dispersion upward – insulator
or
downward – metal

Martin& Allen 1979

Conclusions

- **Satisfying (at least to me) that present-day methods describe important physical phenomena for good physical reasons**
  - **Calculations + fundamental principles**
  - **Continuity principle**
  - **Care with interpretation for T=0**

- **By sticking to fundamental principles and listening to more analytic, mathematical theory we arrive at totally new concepts**

- **Much left to be done!**