Electronic Structure Computation Meets Strong Correlation

Guiding Principles

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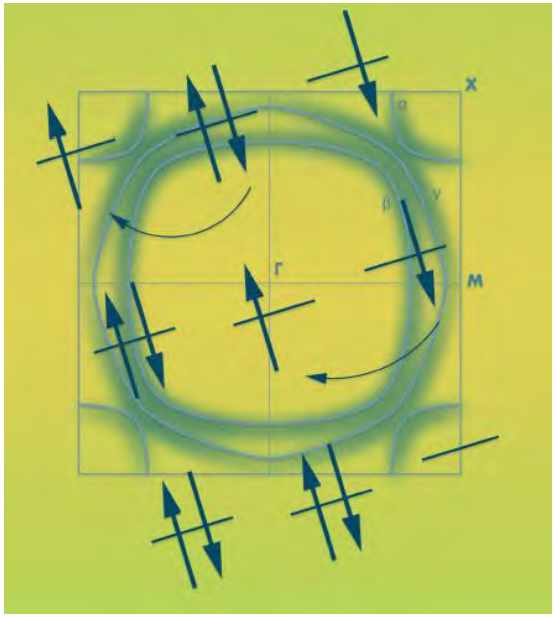
THE PROBLEM

The many-body interacting electron problem

Among the most challenging problems in all of physics, with old and new challenges

Consider the cover picture for this school



The arrows represent electrons that interact so strongly on each site that there is only zero or one electron on each site which act as weakly-interacting localized spins

The fuzzy lines represent the Fermi surface where the electrons act as weakly-interacting itinerant particles

Each picture is supported by experiments.

Each is supported by theory and heavy calculations

The topic of this lecture is how to reconcile these two pictures: concepts, interpretations, models, calculations

Questions for you

What does the term correlation mean?

The general definition in statistics

The definition(s) used in the fields that are topics of this school.

What does "strong correlation" mean?

Strong" relative to what? Meaningful only in a particular context?

What are signatures of correlation?

Experimental evidence?

What are examples of materials and phenomena?

Evidence for something called "strongly correlated"?

What is a "Mott insulator"?

Surely strong correlation to cause a metal to become an insulator!

What is the Luttinger theorem and to what extent is it a "theorem"?

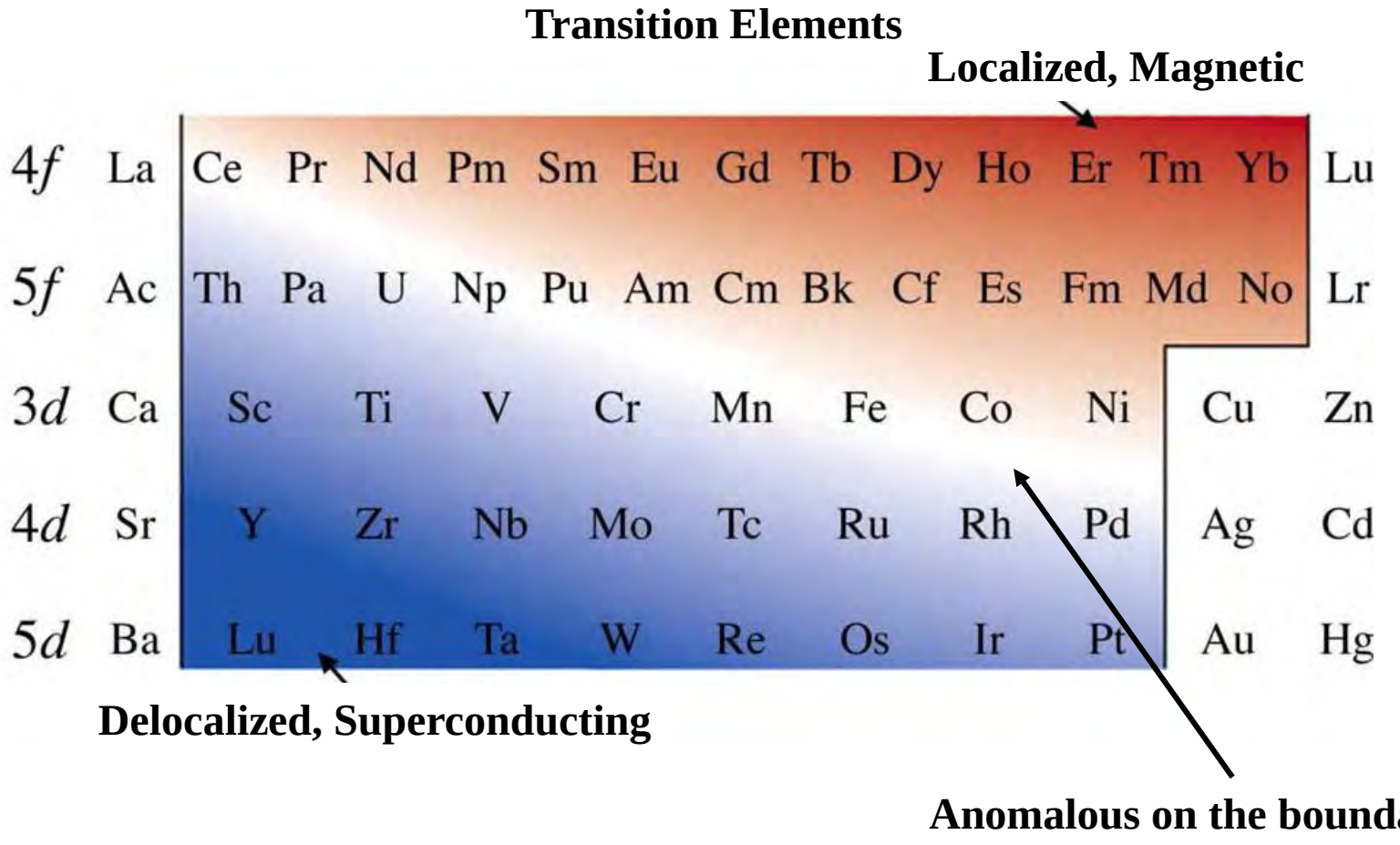
Consider these questions during the school!

What are the materials and systems that are the main topic of this school?

- **Materials where there are strong interactions on localized atomic-like states**

  Typically transition metals, lanthanides and actinides

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



Original due to J. L. Smith

What are the materials and models that are the main topic of this school?

- **Models – the simplest is the Hubbard model**

  A lattice with one state per site and hopping matrix element t between neighboring sites.

  If two electrons are on the same site there is an interaction energy U

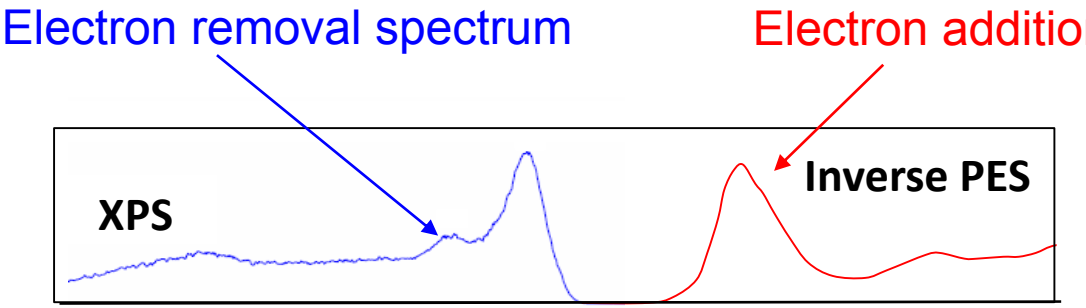
- **In this model strong interaction means U >> t**

- **Real systems are more complicated but the basic idea in an on-site interaction U compared to band width W due to hopping**

- **The most interesting cases are where U and W are comparable – competition that leads to many phenomena**

How do we understand experiments that indicate phenomena very different from independent-particles?

NiO **The original Mott Insulator – Verwey and Mott – 1930's**



Experiment – mainly Ni 3d from L. H. Tjeng

Gap in paramagnetic phase for T > Tc
even though it should be a metal

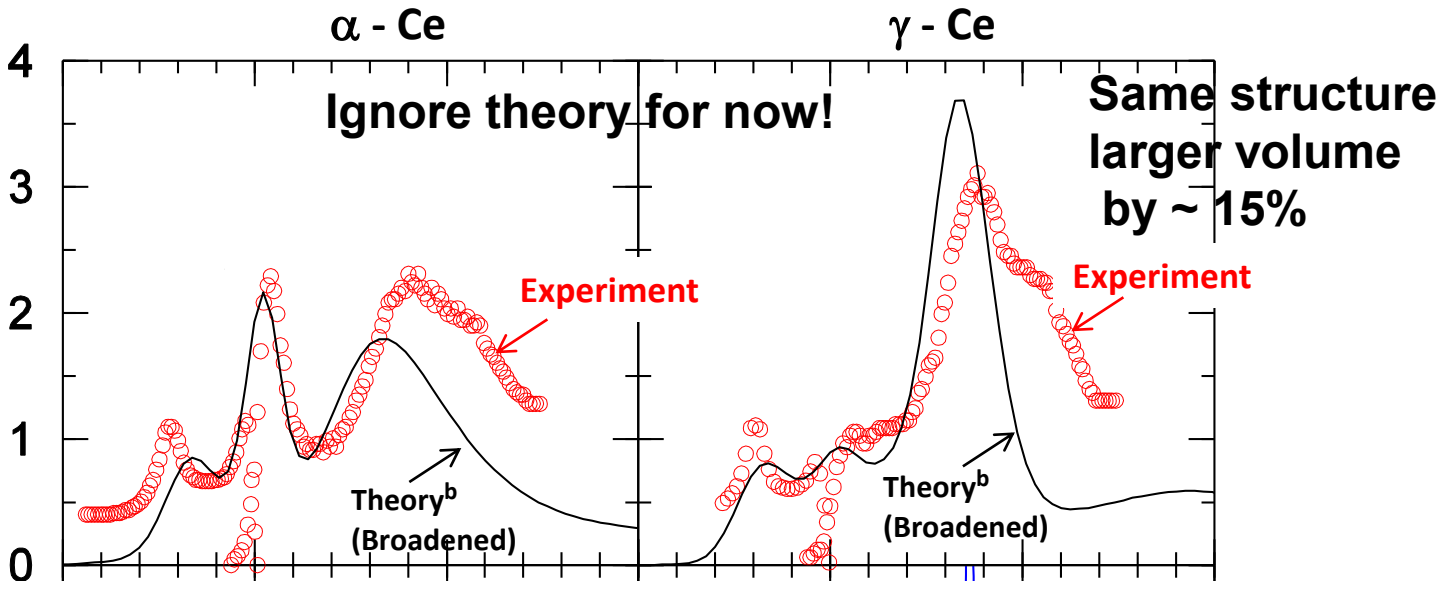
Violation of Luttinger theorem?

Can important aspects of this Mott insulator be understood by perturbation theory?

How do we understand experiments that indicate phenomena very different from independent-particles?

Cerium

Approximately 1 electron in the 4f states per site
Anomalous phase transition where volume changes



Independent electrons would have one peak at Fermi energy

Entropy consistent with electrons acting like spins at high temperature or high volume

Guiding Principles
The Luttinger theorem

The volume of the Fermi surface is conserved – same as an independent-particle calculation – no matter how strong the interaction

Consider "turning on" from zero to the actual value, the volume is the same so long as there is no phase transition

Odd # of electrons per cell – metal

Even # of electrons per cell – insulator or semimetal with multiple partially filled bands

Derived by Luttinger using Green's function perturbation methods -- explicitly for zero temperture

What if the perturbation expansion or the detailed derivation does not converge?

Continuity Principle

Turn the argument around

Like Landau did to propose Fermi Liquid Theory – not an explicit mathematical derivation but instead a statement of continuity

Whether or not a particular expansion converges:

So long as there is no phase transition

The volume of the Fermi surface is conserved – same as an independent-particle calculation – no matter how strong the interaction

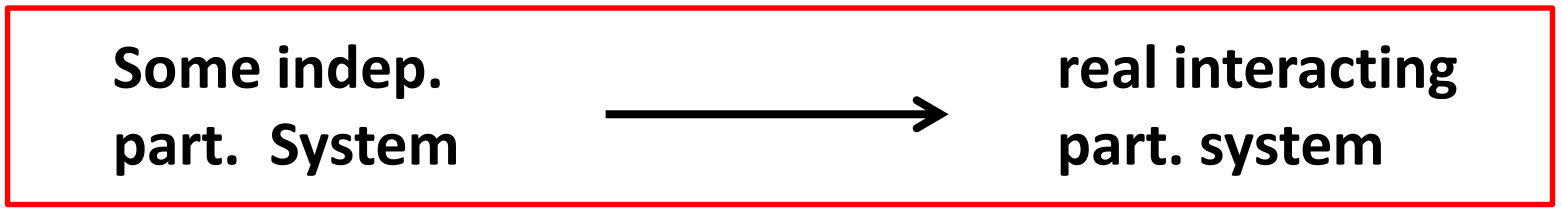
Odd # of electrons per cell – metal

Even # of electrons per cell – insulator or semimetal of multiple partially filled bands

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



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 should not let this get in our way for getting at the properties we can address!

Mott Insulator

A system that "should" be a metal that is an insulator

"Should" may be different for different definitions

But there may be other conditions – different definitions by different people

- **Only in a phase that is disordered**
- **Only for zero temperature**

Many Approaches
Each with advantages - disadvantages

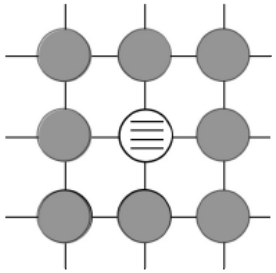
Models

- Exact solutions in some cases – when do they apply?
- Very useful approximate solutions

Numerical calculations (DFT and other methods)

- The only way to treat realistic solids
- For example, using DFT to predict structures

Anderson Model and Kondo Effect



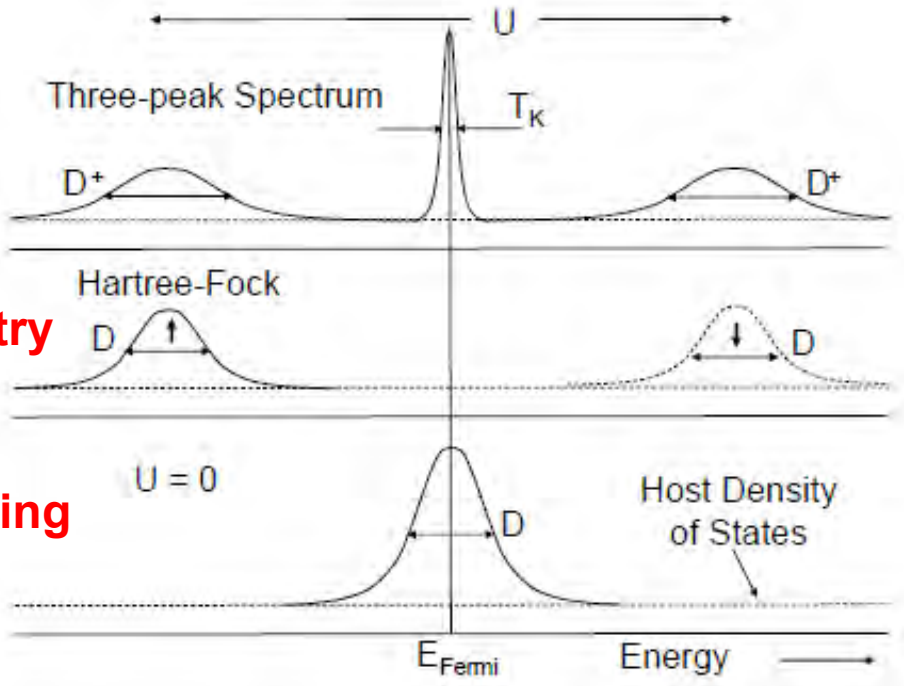
Impurity with interaction U in a metal considered to be non-interacting

Consider zero temperature

Exact

Broken symmetry

Non-interacting



Exact solution agrees with Friedel sum rule

Peak height at Fermi energy same as non-interacting particles

Corresponds to Luttinger theorem applied to an impurity

For temperature $T >> T_{kondo}$ the peak disappears

Electrons decoupled from metal -- act like spins on the impurity site

Heavy numerical theoretical methods

- **DFT - Kohn-Sham equations**

  Very successful for ground state - structures, phonons, static screening,
  Various functionals, extensions make it useful for excited states, …

- **GW – example of many-body perturbation theory**

  Excitations
  Dynamic Green's function G(r,r',ω), screening W(ω)

- **DMFT – example of treating local on-sit correlation accurately**

  Set of methods – requires inputs of parameters from some other method
  Treats longer range correlations only in mean field
  Dynamic Green's function $G_{ij}(\omega)$
  Excitations and temperature dependence

- **Quantum Monte Carlo and Exact Diagonization**

  Very general - Many uses

Density Functional theory

DFT is an approach to dealing with the full interacting electron-nuclei problem

Essential to be clear that there are two step in DFT

Hohenberg Kohn theorem

A formal proof that all properties of the interacting system are determined in principle by the ground state density . That is, each property is a functional of the density

Kohn-Sham approach

Consider only the ground state density and energy.

Leads to a practical method to calculate the ground state density and energy for the interacting system using independent-particle equations

The only approximation is the form of a functional Exc[n] that takes into account effects of exchange and correlation

The great success for ground state properties is due to the fact that there are good approximations useful for wide ranges of materials

But remember that the only things that are supposed to be correct are the ground state density and energy!

It is an independent-particle approximation to interpret the bands from the Kohn-Sham equations as actual energies for electrons

DFT + U

Modify the Kohn-Sham approach

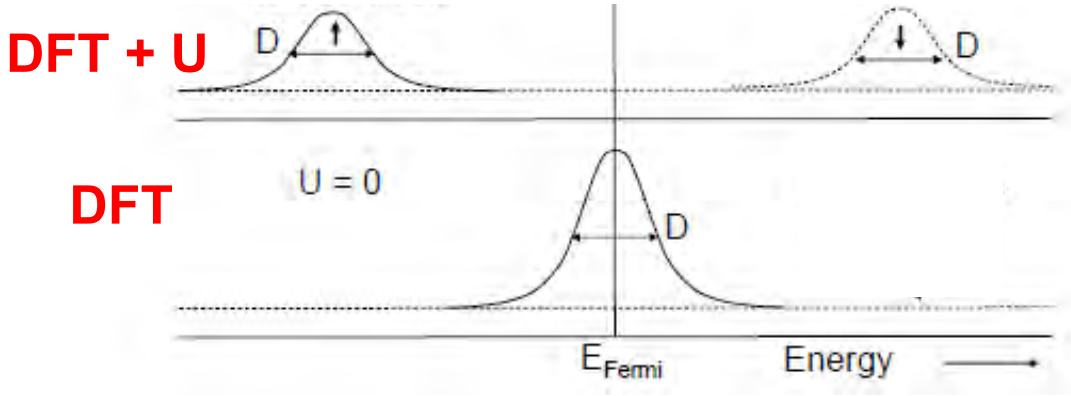
Add a on-site interaction U.

Broken symmetry ordered state like in the unrestricted Hartree Fock approximation for the Anderson impurity problem

The broken symmetry may be physical in a solid, e.g., a magnetically ordered phase

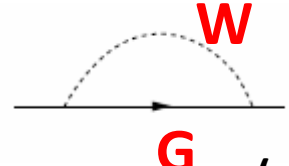
Schematic picture of the effect of U in DFT + U

(analogous to Anderson Impurity model)



Perturbation expansions in the interaction

"GW" Approximation $\Sigma =$



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

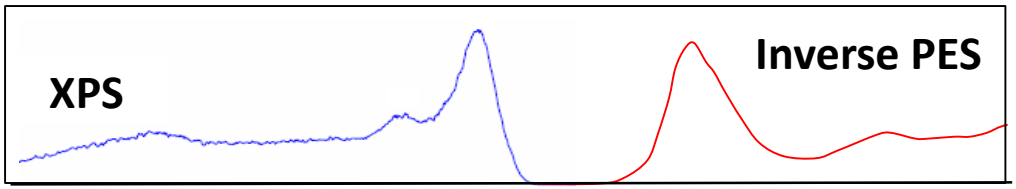
(not bare G_0)

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? ….

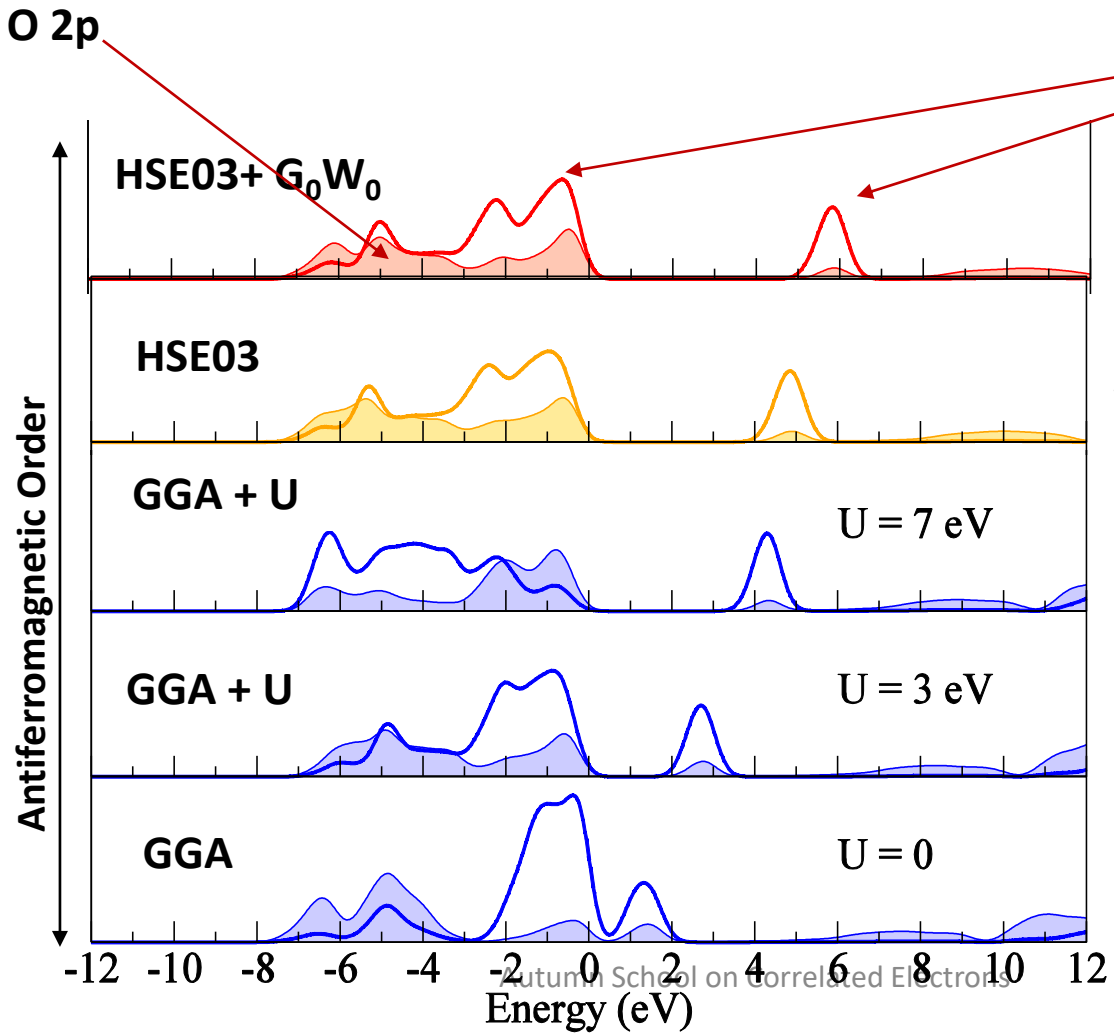
More recently methods been established where the same approach is applied to many materials -- G_0W_0 with well-chosen input – usually NOT LDA or GGA

NiO



Experiment – mainly Ni 3d
from L. H. Tjeng

Similar in ordered antiferromagnetic phase for T < Tc and disordered paramagnetic phase for T > Tc

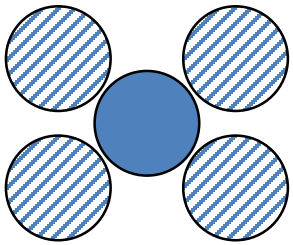


Various Density functional approximations
GGA, GGA +U , and HSE
and
GW perturbation methods
Provided by C. Roedl
(similar to work of others)

Dynamical Mean Field Theory - DMFT

Naturally applicable to high temperature

Solve for atom embedded in average field due to neighbors

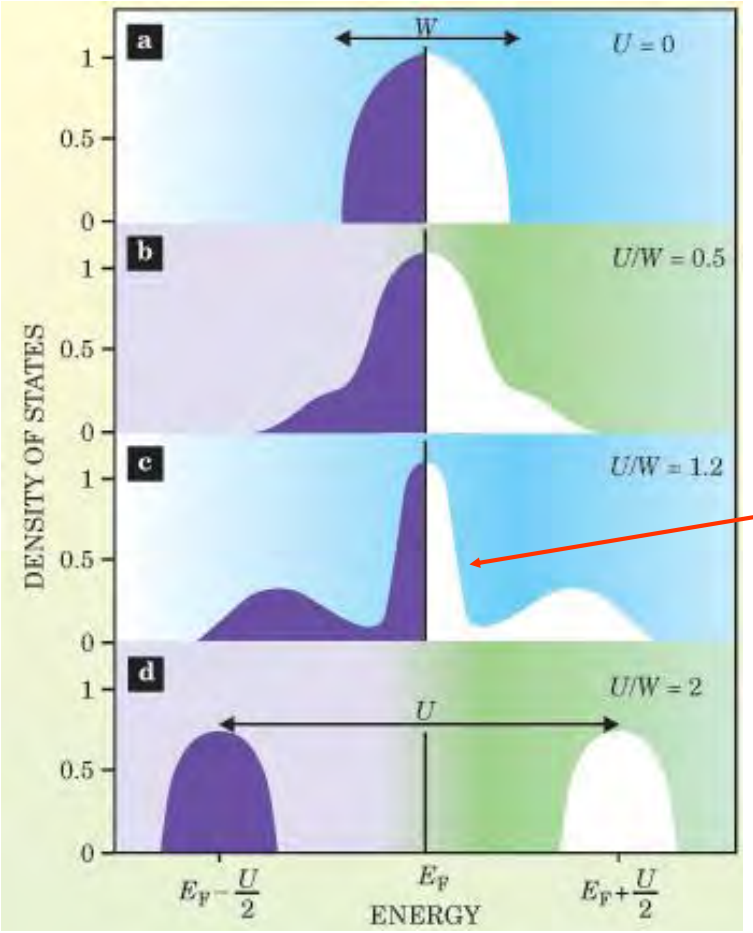


- **Spectrum of Green's function on central site**

  $G(E) = [\, E - H_0 - \Sigma(E) \pm i\delta]^{-1}$

  consistent with neighbors

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



New energy scale

Kotliar and Vollardt, Physics Today 2004

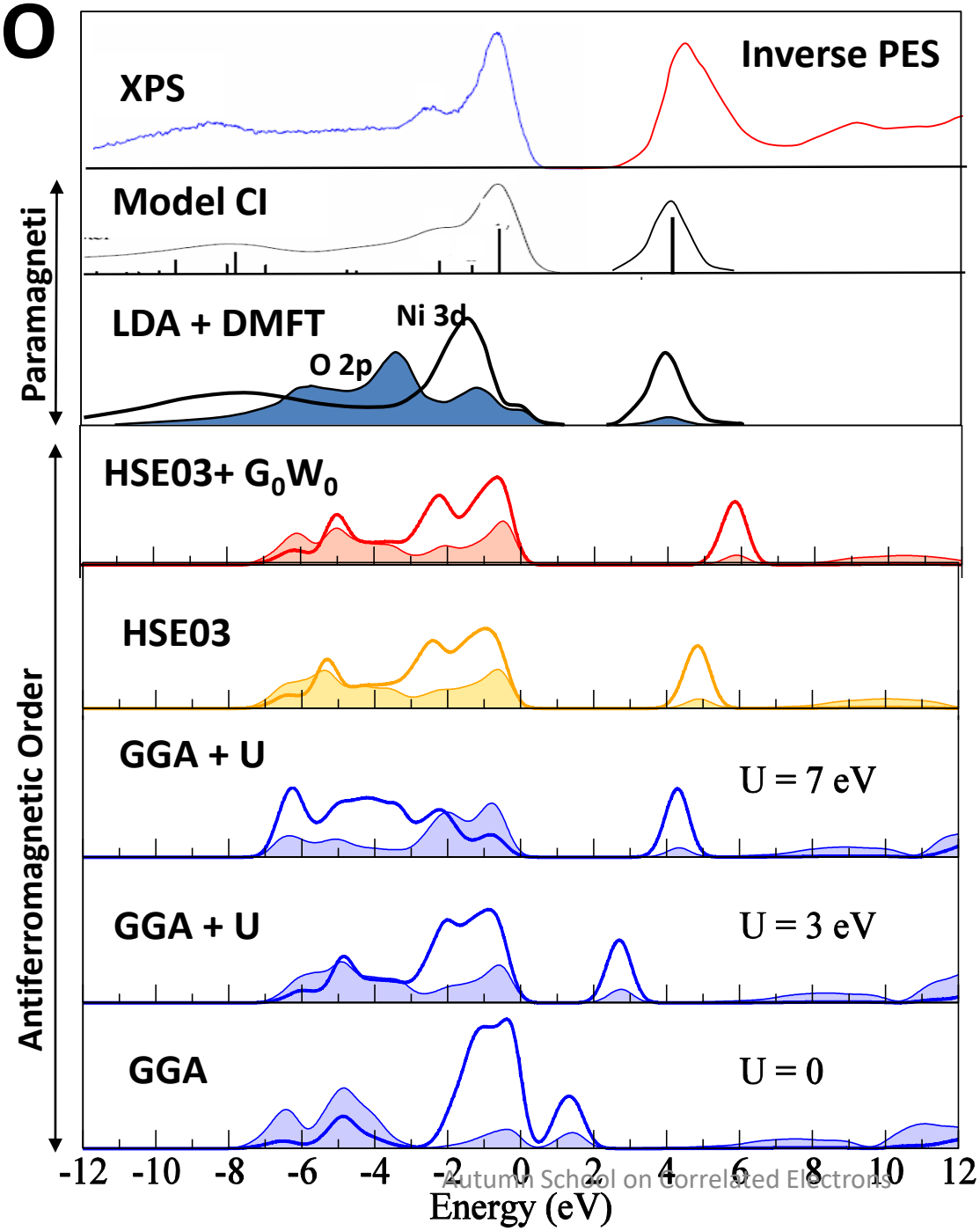
Input to DMFT

DMFT is a set of methods
Needs input for application to real materials

Interaction U
Dispersion of bands
Other bands not included in the strongly interacting d and f bands

Present-day methods
DFT – ad hoc Kohn-Sham since band do not have definite meaning
Static screen U
GW – improved bands with interpretation as quasiparticles
Dynamic screen U(ω)

NiO



Experiment – mainly Ni 3d
from L. H. Tjeng

Calculations by Fujimori

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

Various Density functional approximations
GGA, GGA +U , and HSE
and
GW perturbation methods
Provided by C. Roedl
(similar to work of others)

Conclusion for NiO

It is physically correct (even if approximate) to treat the low T ordered phase of NiO using perturbation theory methods such as GW that apply at T=0

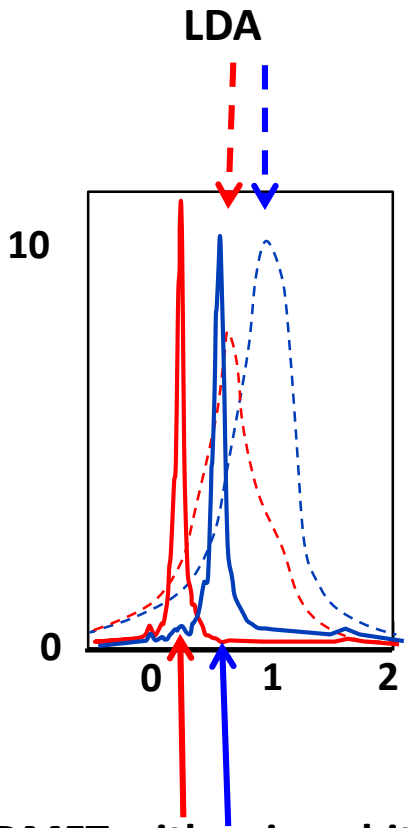
Agrees with Luttinger theorem! Unit cell is doubled – consistent with insulator

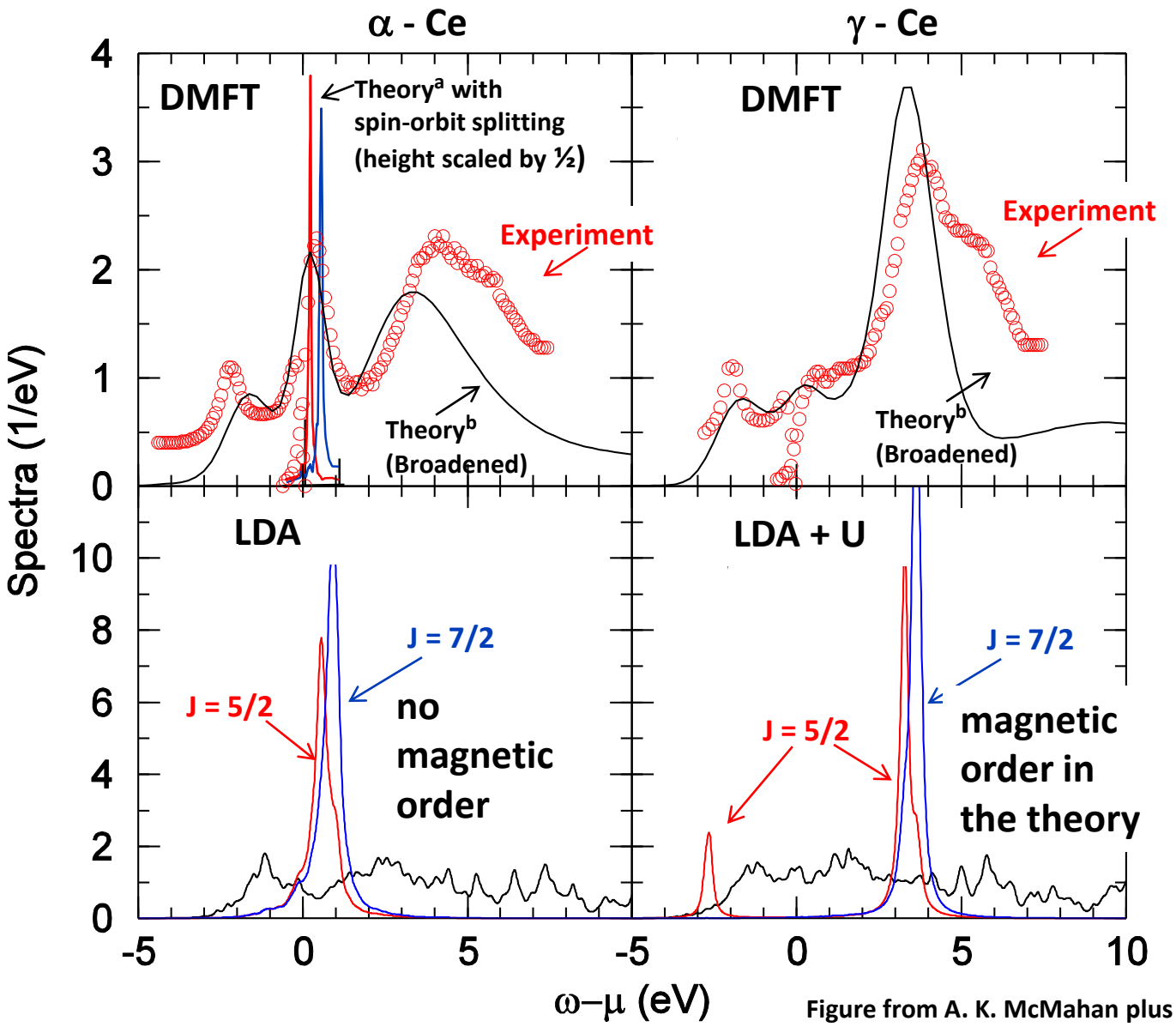
It is physically correct (even if approximate) to treat the high T disordered phase of NiO using DMFT that treats correlation accurately on site and correlation between sites in a mean field approximation – reasonable at high T

Does NOT violate Luttinger theorem which strictly applies only at T=0

Cerium

U = 6 eV from constrained DFT





DMFT with spin-orbit splitting – Haule, et al
Peaks ~10 times narrower than in LDA

Figure from A. K. McMahan plus part taken from figure by K. Haule

[a] Haule, et al, PRB 81, 195107 (2010)

[b] Held, et al, PRL 87, 276404 (2001)

Conclusion for Cerium

It is NOT surprising to have three peaks!

Exactly what we expect from the Anderson impurity model and the Luttinger theorem

Must have a Fermi surface at low T with volume the same as in a Kohn-Sham calculation

The low T approach is appropriate for the α phase
High T for the γ phase

Not proven here but explained in the paper

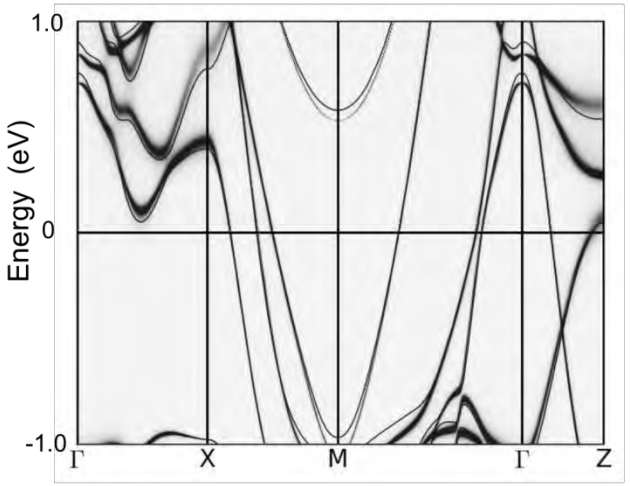
See next slide for a cerium material that shows a VERY large effect

DFT+DMFT -- $CeIrIn_5$

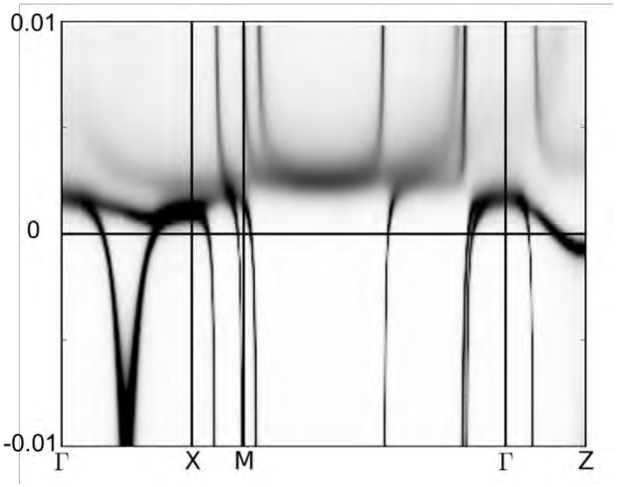
Heavy Fermion Material

LDA+DMFT, single-site approximation

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
4f states act like spins

f states strongly coupled to form narrow band at low T
4f states act like itinerant electrons

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)

Conclusions

- I do not mean to tell you how to think
- My purpose is to tell you what I think ----
  and present some evidence
- We have interesting, challenging problems and powerful methods
  and yet more interesting, challenging and powerful in the future
- I hope I have indicated
  - One MUST have clear ideas to know how to design and interpret calculations, experiments, …..
  - Guiding principles provide a framework, Luttinger theorem, role of temperature, …..
  - Look broadly – classes of materials, models, ….
  - ……..
- These are not theorems in the mathematical sense
  - A real violation is most interesting of all
  - A "Mott insulator" at T=0
  - …….

Mott Insulator - Again

A system that "should" be a metal that is an insulator

"Should may be different for different definitions

But there may be other conditions – different definitions by different people

Only in a phase that is disordered

Only for zero temperature

Much work recently indicates that a Mott insulator at T=0 would have topological order!

Conclusions II

- **Examples:**
- **Experiment indicates cerium does not order magnetically, and there is ~1 4f electron**
- **Given that information alone, the Luttinger theorem requires that there MUST be a peak at the Fermi energy no matter how strong the interaction and how narrow the peak**

- **Ce in Lanthanum is a Kondo system with a small Tk – narrow peak at Fermi energy (Not shown in this talk)**

- **$CeIrIn_5$ may look complicated but the simple answer is the spectacular behavior shown**

- **Despite all this standard calculations nowadays like DFT and DFT+U, plus simple reasoning, reveal the expected behavior before doing heavier calculations!**

Not shown in talk
question for the reader

What about SmB_6?

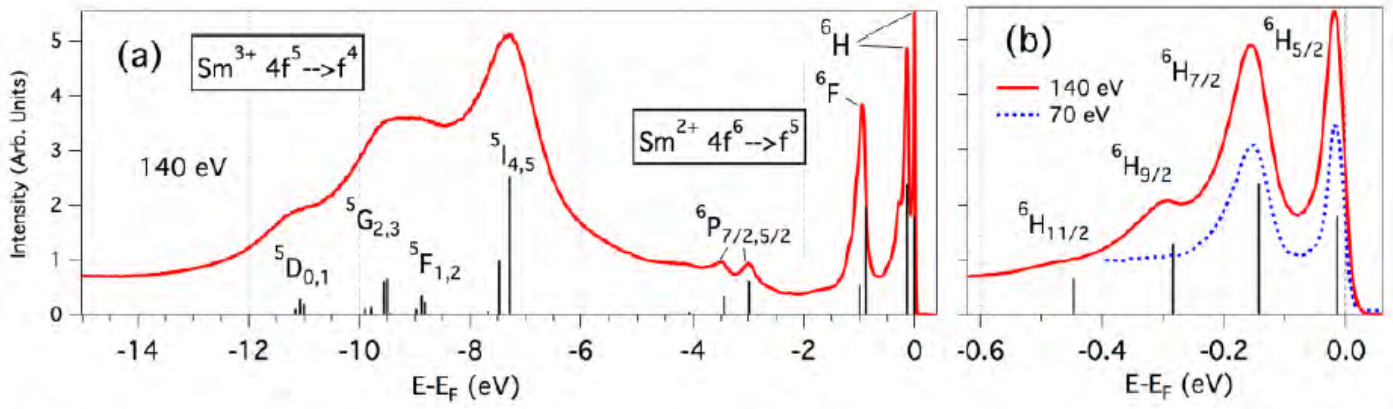
It seems very easy to justify the theory for materials like Si and Na

How can this possibly work for SmB_6 which is now widely investigated as a narrow gap topological insulator.

Photoemission shows interactions of many eV, multiplets, ….

How can be hope to understand a gap of meV?

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



Photoemiossion in SmB_6