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Title: Unravel Electronic Structure in Strongly Correlated Materials

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Los Alamos
NATIONAL LABORATORY

Unravel Electronic Structure in Strongly Correlated Materials

Jian-Xin Zhu (T-4)

LA-UR-24-XXXXX

Outline

- **Introduction and motivation**
  - Correlated electron materials

- **Theoretical approaches to strongly correlated materials**
  - First-principles dynamical mean-field theory (DMFT) framework
  - Applications to *f*-electron correlation effects

- **Summary and outlook**

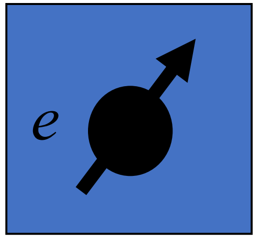
Traffic/congestion

Ordered/organized

Correlation

Courtesy: Houston Chronicle

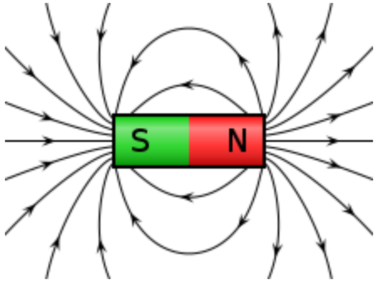
In what ways matter can become ordered



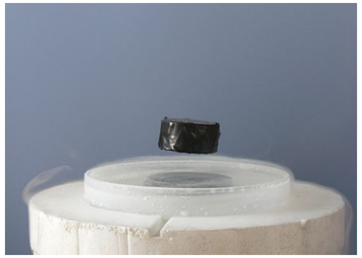
- Landau paradigm

Crystals

Magnets

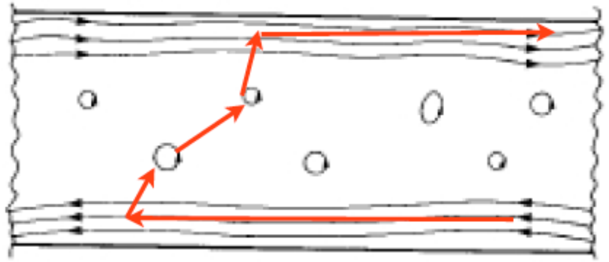


Superconductors

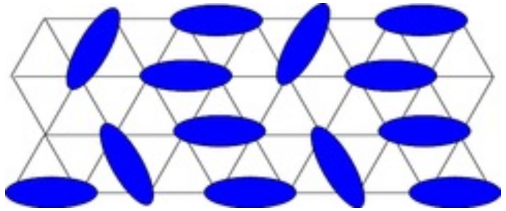


- Beyond Landau paradigm

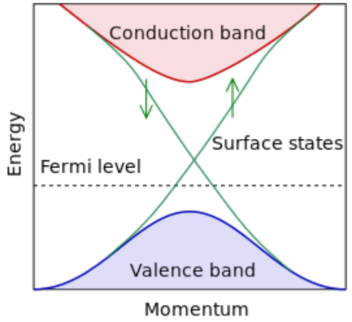
Quantum Hall States



Quantum Spin Liquids

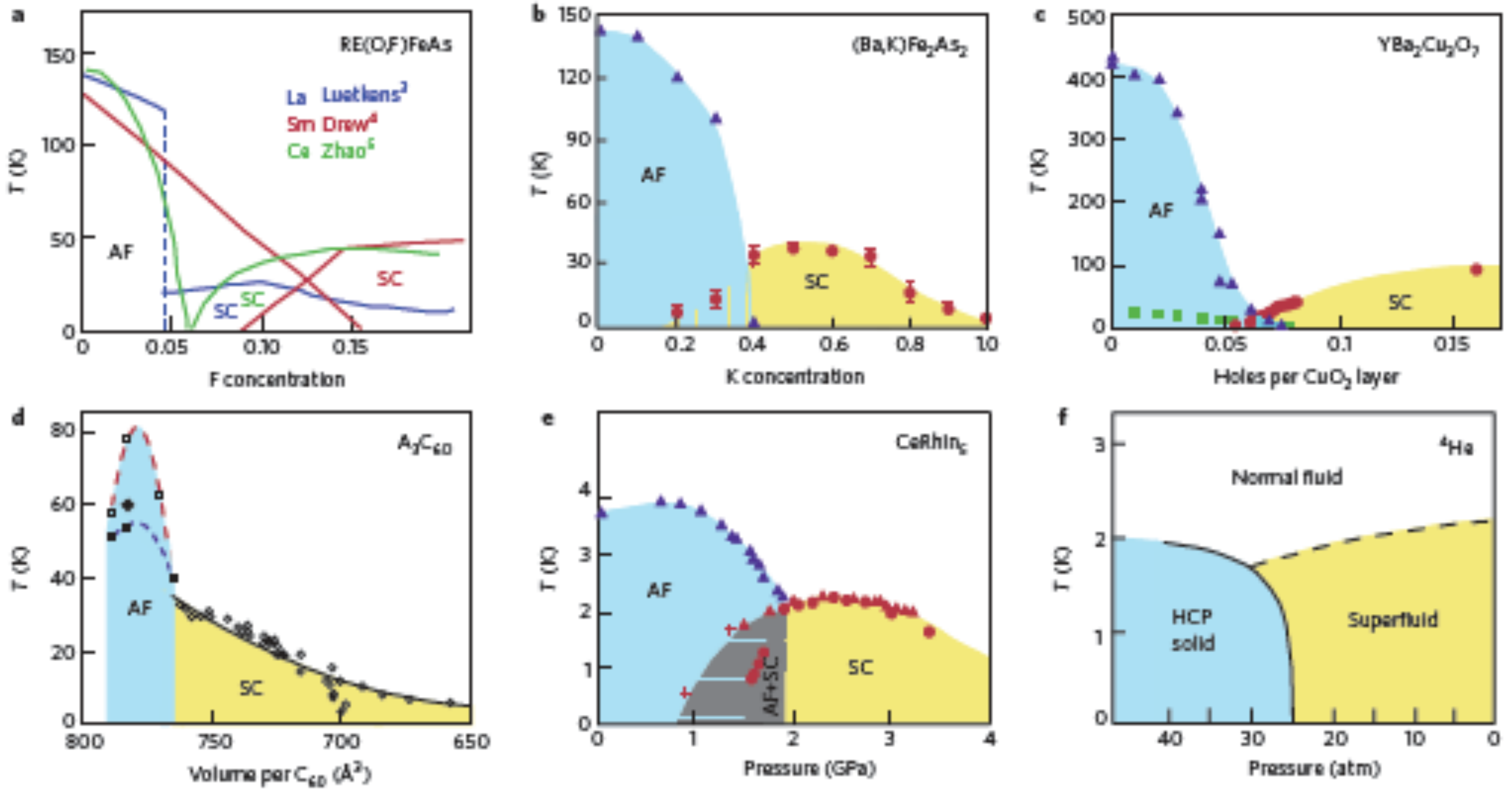


Topological Insulators

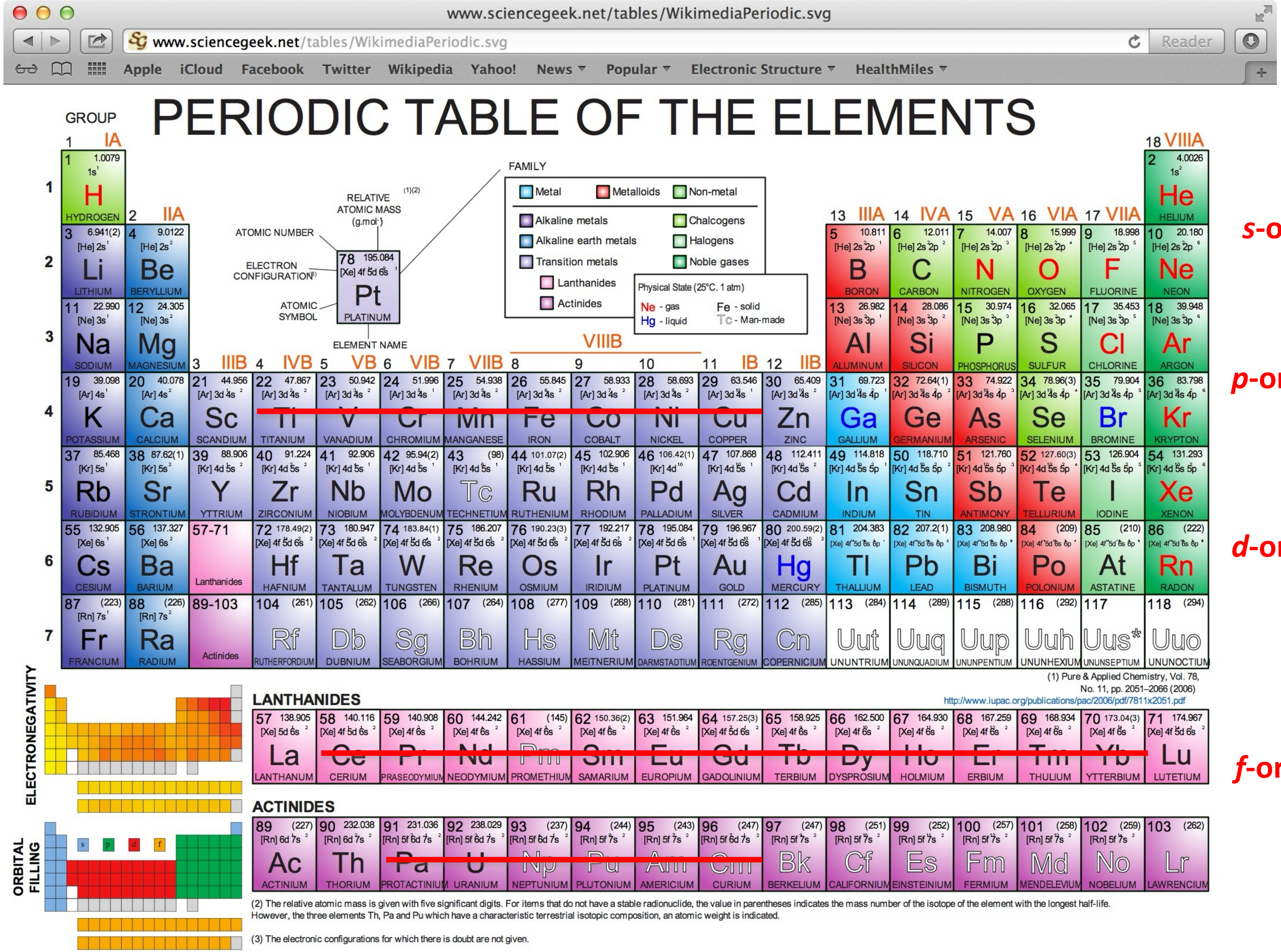


Strongly Correlation Meets with Topology in Quantum Materials

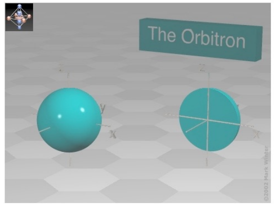
Emergent phenomena from strong correlations



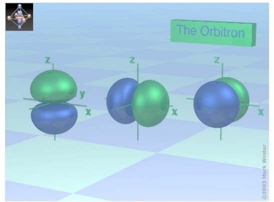
- Superconductivity in close proximity to AF magnetism.
- Ground state in different phases can be tuned by control parameters.



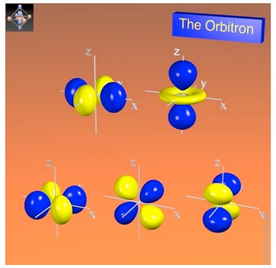
***s*-orbital**



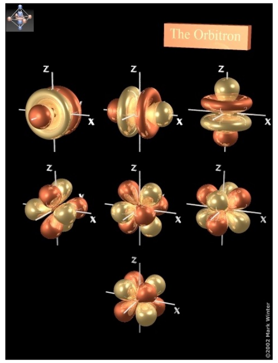
***p*-orbitals**



***d*-orbitals**



***f*-orbitals**



Quantum materials matter (plethora degrees of freedom & functionality)

- Interesting physics

Topology | Entanglement | Many-body interactions | Spin-orbit interactions | Quantum correlations fluctuations

- Emergent phenomena and test ground of fundamental physics

Weyl semimetals | Topological insulators/metals /superconductors | Majorana fermions | Superconductors | Quantum liquids

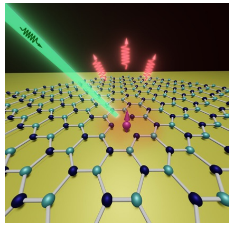
- Emerging technologies (extreme tunability)

Energy

Superconducting Maglev trains

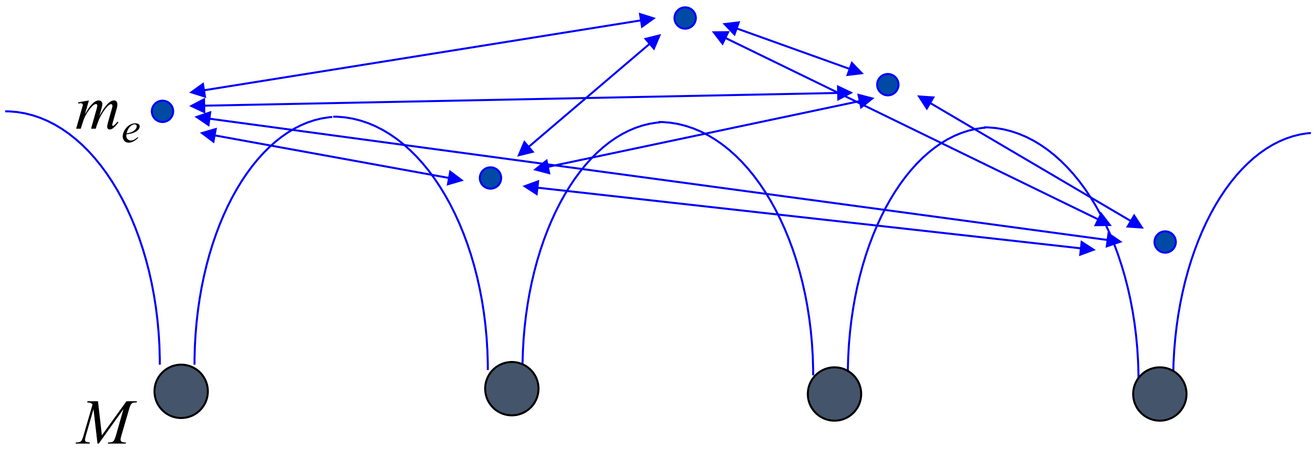
Qubits

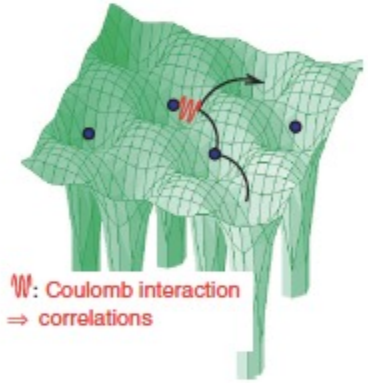
Quantum sensors



Nuclear Technology

In the Beginning, a Theory for Everything

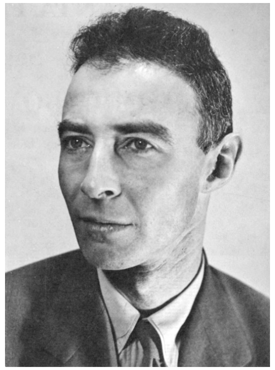




$$H = -\sum_i \frac{1}{2m_e}\nabla_i^2 + \sum_{i,I}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_I \frac{1}{2M}\nabla_I^2 + \frac{1}{2}\sum_{I,J}\frac{e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} \quad (*)$$

- Since $M >> m_e$, the lattice degrees of freedom can be treated adiabatically within the Oppenheimer approximation.

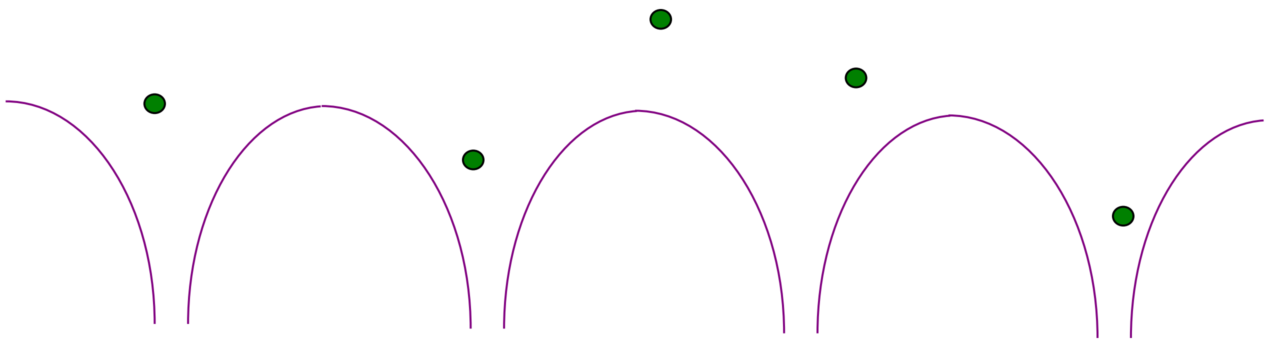
- Even so, electron degrees of freedom are still highly entangled. It is a hard problem and a direct/exact solution is impossible!



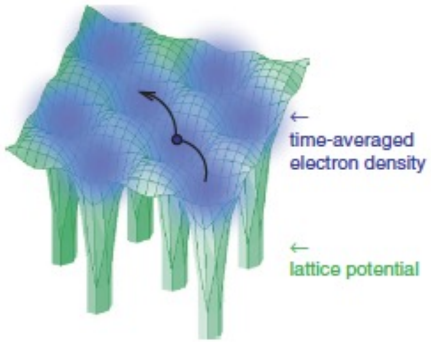
J. R. Oppenheimer

Density functional theory for ground state properties

• It maps the many-body problem onto an auxiliary independent-particle problem. These independent particles are Kohn-Sham particles.



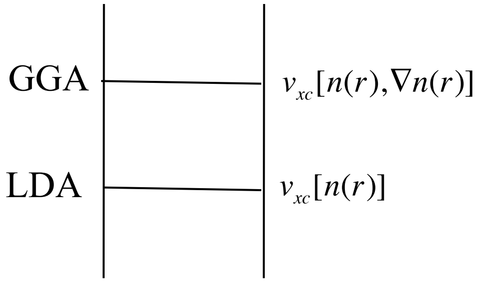
W. Kohn



$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + v_{eff}(\boldsymbol{r})\right)\psi_v(\boldsymbol{r}) = \varepsilon_v \psi_v(\boldsymbol{r}), v = 1,2,\cdots,N$$

$$v_{eff}(\boldsymbol{r}) = v_{e-l}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} dr' + v_{xc}(\boldsymbol{r}),$$

$$n(\boldsymbol{r}) = \sum_{v=1}^{N} |\psi_v(\boldsymbol{r})|^2$$

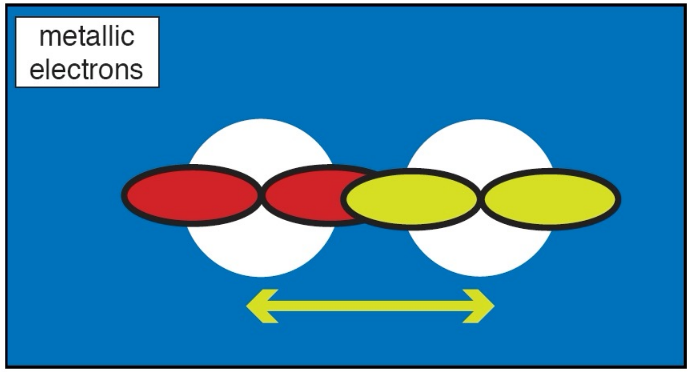


Jacob ladder [Perdew, MRS 38, No. 9 (2013)]

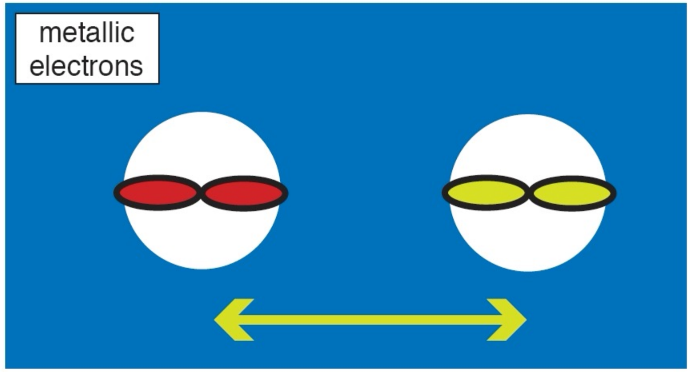
• The LDA-based theory are successful for many *s*- and *p*-electron ordinary materials (including ground state energies and bandstructure).

Hallmark of Strongly Correlated Electrons is the Narrow Band Phenomena

- Energy bands **narrow** as wave function **overlap** is reduced
- At some critical value of reduced overlap, electronic correlation causes states to **localize** rather than to narrow further
- Near the critical region, the LDA fails severely to describe Metal-Mott Insulator transition (e.g., La_2CuO_4, Cr-doped V_2O_3, and NiO)



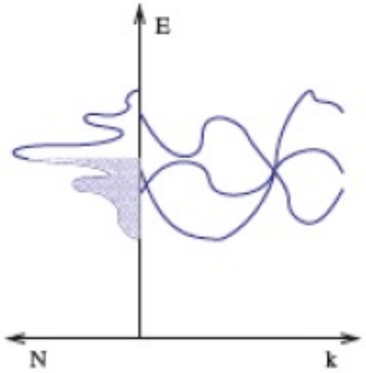
Bonding d-electron

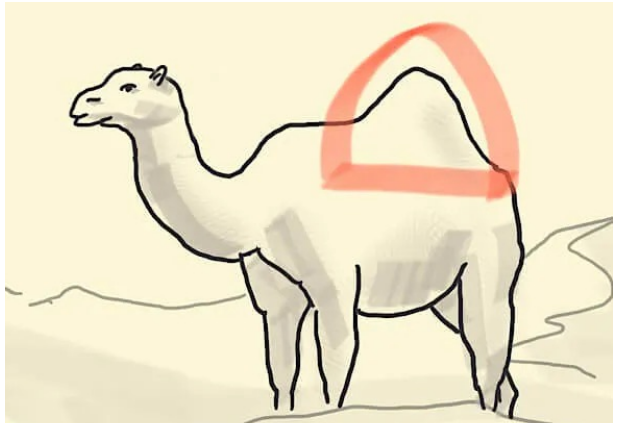


Non-bonding d-electron

Electronic Structure Theory

LDA [Weakly interacting systems]

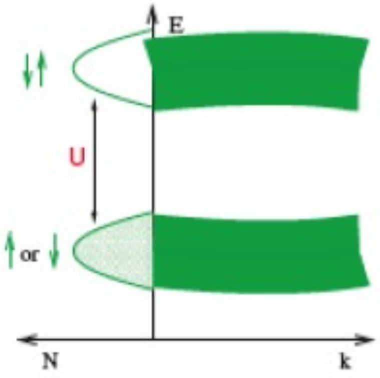


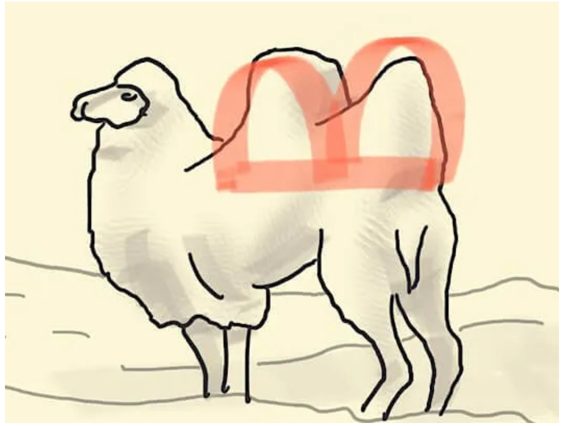


Dromedary

How to describe the transition between two phenomena?

LDA+U [Antiferromagnetic Mott insulator]

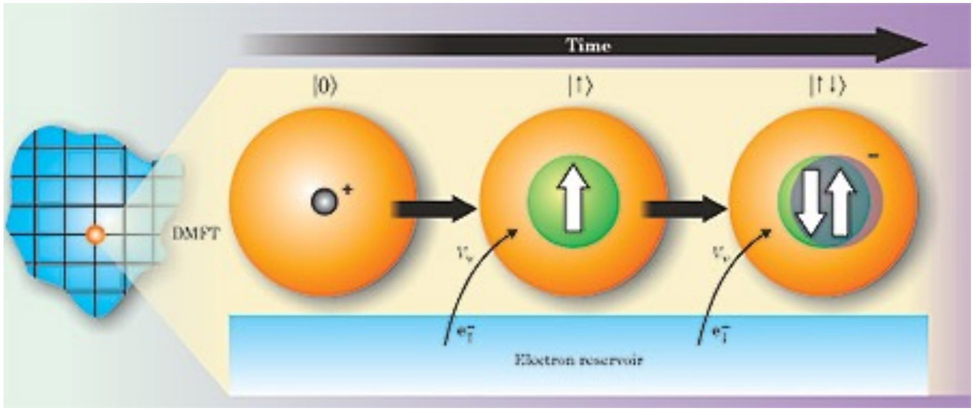


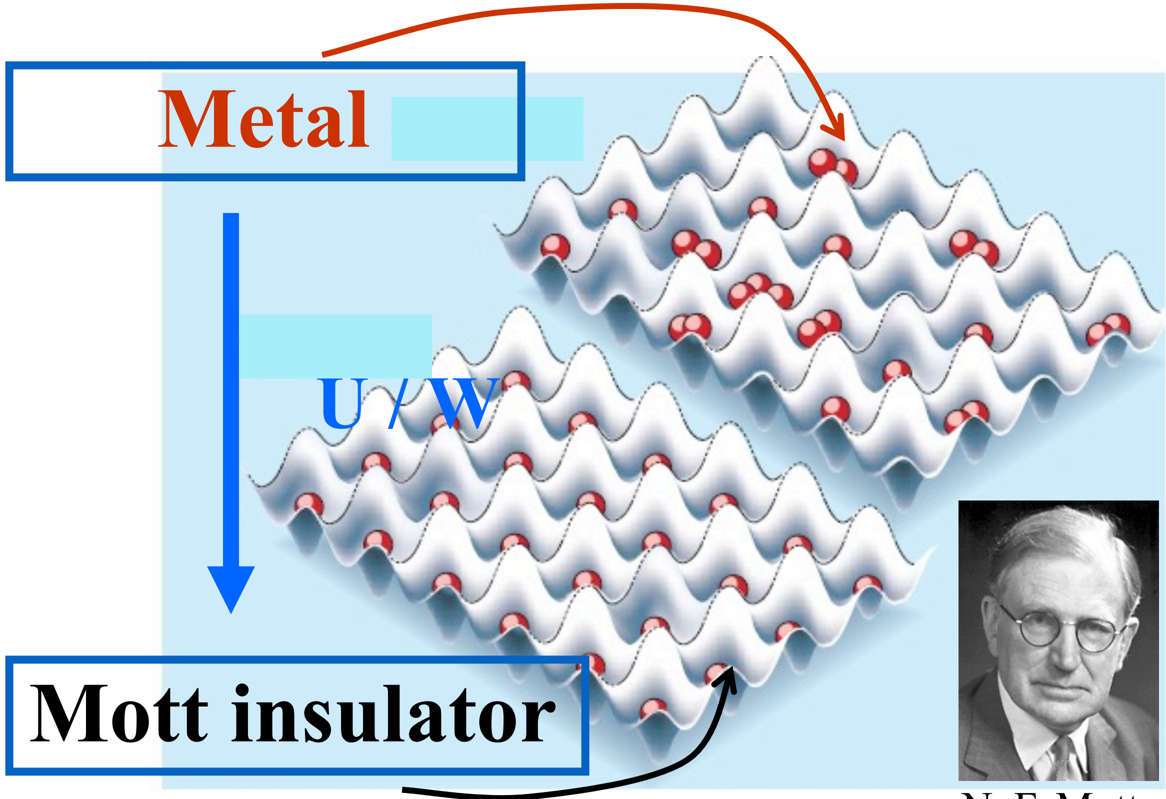


Bactrian

Cartoon taken from sketchplanations.com

DMFT Captures the Metal-Mott Insulator Transition

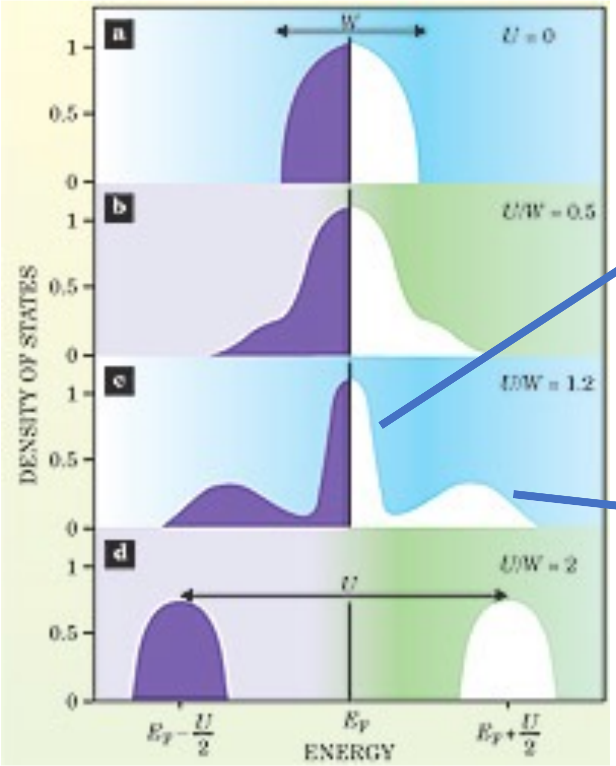


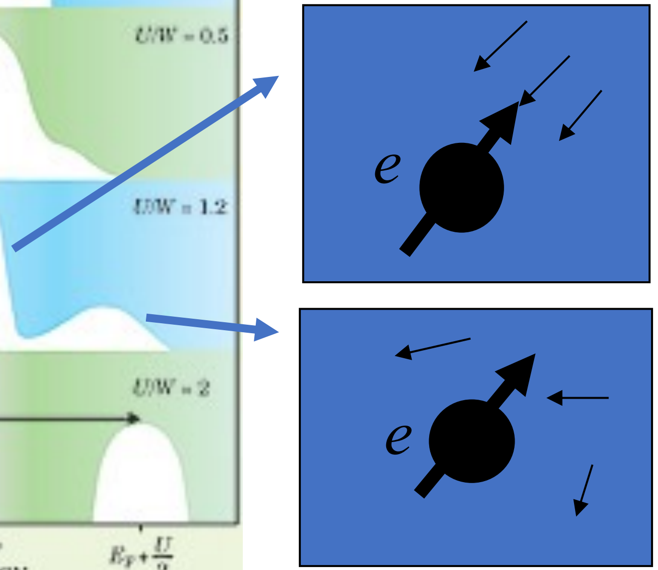


N. F. Mott

$$H = -\sum_{i,j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

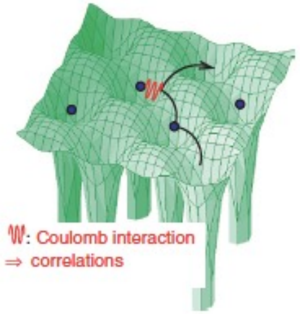
J. Kondo





Spectral density evolves as the ratio of the Hubbard repulsion U to the bandwidth W in a one-band Hubbard model. [Kotliar and Vollhardt, Physics Today (2004)]

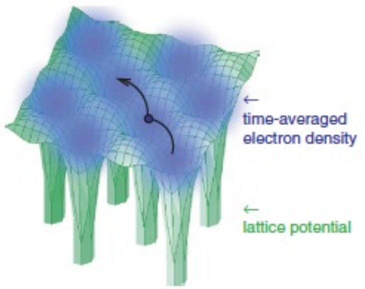
Method: Density Functional theory + Many-Body Approach



LDA+DMFT

$$h^{(LDA)}_{\mathbf{k},\alpha\beta} = \left\langle \chi_{\mathbf{k}\alpha} \left| -\nabla^2 + V_{eff}[n] \right| \chi_{\mathbf{k}\beta} \right\rangle$$

$$O_{\mathbf{k},\alpha\beta} = \left\langle \chi_{\mathbf{k}\alpha} \mid \chi_{\mathbf{k}\beta} \right\rangle$$

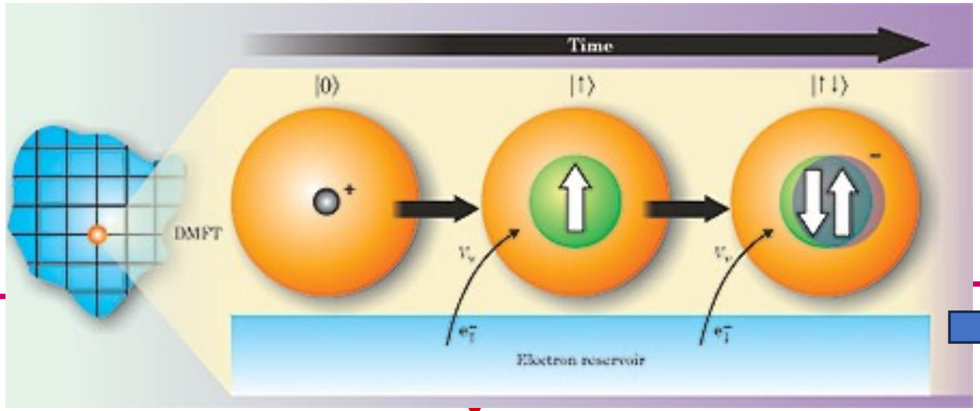


$$G_{loc}(i\omega) = \sum_{\mathbf{k}} \left[(i\omega + \mu) O_{\mathbf{k}} - h^{(LDA)}_{\mathbf{k}} - \Sigma(i\omega) + \Sigma_{dc} \right]^{-1}$$

Σ

$G_{loc} + \Sigma$

DMFT



$$n(\mathbf{r}) = T \sum_{i\omega_n, \mathbf{k}, \alpha\beta} \chi^*_{\mathbf{k}\alpha}(\mathbf{r}) G_{\alpha\beta}(\mathbf{k}; i\omega_n) \chi_{\mathbf{k}\beta}(\mathbf{r}) e^{-i\omega_n \eta}, \ \eta = 0^-$$

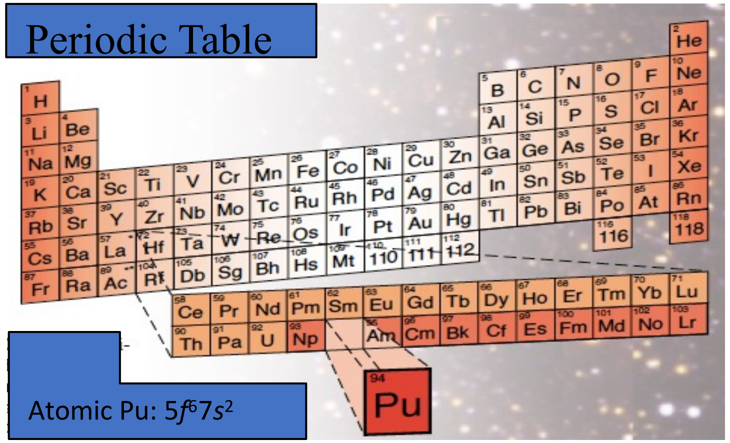
- LDA: Local density approximation; DMFT: Dynamical Mean-Field Theory)
- G (Green's function) and Σ (self-energy) are frequency dependent, capture the temporal quantum fluctuations.

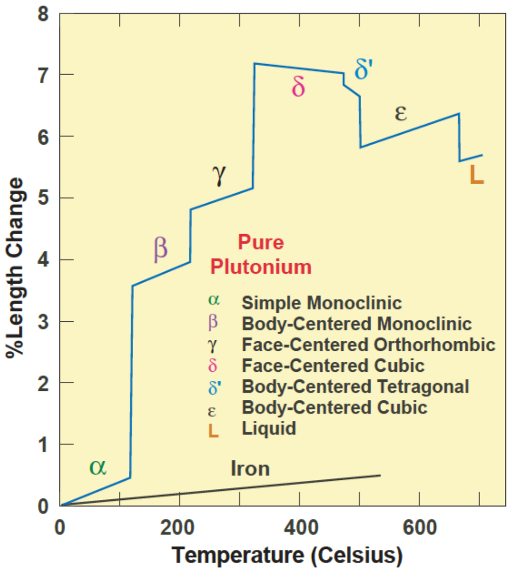
> 5-decades of numerical techniques to quantum impurity problem

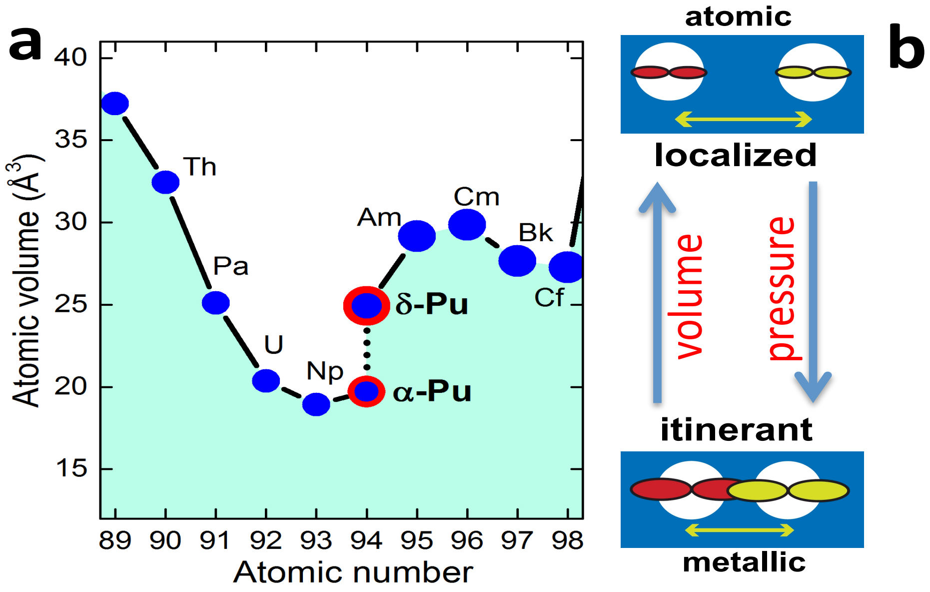
- Quantum Monte Caro
- Diagrammatic perturbation
- Exact diagonalization
- Gutzwiller wavefunction
- …

Kotliar et al., RMP (2006)

Pu: Most complex metal in the periodic table

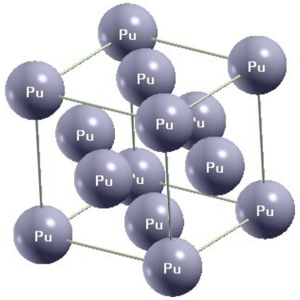






Pu has many anomalous physical properties

How to stitch all pieces of puzzle together?



volume & lattice, bulk modulus

large mass enhancement

spectral properties

- Leverage LANL strategy of integrating theory and experiment

no magnetic order

Theoretical challenge to understanding of δ-Pu properties

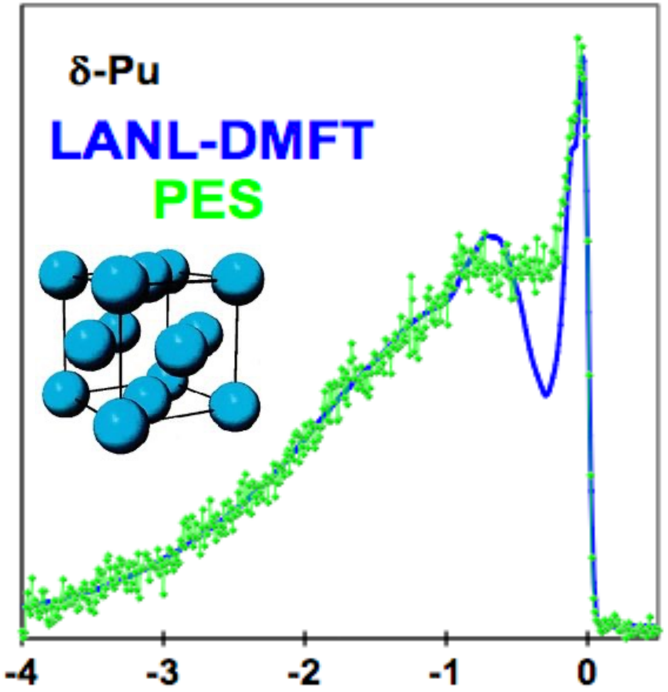
	Volume expansion	Nonmagnetism	Spectral properties
Conventional GGA[1]	✗	✓	✗
Magnetic GGA[2]	✓	✗	✗
LDA+U[3]	✓	✗	✗
Mixed level model[4]	✓	✓	✓
Around mean field LDA+U[5]	✓	✓	✗
LDA+DMFT[6-8]	✓	✓	✓

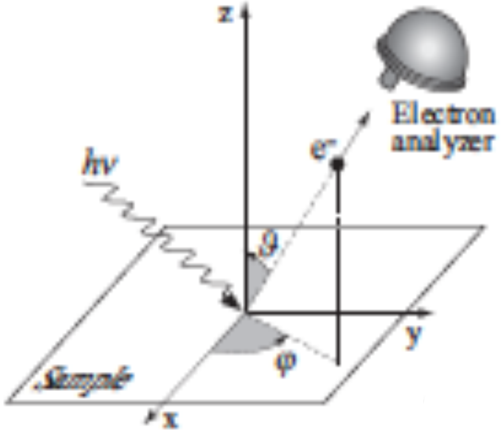
[1] Soderlind et al, PRB 50, 7291 (1994); [2] Soderlind et al., PRB 70, 144103 (2004); [3] Bouchet et al., JPCM 12, 1723 (2000); [4] Eriksson et al., J. J. Alloys and Comp. 287, 379 (2000); [5] Shick et al., Europhys. Lett. 69, 588 (2005); [6] Savrasov et al., Nature 410, 793 (2001); [7] Shim et al., Nature 446, 513 (2007); [8]J.-X. Zhu et al., PRB 76, 24518 (2007).

Recent development: S. Rudin, J. Nucl. Mater. 570, 153954 (2022) – Non-collinear 3Q spin structure

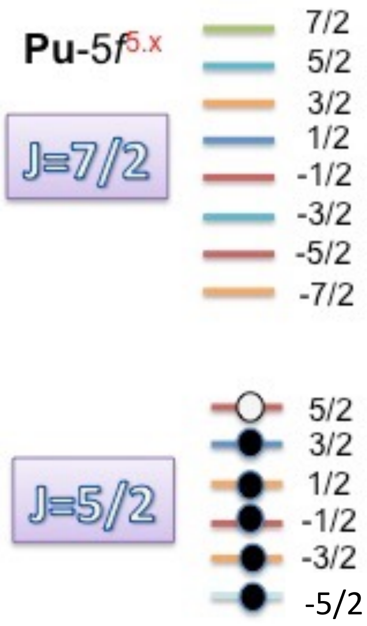
Central to the prediction from the LDA+DMFT: nonmagnetism (no static long- range order) originates from the Kondo screening.

Theory resolves the valence issue of Pu-5*f* electron in δ-phase (Validation)





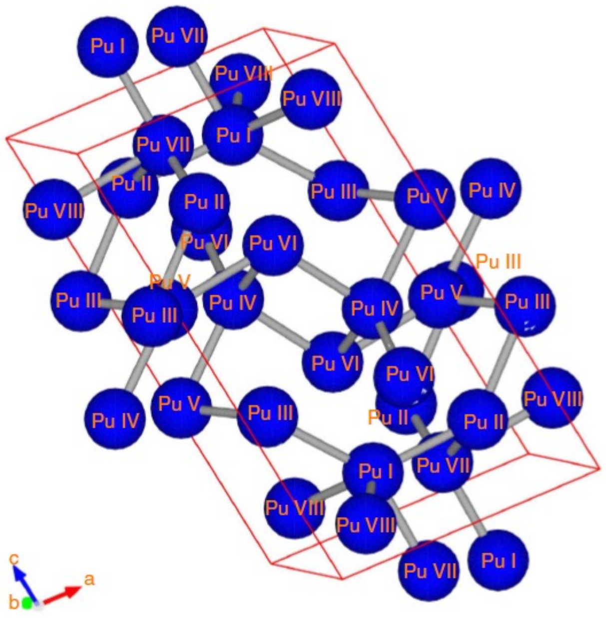
Photoemission spectroscopy (PES)

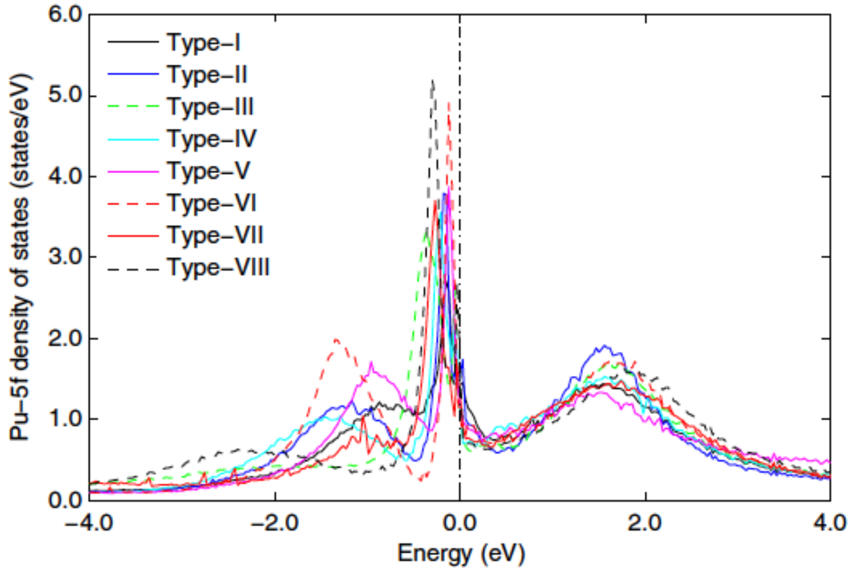


- Best agreement with the photoemission spectroscopy data taken at LANL
- Non-integer Pu-5*f* occupancy impacts understanding of magnetism in δ-Pu

JXZ *et al.*, Phys. Rev. B **76**, 24518 (2007)

Theory predicts site-selective electronic correlations in α-Pu metal (Prediction)



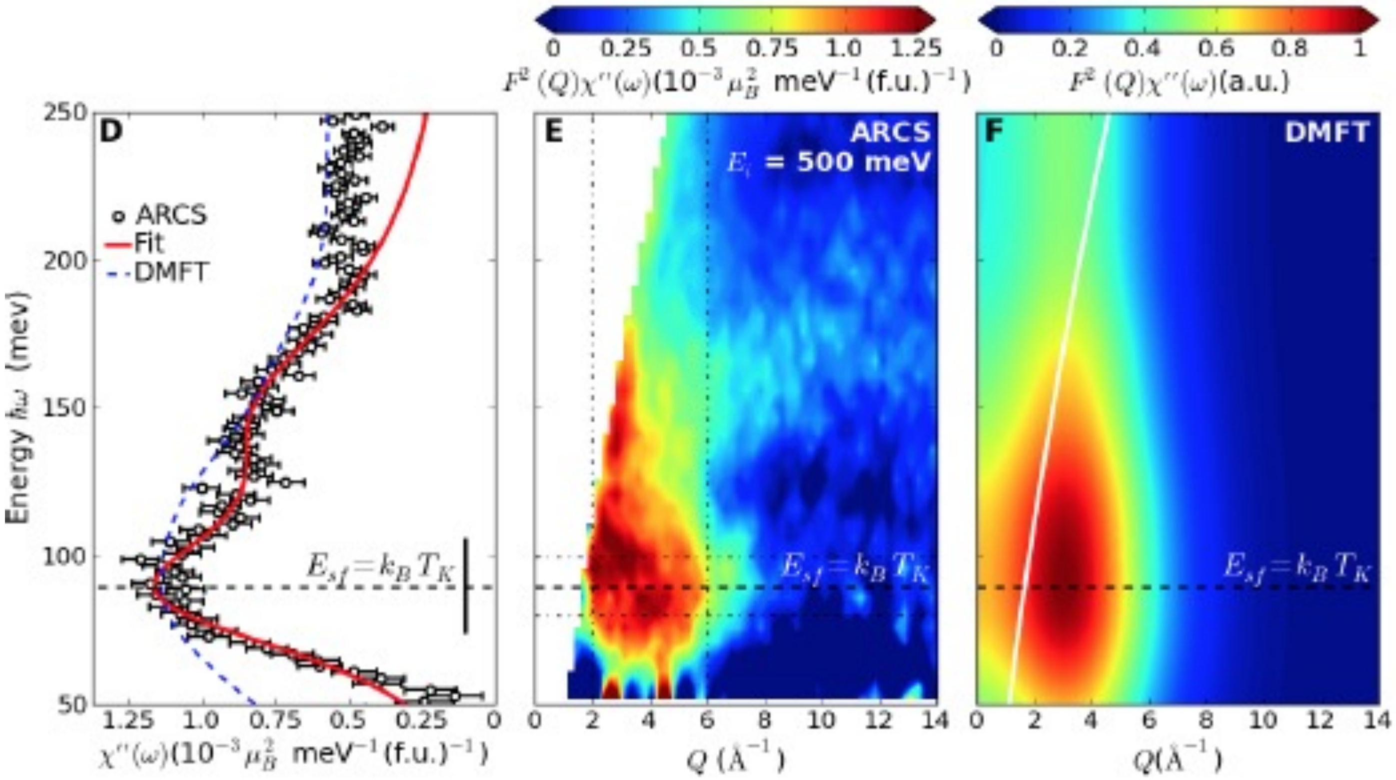


- Uncovers the "invidualism" of electronic correlations of Pu atom in α-structure
- Demonstrates the close structure-function relationship
- Paves the way to explore the entire phase diagram of Pu

JXZ et al., Nature Communications **4**, 2644 (2013)

Track valence-fluctuating ground state in δ-phase of Pu metal (Validation)

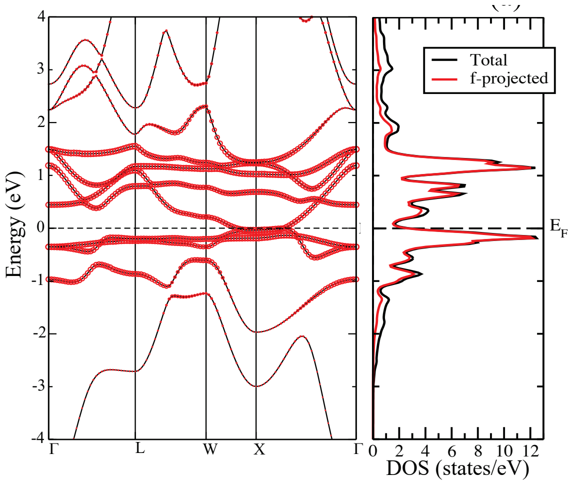
Valence-fluctuating ground state of plutonium

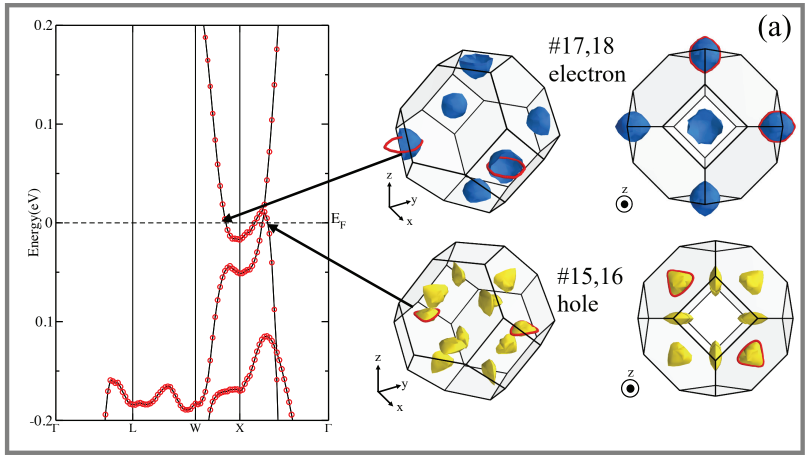


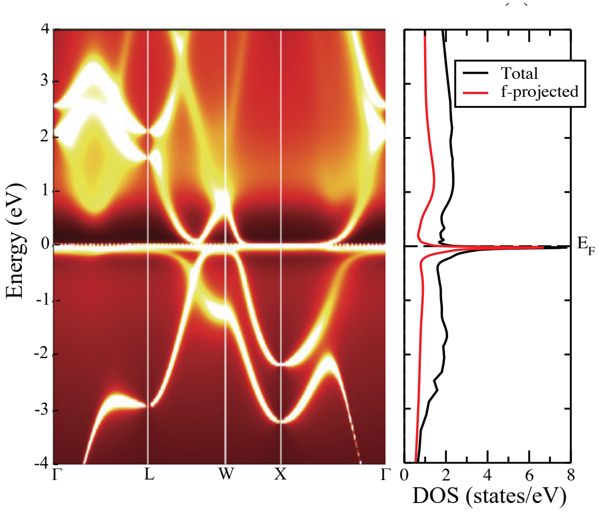
❖ A spin resonance energy at around 80 meV as detected by Inelastic Neutron Scattering, sets an effective quantum fluctuation energy scale – fingerprinting the missing magnetism.

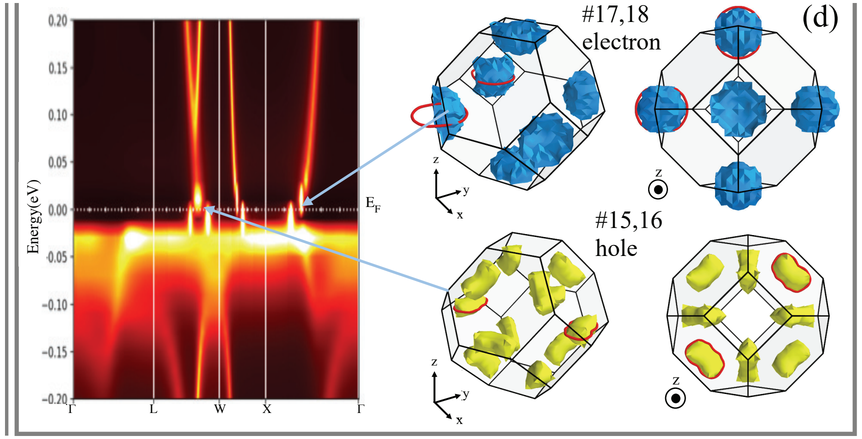
M. Janoschek, JXZ, *et al.*, Sci. Adv. **1**, e1500188 (2015)

Fermi surface topology of δ-Pu (Prediction)





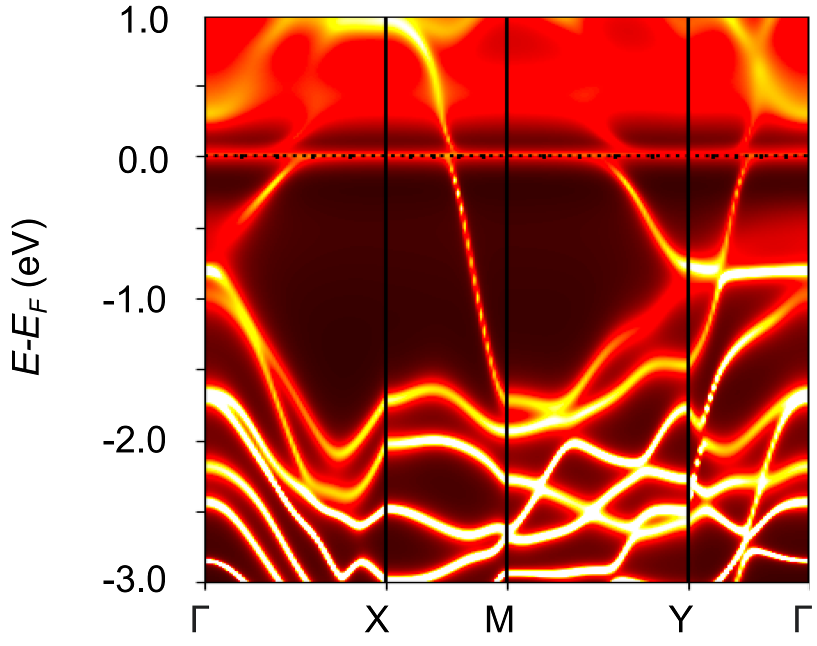


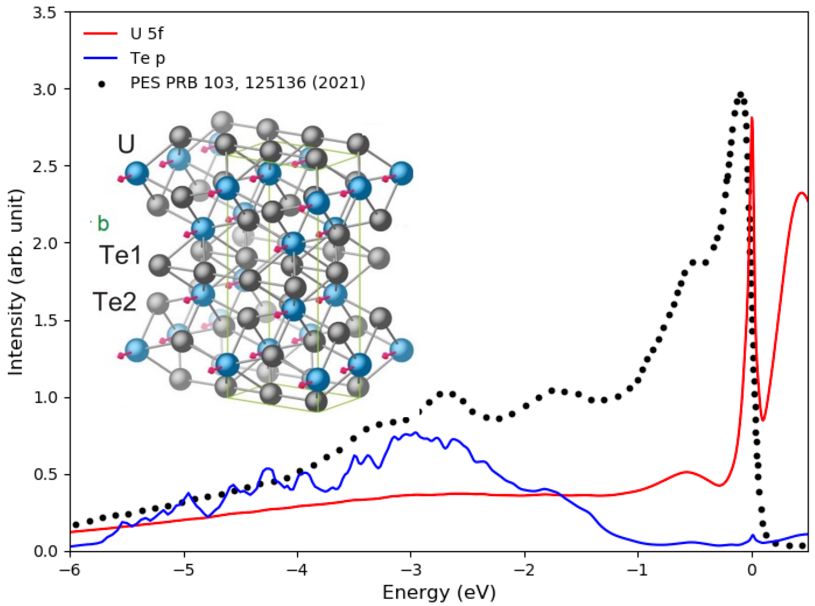


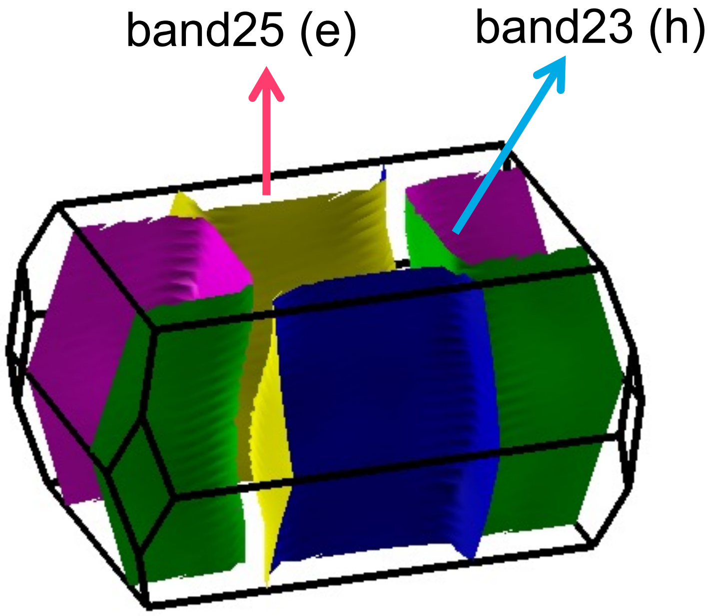
- Correlation induced FS volume expansion

Roxanne Tutchton, JXZ, Phys. Rev. B **101**, 245156 (2020)

DFT+DMFT Band Structure of Topological Superconductor UTe_2



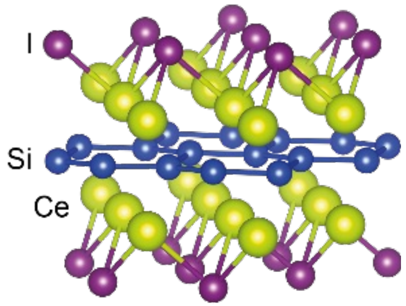


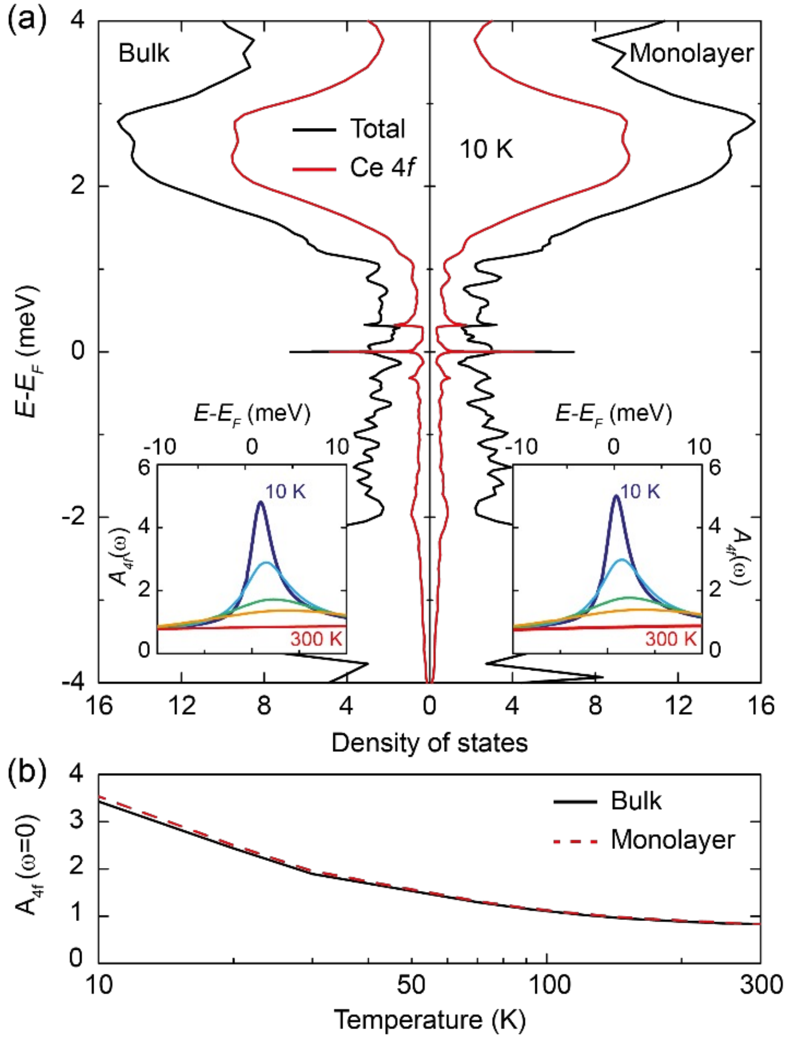


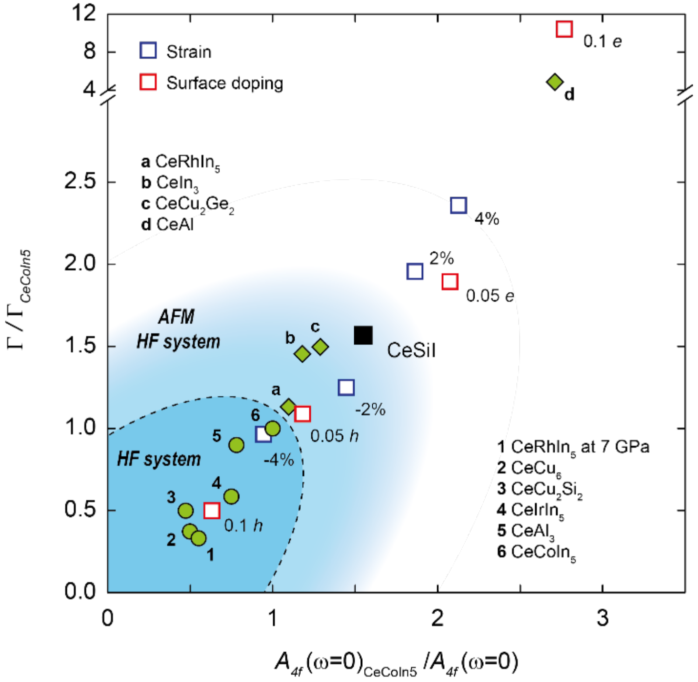
- DFT+DMFT results are in qualitative agreement with the PES measurement
- Kondo physics picture seems also supported by the transport measurements.
- Strongly correlated of U-5f electrons play an important role in driving the metallic behavior and superconductivity

JXZ et al., in preparation

DFT+DMFT prediction of van der Waals of heavy-fermion CeSiI







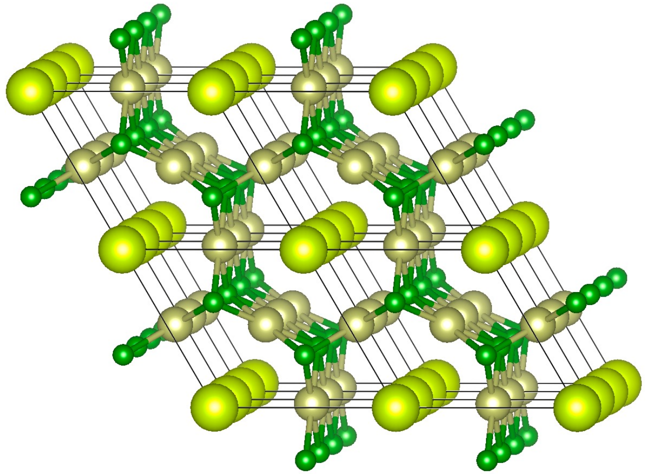
- Kondo resonance peak is clearly observed

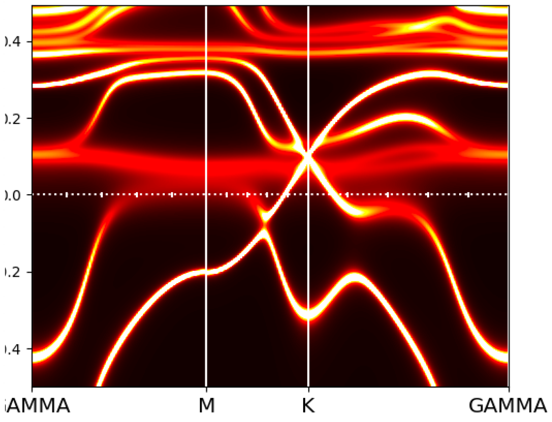
→ Substantial *f-c* hybridization

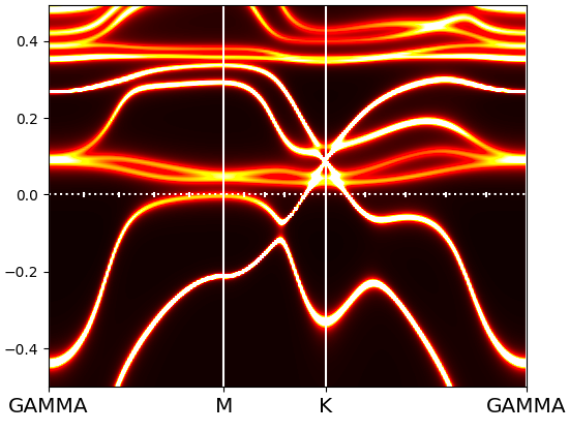
- Kondo resonance peak does not change upon exfoliation
- CeSiI monolayer can be a 2D vdW heavy fermion system

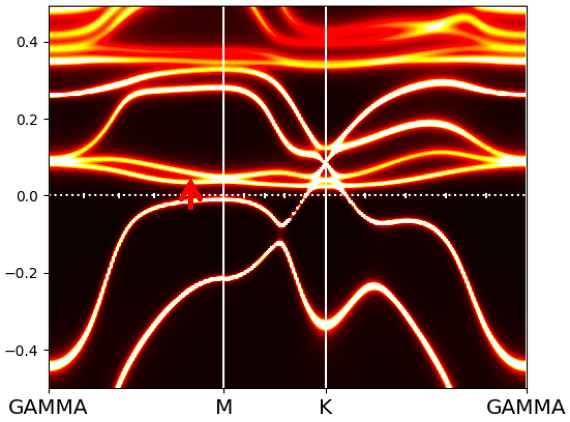
Jang, JXZ et al., npj 2D Mater. Appl. **6**, 80 (2023)

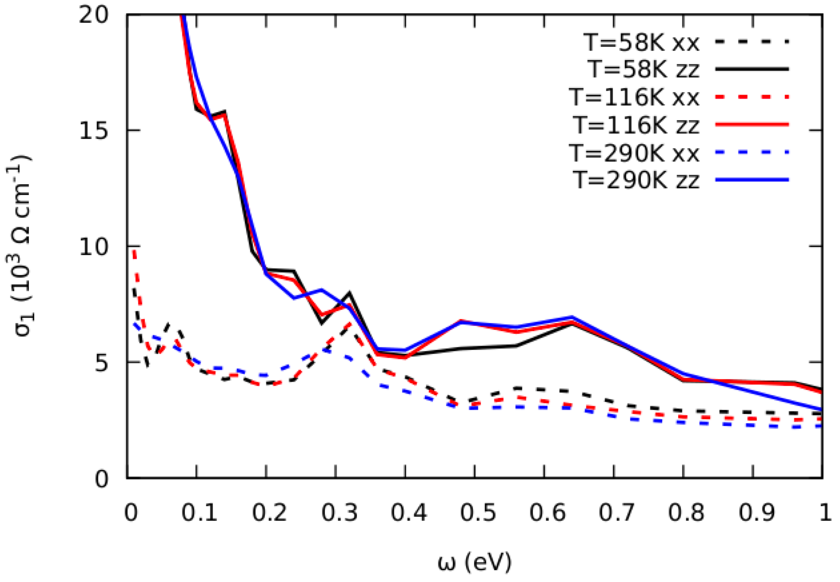
DFT+DMFT Band Structure in Quasi-1D $CeIr_3B_2$











- **The spectral weight is re-distributed and bands are incoherent at *T*=290 K**
- **Electron correlation renormalized bands now enables an optical transition at around 70 meV**

Jang et al., Phys. Rev. B **107**, 205116 (2023)

Summary

- An introduction to strongly correlated electron materials has been reviewed and its challenge to modern condensed matter physics has been highlighted.

- We have also reviewed the methodology of the DMFT to the correlated electrons. As a showcase, we have applied this technique to study elemental Pu solids and other f-electron systems
  - We have elucidated the role of correlation-driven Kondo coherence in spectral properties of Pu.
  - We have also demonstrated the correlation-driven insulator to metal transition in UTe_2, a counter example of Metal insulator transition in transition metal oxides.
  - Heavy-fermion behavior in low-dimensional systems.

Outlook – Future challenges and opportunities

Security and stockpile stewardship mission

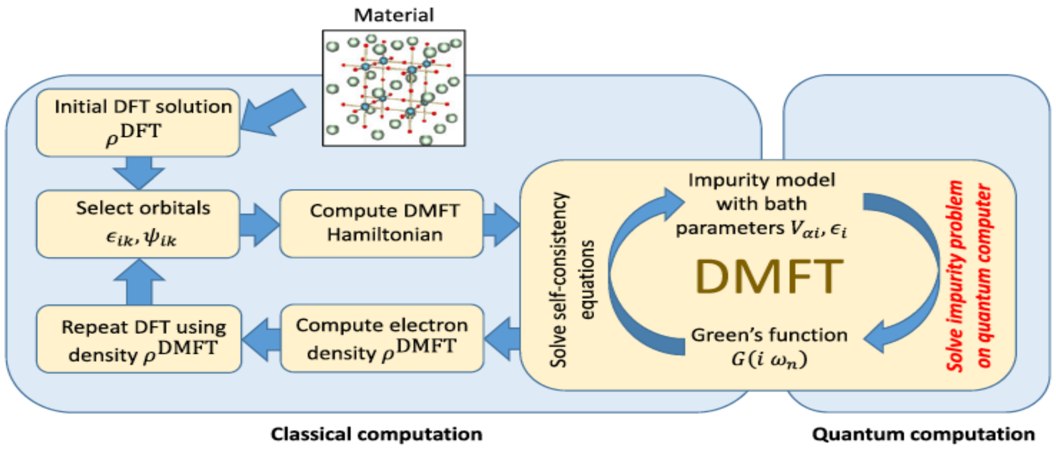
- Give a unified and complete description of phase transformation of elemental Pu.
- Understand the mechanism of impurity/defect induced stabilization of δ-Pu.
- Dynamical phases of actinide under extreme conditions.

Energy and quantum information/computing

- Unravel the topological superconductivity and exotic magnetism in f-electron materials.
- Discovery of strong correlated materials for sensing and energy.

- Accelerate first-principles quantum many-body approaches – computationally cost.
  - ➢ Explore exascale to speed up the algorithms (massively parallelized, GPU)
  - ➢ Explore ML/AI to train the dynamical self-energy corrections to bypass the brutal force simulations.
  - ➢ Explore quantum computing in hybrid quantum-classical algorithms to improve and out-perform classical calculations

→ ***Finite temperature and strong correlation enabled ab initio molecular dynamics.***



→
- **Experimental validation**
- **LANL Material Property Database (w/ automation?)**

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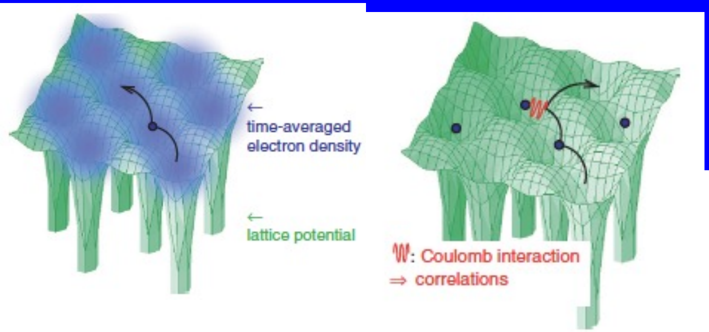
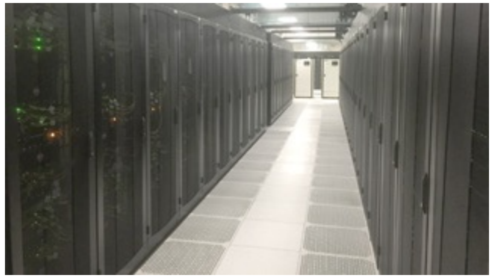


Electronic Structure Theory/Simulation (T)

Controlled synthesis/fabrication (CINT/MPA-Q)

Characteriztion (CINT/MPA-Q/NHMFL)



LANL HPC-Institutional Computing
ASC Computing

- Collaboration with experimental colleagues

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

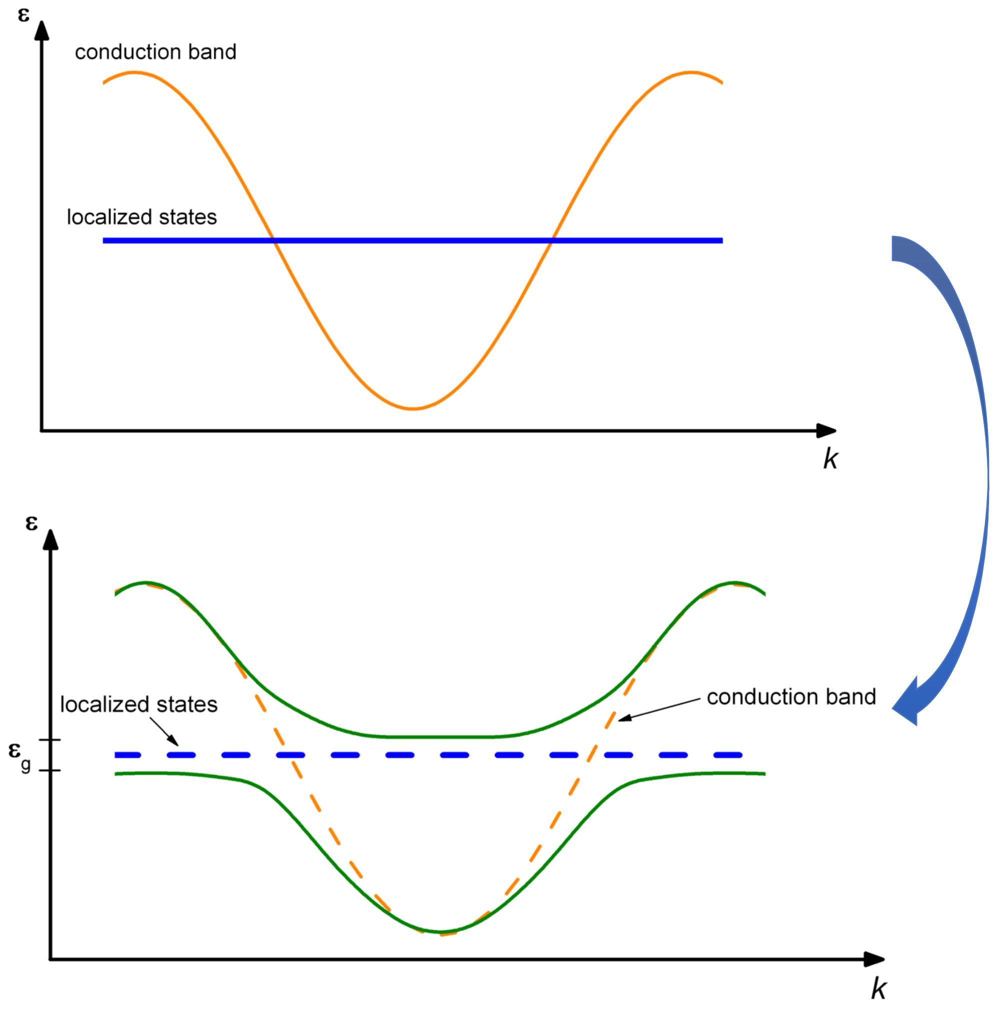
QUANTUM SCIENCE CENTER

Thank You!

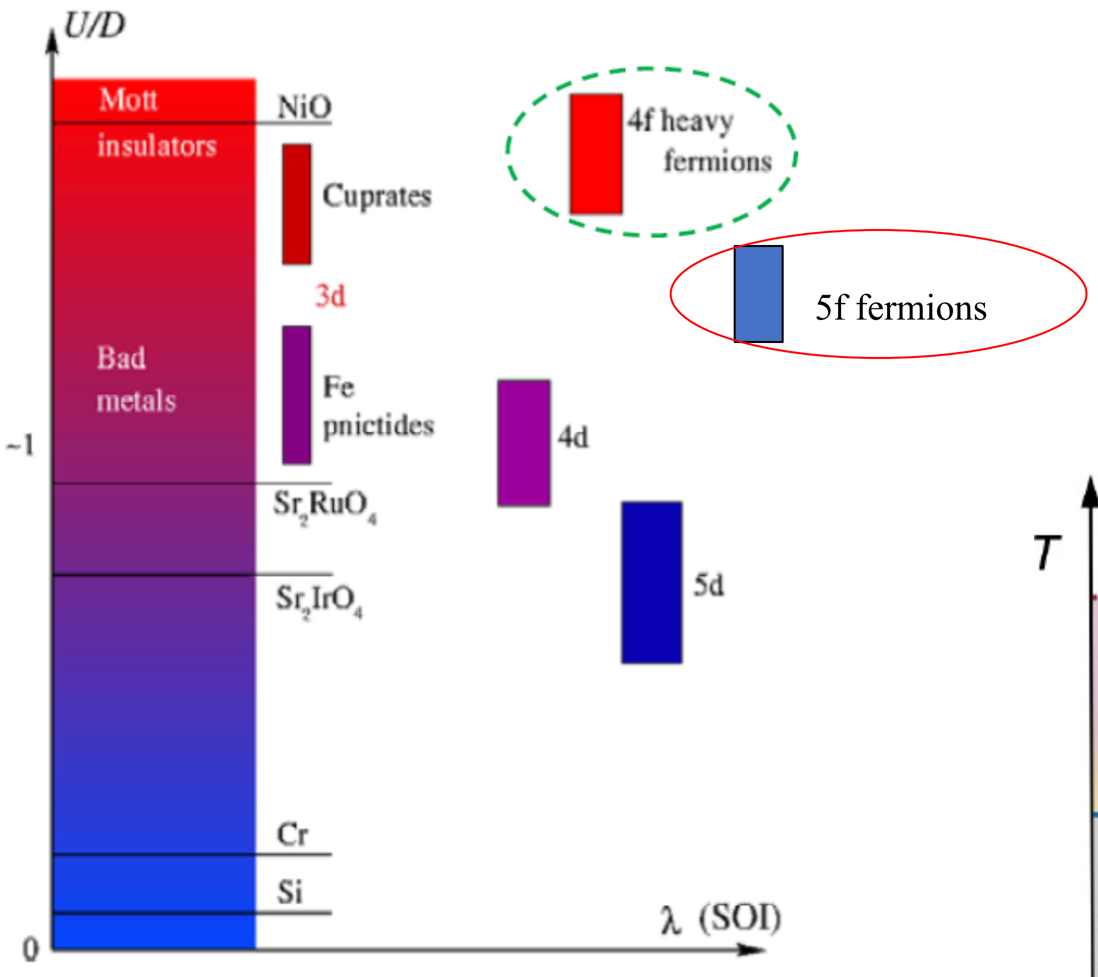
Kondo insulators

- Kondo insulators a direct consequence of electronic correlations

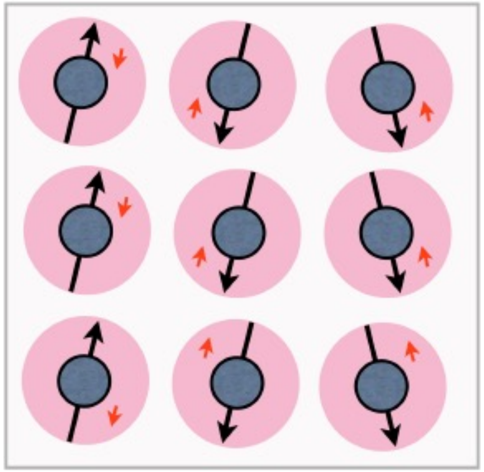
- Hybridization between the localized state and conduction electrons
- Chemical potential is located inside the hybridization gap
- Kondo insulators potentially topological



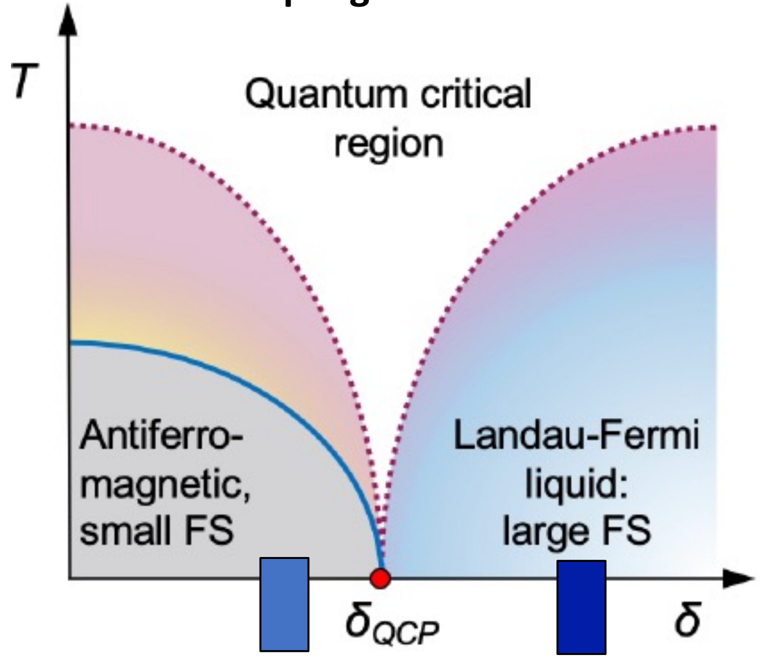
Heavy fermion systems



Courtesy of Sarah Grefe

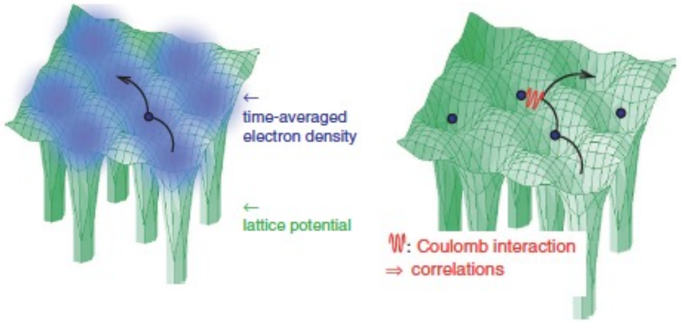


Kondo coupling vs. **RKKY**



- With SOC, topology and interplay?

Co-design approach to f-electron quantum materials



Controlled synthesis/fabrication (CINT/MPA-Q)

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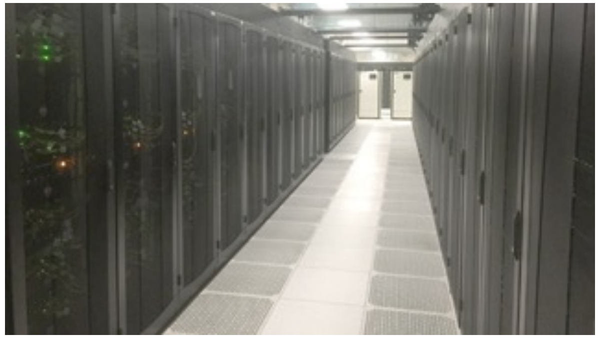

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