### Opportunities and Challenges from Electron Spectroscopy for Realistic Correlated Electron Theory

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*** Work at UM  
Supported by the U.S. NSF.
electron removal (and addition) to study single-particle behavior of many-body system

Spectroscopy of energy and momentum dependence of spectral weight

\[ \rho(k, \omega) = \frac{1}{\pi} \text{Im} \left[ \frac{1}{\omega - \varepsilon_k - \Sigma(k, \omega)} \right] \]

of single particle Green’s function

Both processes together give unbound hole/electron pair the RIGHT WAY TO DEFINE INSULATOR GAP!
Photoemission spectroscopy (and its inverse) to measure $\rho(k,E)$ or $k$-summed $\rho(E)$

Angle variation moves on spherical $k$-space surfaces.

Vary photon energy to change $k_z$

Full electronic structure @ fixed photon energy —3D data set—

Cross-section resonances at core level absorption edges = RESPES

Angles, energy $\Rightarrow k_x k_y$

High photon energy—more bulk sensitive
Mott-Hubbard metal-insulator transition

Hubbard model

Gap in electron addition/removal spectrum due to $U$ gives insulator!

Kin E $\rightarrow$ repulsion $U$

U/t small

U/t large

$E_F$
Mott-Hubbard metal-insulator transition

Old gap collapse picture

Gap in electron addition/removal spectrum due to $U$ gives insulator!

Hubbard model

Kin Energy $E_F$

repulsion $U$

U/t small

U/t large
Mott-Hubbard metal-insulator transition
NEW VIEW from Dynamic Mean Field Theory
(Vollhardt, Metzner, Kotliar, Georges \(\sim\) 1990)

Gap in electron addition/removal spectrum due to \(U\) gives insulator!

Hubbard model

\(K\text{in En t}\) repulsion \(U\)

local orbital electron with magnetic moment

conduction electrons

And. Imp.

\(U/t\) small

\(E_F\)

\(U/t\) large
Mott-Hubbard metal-insulator transition

NEW VIEW from Dynamic Mean Field Theory

(Vollhardt, Metzner, Kotliar, Georges ≈ 1990)

local orbital electron with magnetic moment

hybridized

conduction electrons

And. Imp.

Hubbard model

Gap in electron addition/removal spectrum due to $U$
gives insulator!

$U/t$ small

$U/t$ large

$E_F$
**Mott-Hubbard metal-insulator transition**

**NEW VIEW from Dynamic Mean Field Theory**

(Vollhardt, Metzner, Kotliar, Georges \(\approx 1990\))

Kondo physics—moment loss & Suhl-Abrikosov/Kondo resonance

Gap in electron addition/removal spectrum due to \(U\) gives insulator!

Hubbard model

**local orbital electron with magnetic moment**

hybridized

conduction electrons

And. Imp.

\[ f_0 \rightarrow f_1 \rightarrow f_2 \]

\[ \approx kT_K \]

\[ \varepsilon_f \rightarrow E_F \rightarrow \varepsilon_{f+U} \]

\[ E_F \]

U/t small

U/t large

And. Imp.
Quasi-particle (Kondo) peak at low energy

A Fermi liquid: -- QP peak implied by Friedel sum rule (Langreth 1966)

**Emergent low energy scale:** \( k_B T_K \)

\[ T < T_K \] magnetic moments quenched

\[ k_B T_K = E_F \exp(-1/J) \]

\[ J = v^2/\varepsilon_f + v^2/(\varepsilon_f + U_{ff}) \]

**atomic behavior at high energy**

representing quantum phenomena.
Kondo resonance implied by Friedel Sum Rule (Langreth) for fixed $n_f$

$\rho_f(\omega=E_F) = \rho_f^0(\omega=E_F)$

$V=0, U \neq 0$

$f^1$ moment

$U, V \neq 0$

no moment

$U = 0, V \neq 0$

no moment
Kondo resonance in angle integrated Ce 4f spectra: early experiment and theory

Spectra from photoemission and x-ray inverse photoemission (Xerox PARC) samples: (Maple, UCSD)

Allen et al PRB 1983

CeAl small $T_K$

CeNi$_2$ large $T_K$

Fig. from Allen et al Adv. in Physics 1985

Spectral theory: Gunnarsson & Schönhammer PRL 1983
Ce $\alpha \rightarrow \gamma$ transition: similar spectral change

\[ \Rightarrow \text{"Kondo Volume Collapse" (Allen & Martin 1982)} \]

$\gamma$ stabilized by spin entropy
elastic energy decrease

$\alpha$ stabilized by large Kondo
Kondo binding energy
overcomes elastic energy increase

Magnetic moments
volume large

\[
\begin{array}{c}
\gamma \\
\alpha \\
\gamma
\end{array}
\]

CeAl
small $T_K$

CeNi$_2$
large $T_K$

No moments
15% volume decrease

\[
\begin{array}{c}
800 \\
T(K) \\
0
\end{array}
\]

\[
\begin{array}{c}
25 \\
P(kbar) \\
0
\end{array}
\]

\[
\begin{array}{c}
\text{Ce 4f SPECTRAL WEIGHT} \\
\text{PES/BIS} \\
\text{THEORY}
\end{array}
\]

\[
\begin{array}{c}
\text{(x 2.5)} \\
\text{(x 5)}
\end{array}
\]

\[
\begin{array}{c}
\text{INTENSITY (arbitrary units)} \\
\text{ENERGY ABOVE } E_F \text{ (eV)}
\end{array}
\]
Kondo volume collapse and Ce $\alpha - \gamma$ transition using impurity Anderson model

Kondo Volume Collapse in Ce (Allen & Martin 1982)

- hybridization volume dependence from LDA---elastic energy from experiment
  $-\varepsilon_f$ and $U$ and scaling of $V$ from spectra
- volume dependent $F = (E - TS)$
  from impurity model

CeAl small $T_K$

CeNi$_2$ large $T_K$

PV isotherms

$2^{nd}$ crit. pt. observed
"Dense impurity ansatz" for Ce compounds

Impurity spectral function as an ansatz for local (k-summed) spectral function

$$\Sigma_k \rho(k, \omega) \equiv \rho_{\text{LOC}}(\omega) \approx \rho_{\text{IMP}}(\varepsilon)$$

Impurity model $\Leftrightarrow$ local properties

Use of impurity model for concentrated cerium materials?
angle integrated Ce f-spectrum
find small $T_K$ f-spectrum $\approx x$-independent: e.g. $(La_{1-x}Ce_x)Al_2$

H.-D. Kim et al
Physica B, 2002
RESPES to get diluted f-spectrum

Volume expansion with dilution
$\Rightarrow T_K$ decreases
5K ($x=1$)
$\Rightarrow 0.5K$ ($x=0.04$)
$\Rightarrow$ small change near $E_F$
"Dense impurity ansatz" for Ce compounds

Use of impurity model for concentrated cerium materials?

Impurity spectral function an ansatz
for local (k-summed) spectral function

$$ \Sigma_k \rho(k, \omega) \equiv \rho_{\text{LOC}}(\omega) \approx \rho_{\text{IMP}}(\varepsilon) $$

Impurity model \( \iff \) local properties

For lattice: (Müller-Hartmann, Z. Phys. B 76, 211 (1989))
if self energy k-independent

$$ \rho_{\text{LOC}}(E_F) \equiv \rho_{\text{LOC}, 0}(E_F) $$

i.e. same as exact impurity model sum rule

Possibility for "impurity model" with
$$ \rho_{\text{LOC}}(\omega) \equiv \rho_{\text{IMP}}(\varepsilon) $$

???
Mott-Hubbard metal-insulator transition
new view from Dynamic Mean Field Theory
(Vollhardt, Metzner, Kotliar, Georges ≈ 1990)

DMFT: ⇒ a self-consistent
Anderson impurity model (exact
in \( \infty \) dimensions -- finds \( \Sigma(k,\omega) = \Sigma(\omega) \) )

Hopping \( t \)
Repulsion \( U \)

Hubbard model

Kondo physics—moment loss &
Suhl-Abrikosov/Kondo resonance

Gap in electron addition/removal spectrum due to \( U \)
gives insulator!
Mott-Hubbard metal-insulator transition
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Kondo physics—moment loss &
Suhl-Abrikosov/Kondo resonance

f_0, f_1, ~kT_K, E_F, E_F, \epsilon_f+U

quasi-particle peak
growing in gap as U/t decreases
(“bootstrap Kondo”)
Paradigm material: \((V_{1-x}M_x)_2O_3\) (\(M=\text{Cr, Ti}\))

McWhan, Rice et al.
PRL ’69, PRB ‘73

\(\text{PI} \Leftrightarrow \text{PM}\)
interpreted as Mott transition of 1-band Hubbard model

2\(e^-\) \(V^{3+}\) ion
3 orbitals/ion
4 ions/cell
more complex than 1-band Hubbard

Importance of realism: Ezhov et al, PRL ’99, Park et al, PRB ’00

\(\Rightarrow\) Motivation for LDA + DMFT calculations (Held et al, PRL ’01)
Angle integrated bulk sensitive spectra for Mott transition in \((V_{1-x}Cr_x)_2O_3\)

Experiment: SPring-8 BL 25SU (S. Suga)
- \(h\nu = 500-700\) eV; total \(\Delta E \approx 90\) meV
- Cleaved single crystals from P. Metcalf, Purdue


```
LDA+DMFT(QMC), T=300K
PM (pure), \(h\nu=700\) eV
PM (pure), \(h\nu=60\) eV
PI (Cr=2.8%), \(h\nu=500\) eV
```

“Kondo peak” theory and experiment in M phase

Previous work, 30 years
NO M phase peak

Surface layer more correlated than bulk
Small photon spot also essential for large $E_F$ peak!

Optical micrograph—J.D. Denlinger

With small spot can select probing point to avoid steps and edges as much as possible

$E_F$ peak much reduced with larger spot

Difference for 300 eV to 500 eV range even larger

Steps, edges: even lower coordination than smooth surface
Compare V$_2$O$_3$ PM phase spectrum to LDA + DMFT (t-orbitals, U=5.0 eV, 300K)


Qualitative agreement on presence of prominent $E_F$ peak in spectrum

But experimental peak **width** larger than theory width, roughly by factor of 2

And experimental peak **weight** larger than theory weight
DMFT predicts high T broadening of metal phase $E_F$ peak

- $U=5.0\text{eV}, T=1100\text{K}$
- $U=5.0\text{eV}, T=700\text{K}$
- $U=5.0\text{eV}, T=300\text{K}$
- $U=4.9\text{K}, T=300\text{K}$

$T=300\text{ K}$ (two similar $U$ values)
$T = 700\text{ K}$
$T = 1100\text{ K}$

quasi-particle peak $\rightarrow$ incoherent
Kondo resonance broadening in CeSi$_2$

Garnier et al
PRL 81, 1349 (1998)

低T & 高T spectra

低T & 高T impurity model theory
High T DMFT Landau theory (Kotliar) phase diagram with cross-over regime (red)

\[ \eta \]

\[ \text{Temperature (K)} \]

\[ \text{crossover regime} \]

\[ \text{critical point} \]

\[ \text{PI} \]

\[ \text{PM} \]

\[ \text{AFI} \]

\[ \text{+ Cr} \]

\[ (V_{1-x}M_x)_2O_3 \]

\[ + \text{Ti} \]

\[ \log_{10}[\rho] \text{ (ohm cm)} \]

\[ \text{resistivity on two experimental paths} \]

\[ (V_{0.97}\text{Cr}_{0.03})_2O_3 \]

\[ 0-1-2 \]

\[ 0'-1'-2' \]

\[ \text{Kuwamoto et al 1980} \]

\[ \eta \]

\[ \text{EF spectral weight} \]
Unsuccessful early search for broadening in low $h\nu$ photoemission for PM phase of $V_2O_3$
(no $E_F$ peak to study!)

Two temperatures in the PM phase

One low temperature in the AFI phase

S. Shin et al.
64, 1230 (1995)
New Approach at low $h\nu$ : high temperature PI phase experiment to see correlation gap filling

Home lab, helium lamp $x=2.8\%$ PI phase at 300K

Surface layer more correlated.
So spectra valid to study insulating phase gap filling

Clean by scraping for extended time and multiple measurements
Must calibrate effect of scraping

Low binding energy shoulder
- reduced at low photon energy
- more rounded with scraped surface, but still visible so scraped surface OK to study.
High temperature correlation gap filling in $\text{(V}_{0.972}\text{Cr}_{0.028})_2\text{O}_3$ PI phase: spectra to 800K

![Graphs showing intensity vs. $E-E_F$(eV) at different temperatures and energies.](image)
High temperature correlation gap filling in $(V_{0.972}Cr_{0.028})_2O_3$ PI phase: spectra to 800K

negative curvature near $E_F$, theory and experiment due to gap filling

300K data with 1150 K Lorentizian broadening

800 K data

750 K data

1150 K PI phase theory

Summary for $V_2O_3$

- Metal-insulator transition in $V_2O_3$
- See DMFT “Kondo peak” in PM phase 3d PES spectrum
- Need high $h\nu$ and small photon spot to get bulk 3d
  Surface more correlated---peak hardly seen
- Peak width and weight larger than in theory

- High T gap filling of PI phase
- Qualitatively like DMFT theory in cross-over regime
- Correlates well with high T resistivity

Kondo and Mott physics intertwined!
Ce 4f results provide context for U 5f studies

AF moment very small, can't account for large entropy of URu$_2$Si$_2$ transition at 17.5K
⇒ “hidden order” in low T phase
CeRu$_2$Si$_2$ ARPES on resonance ($h\nu=122$ eV)
CeRu$_2$Si$_2$ ARPES angle sums to impurity model Kondo resonance

angle-integrated 4d RESPES from ARPES
53 angles, normalize at 5 eV, average
CeRu$_2$Si$_2$ ARPES near Z-point like 2-band renormalized Anderson lattice model
LDA for LaRu$_2$Si$_2$ and CeRu$_2$Si$_2$ compared

For Ce LDA and Anderson lattice similar (except for energy scale)---only 1 f-electron
XRu$_2$Si$_2$—3d crystal

k-space arcs for varying photon energy

Brillouin Zones

**ARPES arcs slightly changed in newer work (Denlinger talk)
LaRu$_2$Si$_2$ Fermi surface from ARPES
J.D. Denlinger (data from ALS)

$\nu = 122$ eV

$\nu = 152$ eV

LDA

$h\nu$ fixes $k_z$ and map center's BZ point

Hole sheets (center = Z)

Electron sheets (center = $\Gamma$)
Fermi volume change at Kondo temperature: the f-electron in CeRu$_2$Si$_2$

**Luttinger counting theorem**  $\Rightarrow$

- f-electrons counted in Fermi volume
- IF magnetic moments quenched

(as in Kondo effect)

**Conjecture** (Fulde & Zwicknagl, 1988)

- f-electrons excluded from FS above Kondo temperature $T_K$

Difficult to test with low-T dHvA.

**paradigm** (dHvA) (Tautz et al, 1995)

- **large Z-point hole** FS
  - $f^0$ LaRu$_2$Si$_2$

- **reduced "pillow" hole** FS
  - counts $\approx \frac{1}{2}$ Ce f-electron in Kondo CeRu$_2$Si$_2$
  - --at temperature below $T_K$

**LDA**

- “band 4” hole
- Fermi surface
- no f-electron

- $\approx \frac{1}{2}$ extra f-electron here

($\approx \frac{1}{2}$ f-electron in other multiply-connected complex FS piece)
Same large hole FS for LaRu$_2$Si$_2$ and CeRu$_2$Si$_2$ for $T \approx 120K > 6T_K$ $\Rightarrow$ f-electrons excluded from FS!

XRu$_2$Si$_2$ review: J. D. Denlinger et al, JESRP 117, 8 (2001)

Same conclusion from 2d angular correlation of positron annihilation studies--(Monge et al, PRB, 2002) but didn't actually measure the "pillow"
Fermi surface at high $T$ — 4f weight at low mass $\Gamma$, $Z$ points for CeRu$_2$Si$_2$

$\nu = 91$ eV

$\nu = 122$ eV

$dHvA$: $m/m_e = 4, 2.5, 1.6,$

$m/m_e = 120$

Electron sheets (center = $\Gamma$)

Hole sheets (center = $Z$)
But ... remnant of f-d mixing in high T CeRu$_2$Si$_2$

LaRu$_2$Si$_2$  CeRu$_2$Si$_2$

curvature near $E_F$ for CeRu$_2$Si$_2$ (f') but not LaRu$_2$Si$_2$

f-d mixing in Anderson Lattice model
LDA ThRu₂Si₂ vs URu₂Si₂

for uranium ..... LDA NOT like Anderson lattice
too many (2.5 to 3) f-electrons
Resonant ARPES of URu$_2$Si$_2$
(samples from M. B. Maple, J. Serrao)

Comparison to LDA

LDA with 5f’s bad especially near E$_F$
---better agreement with LDA
calculated for f$^0$ compound!
New idea for U 5f”s: \{f$^2$ core + 1\}
(Zwicknagl, Fulde)
Idea applied to δ-Pu and PuCoGa$_5$: \{f$^4$ core + 1\}
(Wills et al, Joyce et al)

f-weight confined to d-band hole pocket

like in renormalized Anderson lattice model
**URu$_2$Si$_2$ X-point f-weight T-dependence**

X-point, 108 eV, $T = 100 \rightarrow 15$K

Optical relaxation time shows coherence developing $\leq 40$K (Bonn et al PRL ’88)
**URu$_2$Si$_2$ f-weight T-dependence**

X-point, 108 eV, T = 100 → 15K

Specific heat implies gap opening at 17K “hidden order” transition (Maple et al ’86)

Optical conductivity shows gap in “hidden order” phase (Bonn et al ’88)
**UGe$_2$ Phase Diagram and models**

PM $\rightarrow$ FM$_1$ transition at 53K  
FM$_1$ $\rightarrow$ FM$_2$ at 30K  
Superconductivity in FM phase  
SC $T_{sc}$ highest at $P_x$

**Coupled CDW-SDW fluctuation model**  
--Phase boundary $T_x(P)$ is related to coupled CDW and SDW formation  
--FM Superconductivity  
Assumes Fermi Surface Nesting

**FS topology driven Model**  
— Sandeman et al., PRL 90, 160075 (2003)  
--Mean field Stoner treatment  
--Quasi 1-D 2-Peak DOS model  
Assumes Fermi Surface Nesting

**Moderately heavy fermion**  
$\gamma = C(T)/T = 35$ mJ/mol K$^2$

Nature of the 2$^{nd}$ FM phase transition and how they are related to the development of SC are still not clear

**Graphical Diagram**

- Phase boundary and transitions
- Disorder, superconductivity, and nesting
- ARPES results and implications
**UGe$_2$ crystal structure and Brillouin zone**

**Crystal Structure**
- Czochralski grown single crystal
- Cleaved in-vacuum at $T<100K$
- Cleaving surface normal to $b$

**Brillouin Zone**
- Orthorhombic (Cmmm) — base-centered ($b>a$)

**Parameters**
- $a = 4.009$ Å — Magnetic Easy axis
- $b = 15.089$ Å
- $c = 4.095$ Å

*(Oikiwa, et al JPSJ 65, 3229 (1996))

**Czochralski grown single crystal**
- Cleaved in-vacuum at $T<100K$
- Cleaving surface normal to $b$
UGe$_2$ Fermi Surface --- LDA vs. LDA+U

Quasi-2D FS sheet primarily \( \{m_s=\uparrow; m_L=0\} \)

dHvA: \( \alpha: f=7.76 \text{kT} \rightarrow r=0.486 \text{Å}^{-1} \)


Experimental Fermi Surface and Band Structure
\( h \nu = 92 \text{ eV and } T = 30\text{K} \)

**Fermi Surface**

- Large FS observed in multiple BZs, defined by non-f band dispersion
- Diamond shape FS simpler than calculations
- FS more connected in one direction than the other

**Diagonal FS nesting, different from LDA/LDA+U**
Fermi Surface and Band Structure Details

BS details

FS details, $h\nu = 92eV, T = 30K$

- Band curvature: f-p/f-d hybridization in the Anderson Lattice Model
- Broadened FS feature due to integration
- FS size agrees with dHvA

Anderson lattice Model

Integration window

Integration window

Integration window

Integration window

Integration window
FS topology – compare to quasi 1-D model

Subtle connectivity in one direction (c*), but not the other \(\rightarrow\) quasi 1-D signature?

- Our FS topology
- FM-SC and both phase transitions reproduced

- FS topology driven Model
  - Mean field Stoner treatment
  - Quasi 1-D 2-Peak DOS model
  - Lead to SC in FM and the 2\(^{nd}\) FM phase transition

ARPES spectra: compare with LDA

Photon energy 92 eV, $T=300K$

ThGe$_2$ LDA calculation by A. B. Shick

UGe$_2$ LDA
H. Yamagami et al., Physica B186-188 (1993)

better agreement with $f^0$ bands
(will try $f^2$ core plus 1)

Samples:
A. D. Huxley
J. Flouquet
Fermi Surface – Experiment vs. Calculation -- Summary

**Experiment**
- ThGe$_2$ LDA

**Calculated by**
- A. B. Shick

**UGe$_2$ LDA**

**ThGe$_2$ LDA**
- matches a dHvA orbit area

**UGe$_2$ LDA+U**

Quasi-1d hint
FM ↔ PM Transition


ARPES

T=70K

T=20K
FM-PM transition
dHvA measured FS size change small

Orbital size calculated from the dHvA frequency

• Anderson impurity ansatz in Ce systems good for angle integrated spectra
• Kondo effects and Luttinger in CeRu$_2$Si$_2$ high and low T need theory for k-dependence e.g. issue of f-weight
• LDA much like Anderson lattice for cerium—only f$^1$
• Uranium compounds: e.g. URu$_2$Si$_2$, UGe$_2$
  LDA f-bands bad, distort non-f bands and FS too many f-electrons
  LDA for f$^0$ gives better description of non-f bands idea of core f$^2 + 1$
• Anderson lattice f-weight confined to hole pockets
• T-dependent f-weight in URu$_2$Si$_2$
• UGe$_2$
  FS consistent with LDA, little change in FM transition diagonal nesting, not like LDA or LDA + U not enough low d character for 1d model