INVITED PAPER

ELECTRON SPECTRA OF HEAVY-FERMION SYSTEMS

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An overview is presented of current understanding and recent approaches and issues in studies of the single-particle electron spectra of heavy-fermion materials, with emphasis on uranium compounds.

1. Introduction

The various ground state and low-energy phenomena associated with heavy-fermion materials are generally taken to be electronic in origin, specifically due to the f-electrons of these materials, 4f for the rare earths, and 5f for the actinides. It is thus of fundamental interest to characterize the electronic structure of the f-electrons. For non-interacting electrons it is obvious that if one measures the spectrum of ionization and affinity energies for the electrons, that is, the spectrum to remove and add electrons, one will have learned all there is to know about the electronic structure. However, it is a near-certainty that the f-electrons of interest constitute a strongly interacting Fermi system, and that the interactions are responsible for the properties that make these systems interesting. What then should one measure?

For the interacting system, the spectrum to add and remove electrons continues to be of fundamental importance, as the only single-particle spectroscopic information allowed by the principles of quantum mechanics. In general the added hole or electron interacts with the remaining electrons, and the spectrum thus carries information about the interactions, which are, of course, operative to produce the ground state properties of interest. Two-particle spectra, e.g., those of a hole–electron pair, or two holes, in general carry new information, but can be more complicated to analyze because the two extra particles interact, not only with the remaining electrons, as occurs also with a single extra hole or electron, but also with each other. Examples of two-particle spectra are optical, neutron scattering and Raman scattering spectra, which involve electron–hole pairs with the same or opposite spins, and Auger spectra, which involve two holes.

This paper focuses on the single-particle electron spectrum. Theoretically the spectrum is given by the spectral weight of the single-particle Green’s function $G$, and the closest experimental realization is provided by photoemission and inverse photoemission, or bremsstrahlung isochromat spectroscopy, (PES and BIS, respectively). In making the connection of PES and BIS to $G$, it is assumed that for the photon interaction the sudden approximation holds, i.e., that, respectively, the outgoing or incoming electron in PES or BIS has large enough kinetic energy that its interactions with the system after or before the photon event can be neglected. Then the photon event can be characterized by a cross section. It is important to remember that $G$ was not invented to describe the results of PES/BIS experiments, but is a fundamental theoretical construct for characterizing an interacting many-body system.

The remainder of the paper describes current understanding, and recent approaches and issues, with emphasis on uranium systems because they are the least well understood at the moment.

2. Rare earth systems and the Anderson impurity Hamiltonian

Strongly interacting Fermi systems have multiple energy scales, most of which are displayed in the single-particle spectrum. Electron spectroscopy has had a major impact on heavy-fermion physics by revealing, and forcing cognizance of these energy scales for heavy-fermion rare earth systems containing, for example, cerium and ytterbium. For the rare earth systems, the spectra can be described in considerable detail using the degenerate impurity Anderson Hamiltonian.[1]

The degenerate impurity Anderson Hamiltonian is a model for an $N_f$-fold degenerate local
orbital hybridized to a band. It contains explicitly
the charge fluctuation energy scales, $U_{ff}$, $\varepsilon_f$, and
$\rho N_f V^2$, which are, respectively, the $f$ Coulomb
repulsion, the $f$-binding energy relative to $E_F$, and
the hybridization width involving hybridization $V$
of the $f$-state to the conduction electrons having
density of states $\rho$. There is then a derived low
energy scale, the Kondo temperature $T_K$, which
depends exponentially on $(-1/J)$ where $J$ is the
Kondo coupling constant formed from the Ham-
iltonian parameters, roughly as $J = (\rho N_f V^2)/\varepsilon_f$
when $U_{ff}$ is very large. All these energy scales are
both observable and observed in the spectra. [1,2]
The largest energy scale, essential for understand-
ing heavy-fermion behavior, is $U_{ff}$, which sepa-
rates a PES ionization peak at $\varepsilon_f$ and a BIS
affinity peak above $E_F$. The low energy scale $T_K$
is observed as a peak, the Kondo resonance, at
$E_F$, and controls thermodynamic properties such
as the $T$-linear specific heat coefficient, which is
proportional to $1/T_K$. The volume dependence of
$T_K$ gives rise to the $\alpha-\gamma$ phase transition in cerium
metal [3,4]. Another energy scale, the $4f$ spin–orbit
energy $\Delta_{so}$, is observed [2] as fine structure on the
Kondo resonance, and in principle, the resonance
should also show structure associated with the
lattice effects neglected in the impurity approach.
This renormalized bandstructure [5] of the qua-
siparticles has yet to be observed, or identified in
electron spectra.

A screening description of cerium spectra also
exists. Although the single-particle density of states
obtained from the eigenvalues of the local density
approximation (LDA) to the density functional
method does not give a good description of the
measured PES/BIS spectra of rare earth materi-
als, it has been possible to use supercell LDA
calculations [6] to obtain the site $4f$ excitation
energies, i.e., the energies of the PES and BIS
peaks that lie away from $E_F$. In the calculation
the $4f$ occupancy of a central site is constrained to
be, in the case of cerium, 0 or 2 for PES and BIS
respectively. The physical interpretation given to
this approach is to regard the peaks away from $E_F$
as poorly screened, or valence-electron screened
final states, and the peak cut by $E_F$ as a well
screened or $f$-screened final state, because it corre-
sponds to the ground state charge density in which
there is nominally 1 $f$-electron.

This screening approach has both a great simi-
larity to and a great difference from that of the
impurity Anderson Hamiltonian. The similarity
[7] is in the screening description, because in the
Anderson Hamiltonian spectrum, the final states of the peaks below and above $E_F$ have roughly 0
and 2 electrons, respectively, while those of the
Kondo resonance have a number of $f$-electrons
equal to that of the ground state. As has been
pointed out in a pedagogical discussion [7], the
spin–orbit fine structure can be interpreted as
screening, or relaxation, in which the ground state number of $f$-electrons is obtained, but with the
higher energy internal arrangement of spin and
orbital angular momentum. The great difference is
that the Kondo resonance has associated with it
the small energy scale $T_K$, which governs its width
and weight, and controls ground state properties.
The LDA approach does not obtain the low en-
ergy scale, and so for heavy-fermion systems, the
LDA eigenvalues have physical meaning only at
the Fermi level, where they appear to give a
reasonable description of the Fermi surface geom-
etry in some systems. A related aspect is that LDA
calculations do not now give the relative weights
of the screened and unscreened peaks, which are
also related to $T_K$.

One current disagreement for rare earth materi-
als involves YbAl$_3$. There exist two sets [8,9] of
PES/BIS spectra and two sets of Anderson Ham-
iltonian parameters in the literature for YbAl$_3$.
For one set [8] the spectra are remarkably similar
to those of YbAl$_2$ [10], and the valence and ther-
modynamic properties deduced therefrom are con-
sistent with those deduced for YbAl$_2$ from other
measurements. For the other set [9], the spectra
are quite different from YbAl$_2$, and the valence
and thermodynamic properties deduced spectro-
scopically are consistent with those of YbAl$_3$.
Detailed comments on this discrepancy will be
published by the two groups in due course. Here I
offer the brief, and purely personal opinion, de-
vided from experience with a number of YbAl$_3$
and YbAl$_2$ samples, that this difference does not
reflect an overt lapse of proper experimental tech-
niques by either group, but rather that there are
subtle materials science issues involved, possibly
concerning the grain boundaries of different sam-
ple. The general consistency [1] between thermo-
dynamic and spectroscopic data found when the
theory is applied to other systems is a strong
motivation to think that the consistent set of data [9] is, in fact, the one that is characteristic of YbAl₃. However, additional work will be required to clarify this important issue.

3. Concentrated uranium systems and alloys

3.1. Introduction

For metallic actinide systems, building up a picture as unified as exists for the rare earth materials is a focus of active research. This discussion concentrates on uranium, for which the largest amount of work has been done. In general, the f-spectra [11] of metallic uranium materials do not resemble those of the rare earth materials. For the latter the 4f spectra never agree with band calculations, and for the former, the 5f spectra nearly always have a bandlike appearance and sometimes agree rather well with band calculations. Thus uranium spectra do not display well-separated peaks showing \( U_{n\uparrow} \), and for the heavy-fermion materials there is much more weight in the vicinity of \( E_{\uparrow} \) than would be expected from the small value of \( T_K \) implied by the very large \( T \)-linear specific heat coefficient \( \gamma \), or by looking at cerium spectra for materials with very large \( \gamma \). The famous exception is UPd₃, for which the PES/BIS spectrum [12] shows a gap around \( E_{\uparrow} \). The standard understanding [12-14] of the UPd₃ gap is that the 5f electrons are localized and that the gap measures \( U_{\uparrow\uparrow} \). UPd₃ is discussed further below in the section on dilution studies.

3.2. Use of resonant photoemission

Resonant photoemission (RESPES) for uranium [13] has been used to extract the 5f spectrum of uranium materials in which there is strong competing emission from other elements, such as transition metals with nearly filled d-bands, or systems where the uranium is very dilute. The most commonly used resonance occurs for the photon energy near the uranium 5d absorption edge. Viewed atomically, photons excite \( 5d^{10}5f^n \rightarrow 5d^{10}5f^{n-1} \) transitions, and the resulting intermediate state decays via a super Coster–Kronig (sCK) Auger process, \( 5d^{9}5f^{n-1} \rightarrow 5d^{10}5f^{n-1} + \) electron, to produce the same final state as in direct 5f photoemission. It is thus a resonance in the 5f emission cross-section and interference between the resonant and direct processes produces a Fano-type lineshape.

Recently it has been claimed [15] that in many uranium materials, the width of the 5f spectrum determined by RESPES is greater than that determined at other photon energies. This conclusion was reached by studying materials such as USi₃, in which RESPES is not necessary to extract the 5f emission because it dominates spectra at other photon energies, e.g., that from X-ray photoemission spectroscopy (XPS). This extra width was attributed to a decay mechanism additional to the sCK one. In this mechanism, most easily described in a band picture for the 5f electrons, the intermediate state is a 5d core hole and a 5f electron above \( E_{\uparrow} \). This state decays by a conventional Auger transition involving two electrons below \( E_{\uparrow} \), accompanied by a transition of the 5f electron above \( E_{\uparrow} \) back to \( E_{\uparrow} \). The result is a final state with a valence band hole and a hole–electron pair excitation with the excited electron being at \( E_{\uparrow} \). Because of the second hole, the width appears to be potentially twice that of the "legitimate" one-hole spectrum.

Actually, the width associated with this mechanism is probably a legitimate part of the 5f one-hole spectrum. Viewed in more general terms the final state proposed has only one 5f hole, and the remaining 5f electrons are in an excited state of the \((n-1)\) electron system. A familiar example of this situation is rare earth 4f photoemission in which \( 4f^{n} \rightarrow 4f^{n-1} \) transitions produce a spectrum in which excited multiplets of \( 4f^{n-1} \) appear in addition to the lowest energy one. In this case it is understood by all workers that the 4f Coulomb interactions are responsible for a spectrum with total width much larger than that due to the one-electron bandwidth. The proposed uranium final state is essentially equivalent to that for the Ni valence band satellite, in which the Ni 3d Coulomb interaction produces in the one-hole spectrum extra structure due to final states with two holes and one excited electron. Although this structure in Ni is enhanced by RESPES, it can be observed away from resonance.

In fact, the claim of an extra width found only in RESPES has been challenged [16], convincingly in my opinion, on experimental grounds, based on measurements at various photon energies for
several of the compounds, including UGe$_3$, UBe$_{13}$, and USi$_3$, where an extra width was reported. It was found that the RESPE spectrum completely matches the spectrum measured at a photon energy well below the resonance, and that differences from the XPS spectrum are entirely due to the different resolution in the XPS case. It is asserted that there is not extra width in a RESPES spectrum if differing resolutions are taken into account properly, and if the off-resonance and on-resonance spectra are properly normalized before extracting the 5f spectrum.

3.3. Comparison to LDA

One approach to understanding uranium spectra is to search for evidence of the Coulomb interaction by direct comparison of a full RESPES/BIS spectrum with the LDA density of states. For heavy-fermion uranium materials the first such comparison [17] was made for UPt$_3$ and UAl$_2$. It was pointed out that both the PES and BIS 5f spectra are broader than the LDA density of states, and that this additional width must be attributed generically to uranium 5f Coulomb interactions. It was also suggested that the large weight around $E_F$ in the spectra might be due to a sequence of sidebands on a Kondo-type resonance, analogous to the spin-orbit fine structure observed in cerium, but involving the multiplet structure of the relevant valence states. In assessing the roles of various Coulomb interactions, it is important to remember that even though the repulsion $U_{ff}$ may be screened nearly to zero, the same screening mechanisms do not apply for multiplet splittings, which are less well screened [18].

Recently there have been quantitative theoretical predictions [19,20] of the XPS valence band spectrum based on the LDA for two heavy-fermion materials, UBe$_{13}$ and UPt$_3$, and two other compounds UAu$_3$ and UIr$_3$. The theory gives a fully relativistic description of the photoemission process, and associated surface and matrix element effects, in an independent-electron approximation appropriate for LDA theories. After broadening appropriate to the typical resolution of an XPS experiment, and if the Fermi level is adjusted somewhat, it is found that the predicted spectra are in good agreement with measured ones. It was concluded [19] for UPt$_3$ that the excellent agreement suggests that the band-structure or itinerant model for the uranium f-electrons is correct, at least at room temperature where many-body renormalizations are presumably weak.

The two conclusions of the work described in the two preceding paragraphs are clearly inconsistent. The situation is that the higher resolution of the RESPES spectra, relative to that of XPS spectra, shows that the experimental width is larger than the calculated one, even when the resolution is less than the calculated width. The authors of ref. [19] point out that the theory used to calculate the XPS spectrum is not applicable for the spectra taken at the lower photon energies, because at these energies the photoelectron is much more sensitive to multiple-scattering and surface effects, which were neglected. The implication is that surface effects may invalidate the lower photon energy data. However, the finding of ref. [16] that XPS and lower photon energy spectra agree apart from resolution differences is strong evidence to the contrary. Also, for UIr$_3$, angle resolved photoemission spectra [21] taken at lower photon energy agree quite well with band theory. Thus it seems that in the case of UPt$_3$ (and also UBe$_{13}$) the favorable theoretical comparison with XPS spectra is fortuitously good because of the low XPS resolution, and that there are significant differences of widths of experimental spectra from those of LDA predictions. The BIS/PES spectra of other heavy-fermion systems, UBe$_{13}$ [22,23], U$_2$Zn$_{17}$ [24], and URu$_2$Si$_2$ [25] show similar widths.

3.4. Satellite analyses

The observation [17] of excess width in the experimental 5f PES spectra of heavy-fermion materials, relative to the LDA densities of state, has been pursued vigorously by Arko and co-workers, [14,26] who have developed the idea that the extra width should be regarded as a satellite. In this work, the PES spectrum is analyzed into two components, which are thought of as a poorly screened state lying at higher binding energies and a well screened state lying at small binding energy. The well screened state would be expected to have larger intensity for larger hybridization and UPd$_3$ is then taken to be an example in which only the poorly screened peak occurs. If the spectra of cerium are also interpreted in terms of two screen-
ing channels, some commonality for the systematics of uranium and cerium are obtained. In this connection it is interesting that in URu$_2$Si$_2$, a similarity to cerium has been found in RESPES, that for the resonance between 102 and 108 eV, the 5f spectral weight closest to $E_F$ resonates at slightly lower energy than the portion further from $E_F$. [25] For cerium this behavior [1] can be described [27] by the Anderson model, and it will be interesting to see if it occurs in other uranium materials. For BIS spectra, the extra width has also been analyzed from a satellite viewpoint by two groups. Sarma and co-workers [28] have employed a Hubbard model to describe the effect of $U_{U1}$, adapting a perturbation calculation [29] used to describe the Ni PES satellite. The essential idea underlying this approach is that the ligand–U5f hybridization is sufficiently large that the single-particle 5f spectrum is dominated by uranium–uranium coupling through the ligands, permitting a Hubbard description based on hybrid-Wannier orbitals. Sarma et al assert [28] that such a satellite should appear only in the BIS spectrum, and have argued that extra width in the PES spectrum either does not occur or has other than a satellite interpretation. [15] In contrast, Laubschat and co-workers [30] have recently extended Arko’s PES analysis to include the BIS spectrum of UBe$_3$, and some U–Pt compounds. Both the PES and BIS spectra are decomposed into two components, producing a picture crudely like that of cerium, with peaks lying above and below $E_F$, and a peak cut by the Fermi level. As part of the screening picture, the latter feature is taken to be the LDA density of states.

4. Uranium materials–dilution approach

Another approach to obtaining an understanding of uranium spectra is to study the effects of diluting the uranium with a chemically similar element lacking 5f electrons, such as yttrium. The motivation stems from the fact that the near neighbor uranium–uranium separation in many heavy-fermion and other uranium compounds precludes direct hybridization of 5f wavefunctions with one another so that the Anderson lattice model should apply at least as well for these materials as it does for rare earth compounds. The success [1] in understanding cerium spectra is entirely because the impurity approximation, for which high quality theoretical solutions exist, provides a good description of the spectra. Similarly, the LDA treatment [6] of poorly screened peaks also relies on the dominance of single site effects in modeling the final state. It is thus of considerable interest to distinguish single site from lattice effects in at least the large energy scale features of the 5f spectra.

Two published studies are for the 5f PES and BIS spectra of $U_iY_{1-x}B_4$ with $x = 0, 0.1, 0.3, 0.6$ and 1.0, [31] and for the PES spectra of $U_iY_{1-x}Al_2$ with $x = 0, 0.02, 0.1$ and 1.0 [32]. Both of these systems have the same crystal structure for all $x$. For the PES spectra, especially with $x$ as small as 0.02, RESPES can be very useful for enhancing the 5f emission. For BIS, it is necessary to determine the 5f spectrum by subtracting the $x = 0$ spectrum, a method that can also be used for PES. The latter method has the difficulty of properly relating spectra taken on different samples. In the $U_iY_{1-x}Al_2$ system, assuming random Y and U site distributions, it is straightforward to compute that the probability of at least one uranium nearest neighbor decreases from 0.35 to 0.08 as $x$ decreases from 0.1 to 0.02. It is thus difficult to achieve truly isolated uranium atoms, but for $x$ as small as 0.02 it is possible to be far from the band limit. In both the systems the PES spectra were found to be essentially independent of $x$, indicating that the large energy scale features are dominated by hybridization to near neighbors, as in the Anderson impurity model. Fig. 1 shows the spectra for the $U_iY_{1-x}Al_2$ system, as $x$ decreased, a small increase in the portion of the BIS spectrum furthest from $E_F$ was reported, but no qualitative change occurred. Thus it appears likely that an impurity approach could work for the major features of the two concentrated compounds.

The 5f PES spectrum has also been measured [33] for $Y_{1-x}U_iPd_3$, with a quite surprising result. As mentioned above UPd$_3$ plays a special role as an archetype of localized 5f electron behavior, for which the absence of 5f weight at $E_F$ is taken to be a signature [12–14]. Within the standard picture of localized 5f electrons one would expect that dilution of the uranium would, if anything, enhance this localization, so that the 5f spectral weight would remain peaked below $E_F$, and per-
haps decrease its width. One finds instead the completely counter-intuitive result shown in fig. 2, that although the 5f spectrum does sharpen, its peak moves to $E_F$. A large fraction of the shift occurs for $x$ between 0.1 and 0.5, and so the shift does not seem to be especially correlated with a crystal structure change that takes place between $x = 0.5$ and 0.9. Taking the standard picture at face value, one would infer that uranium dilution has caused the 5f electrons to delocalize. This inference seems very implausible, and a more probable conclusion is that the suppression of 5f weight at $E_F$ in UPd$_3$ is somehow a lattice effect, requiring many uranium atoms. It is found that there is a considerable shift in the Pd 4d peaks towards $E_F$, and the possible connection of this with the 5f behavior is discussed in ref. [33]. Also, the presence of 5f weight at $E_F$ in the dilute samples implies that this is not a good signature of 5f delocalization in the sense of 5f band formation.

5. Uranium materials-relation of thermodynamics and spectroscopy

For all of the various approaches described above it is not obvious how to understand the large mass enhancements of the heavy-fermion materials. The screening pictures intrinsically do not address this question, and for the parameters that have been deduced, [28] the mass enhancement available from the Hubbard model is too small. By far the most effective mass enhancement mechanism is that of the Kondo properties of the impurity Anderson Hamiltonian, where it is proportional to $1/T_K$. However, if the finding from LDA calculations of $n_f$ near 2.5 is correct, as might be expected for this average ground state property, then even for the impurity Anderson Hamiltonian it may be difficult to account for the heavy masses, extrapolating from current results for cerium that $n_f$ near 0.5 corresponds to the mixed valent regime with very large values of $T_K$ and therefore very small mass enhancement. However, the impurity Anderson model seems to be rife with theoretical surprises. In the only theoretical work to date on the interplay of spin and charge fluctuations, addressed specifically at uranium, Rasul and coworkers have found [34–36] numerically in an inverse degeneracy treatment that the impurity Anderson Hamiltonian with fluctuating valence between $f^2$ and $f^3$ can have a small energy scale even for $n_f$ near 2.5. This treatment did not include multiplet splittings. In a theory including multiplet and crystal field splittings for a uranium ion, but in the integer valence limit, Cox has described a novel quadrupolar Kondo effect [37]. These theories offer hope that the impurity Anderson Hamiltonian can provide
insight into heavy-fermion uranium compounds. Since the screening pictures being developed for uranium spectra can be regarded as an aspect of the Anderson model behavior, the plea [17,32] for a theoretical treatment of both the ground state and spectroscopic properties of an impurity Anderson model which is realistic for uranium is made here again.

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References


