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f-ELECTRON SYSTEMS: PUSHING BAND THEORY*

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ABSTRACT

The f-electron orbitals have always been the "incomplete atomic shell acting as a local moment weakly interacting with the remaining electronic structure" in the minds of most people. So examining them using a band theory where one views them as itinerant once was -- and to some extent even today still is -- considered with some skepticism. Nonetheless, a very significant community has successfully utilized band theory as a probe of the electronic structure of the appropriate actinides and rare earths. Thopse people actually using the approach would be the first to declare that it is not the whole solution. Instead, one is pushing and even exceeding its limits of applicability. However, the appropriate procedure is to push the model consistently to its limits, patch where possible, and then look to see where discrepancies remain. I propose to offer a selected review of past developements (emphasizing the career to date of A.J.Freeman in this area), offer a list of interesting puzzles for the future, and then make some guesses as to the techniques one might want to use.

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INTRODUCTION

This workshop is being held in recognition of A.J.Freeman reaching the maturity of his 60th year in 1990. It offers the opportunity to remember the things we have learned together and consider what lies ahead. The area to be considered here is that of materials exhibiting electronic orbitals which can't decide whether they are localized atomic orbitals or itinerant conduction electrons (of course, it is actually the observer which is confused, not the electrons). A.J.Freeman introduced me to problems in that area and they have been a major component of our interactions ever since. In a way, J.L.Smith neatly pictured our interests whaen he proposed his specialized periodic table[1] where the rows are ordered according to increasing relative size of the more atomic like orbital, i.e. 4f,5f,3d,4d,and 5d. Ordered in that way, there is a diagonal strip going through Ce, {U,Np,Pu}, {Mn,Fe,Co,Ni, and now Cu}, and Pd that separates the magnetic moment systems on the upper right from the itinerant or bonding systems on the lower left. That strip represents the transition from local orbital behaviour to itinerant behaviour or vice versa, as more appropriate to our approach. The materials away from this transition regime tend to have a cannonical behaviour with only variations in parameters. It is those in this regime that exhibit the widest variety of properties which offers numerous technological possibilities. This comes as a result of there not being a single dominant factor but competing factors of Coulomb replusion, hybridization, and bonding making the theoretical description more involved and in many cases still unresolved.

Freeman moved from the National Magnet Laboratory to Northwestern University in 1967. For the prior 15 years, he had been a member of the Slater's Solid State and Molecular Theory Group (SSMTG). The SSMTG had celebrated its 15th aniversary in 1966 and in Quarterly Progress Report #61 of July, 1966, Slater recounted that history. Included there were the vitas of all persons that had been associated with the group over its 15 year history and that included Freeman's. Along with showing a very extensive list of classic publications, that vita revealed two interesting things: (1) that he was born in Poland in 1930 -- which is the reason this workshop was organized. and (2) that his thesis topic was "A Theoretical Study of the Electronic Structure of the OH Molecule by the Method of Configuration Interaction" -- which should be of some interest to those people who think of him as "Mr. Band-Structure". To illustrate how far computers have come in the intervening 35 years, that calculation was done on Whirlwind I whose compute power and memory is now exceeded by *pocket* computers.

Shortly after moving to Northwestern, Freeman formed his Magnetic Theory Group (MTG) which can in many ways be viewed as a true child of the SSMTG. It is instructive to consider Slater's characterization of the situation in that same QPR #61:

> "Much of the discussion which went on in the group during the mid-1950's dealt with magnetic problems, and also with impurity atoms, excitons, and other related problems which deal with localized excitations in crystals. We were investigating the methods of treating these problems, by means of Wannier functions and other forms of localized functions. However, the techniques we had worked out for handling these problems all had to start by assuming that the energy-band problem had been solved, so that one the one-electron solutions of a self-consistent field problem would be known. Since at that time the energy-band problem had not been worked out to this point, these problems were mostly postponed, and the major effort was put onto the solution of the energy-band problem. Now that that problem, as a one -electron approximation, is essentially mastered, the time has come to return to localized impurities and excitations, and it seems likely that a major part of the effort, during the next few years, will be along those lines. "

As it turned out, a very sizable effort was still required within the MTG and elesewhere to extend the capabilities of band theory to really begin that program. Problems like relativity, asymptotes, shape approximations, and efficiency had to be dealt with. Twenty four years later, we as a community and the MTG specifically really are into that program. Such is the necessary optimism of the physicist! During my stay in the MTG, I was inculcated with some basic philosophical precepts that are worth noting here:

°Push the "simple minded" explanation to the limit before appealing to the "exotic". More than once a many body explanation has turned out to be a band-structure effect -- which is also a many body effect but simpler.

°If you can't calculate it, you don't really understand it. Perhaps that is why Freeman has another characterization as "Mr. Large-Scale-Computer".

°Nothing resembles a new effect like a mistake. Actually, this is the physics-relevant part of a basic conservatism, the other half of which is "There's no free lunch."

In what follows, I will recall some of the lessons from the early actinide element work and then from the work on rare earth and actinide compounds. Thereafter, some of the efforts beyond standard band theory will be considered. The focus is on the contributions of Freeman and the MTG in these areas. To be sure, a lot of good work was done elsewhere, but this is not their 60th birthday. The fact that this review is so focussed is based solely on the observation of event. Finally, to be sure that this not taken as a memorium but as a celebration of a coming of age, I will offer some of the outstanding problems that intrigue me and will no doubt be a part of the MTG's future.

EARLY WORK ON THE ACTINIDE ELEMENTS

When I joined Freeman at Northwestern, we were interested in Pd, Sc, and $LaSn_3$. (As a parenthetical note, it is unfortunate that the antiparamagnon debate that took over our APS presentation of the Sc band structure did not get more play. It could have been quite useful when heavy fermions came along.) It was from this background, Freeman's interest in rare earths, and the extensive experimental effort at Argonne National Laboratory that we soon became interested in the actinide elements. The argument of interest was that f-orbital overlap was sufficient to broaden out the f-levels into f bands -- at least for the occupied states in the light actinides. Recognizing that the extent of the outermost reaches of the f-orbital tails was the critical issue, we utilized the higher (fourth) moments of the orbital to see whether they had an adequate reach[2]. To put a numerical basis under such thinking, we were performing fully relativistic but non-selfconsistent band calculations. At the same time, Hunter Hill was making similar arguments of itineracy based on materials systematics which gave rise to the Hill plots[3] while Ed Kmetko was performing self-consistent but non-relativistic band calculations[4]. The difference in band results led to a spirited rivalry. We were questioning whether one could do the self-consistency to adequate precision (we were wrong on that point) and Hill-Kmetko claimed the non-relativistic approximation was adequate (they were wrong on that point). The neglect of relativistic effects caused the s-p states to lie unphysically high in energy[5] so that they were eliminated from the bands causing Hill and Kmetko to propose a d-f transition series. Interest in the differences wained with the deaths of both Hill and Kmetko although a real culprit was beginning to emerge: the use of the Herman-Skillman mesh which they used even in their semi-relativistic calculations[6]. The Herman-Skillman mesh does not penetrate close enough to the nucleus so that one must go to very high order expansions to properly start the radial integration. Later calculations[7] have ruled in favor of having f-bands inserted into an already transition metal like band structure. The extensive use of logarithmic meshes and linear techniques has greatly diminished the significance of that issue. However, as it becomes desirable to redesign meshes for speed needed for some of the newer simulation based technology, it will be well to remember that history.

Another technology advance was required to make further progress. In the early actinide work, we felt it necessary to draw large hatched regions just above the Fermi energy where we declared the results unreliable. This did not disturb us because we felt the f-orbitals were too localized there to be significant anyway. In dealing with compounds, however, we did not have that luxury and the problem had to be dealt with. The problem occured because, in the standard APW method, the design of the APW basis function specifies that one continuously match the radial solution to the Bessel function of the planewave. That cannot be done when the radial solution has a node at the matching radius -- which occurs at an energy just above the band of that given character. The problem is exacerbated in the relativistic case because there exists two such energies and the numerical precison becomes suspect. The interest in eliminating this problem caused us to consider alternate basis set formulations[8] and was the basis of the initial interest in the energy derivative rather than the linearization. The author had unfortunately accepted the energy window estimates of Marcus[9] (15-25 mRy) rather than of Anderson[10] (a band-width): the belief in "no free lunch" was a bit too strong. (The essential genius of Anderson was the realization of that wide energy window which seems so obvious in hind sight. Were it so obvious in forsight, Slater[11] would have proposed a linearized method in 1953.) Because they join two radial functions continuously also with continuous derivative, the linearized basis functions also eliminate the asmptote problem which is a very significant contribution in the calculations for compound materials. The much needed speed enhancements of the linearized methods came as an unexpected bonus.

One last aspect deserves comment before turning to actinide compounds more because of its reflection on our celibratee. A major concern in the calculations of band structures has been the choice of exchange -correlation potential. (Interestingly, the more dominant the Hubbard U, the less critical that choice becomes.) When the first gradient correction was proposed[12], we immediately recognized that it could be obtained as the result of a local averaging much as the relativistic Darwin term is obtained as a consequence of the Zitterbewegung. It is a badge of honor that the resulting manuscript was *not* published because of our disagreement with the referees over the appropriatenes of testing in atomic calculations. The technique of averaging homogeneous results was a reasonable one and has more recently been used in another context of density functional theory[13].

ACTINIDE AND RARE EARTH COMPOUNDS

Effort began on the rare earth and actinide compound materials occured after the author had left the MTG and come to Argonne National Laboratory. There was a long period of very little progress because the problem was really waiting for developements in technology. Rare earth and actinide materials are among the most computationally demanding band structure efforts one can undertake. The cuprate superconductors, which are just beginning to sort out, benefitted from the efforts targetted to these materials. However, some things were possible with the older technology such as the sorting out of the Fermi surfaces of URh_3, UIr_3, and UGe_3. During that phase, other problems received greatewr attention and this interesting area was more discussed than worked. Freeman shared a fascination with the $L1_2$ structured compounds that developed during that period. Freeman later did a study of the relative hybridization for the transition metal B atom materials[14]. During that time, we developed an appreciation of the curious utility of the Hill plots. The left hand or close separation side of the Hill plot is supposed to contain the itinerant f materials and they are indeed found to be "non-magnetic" or superconducting unless the presence of iron or nickel drives the system magnetic. This is not always the result of f-f interactions as we found out later in the case of the Ce based cubic Laves phases[15] but nonetheless the correlation is perfect. On the right hand or large separation side of the plot, however, the correlation is quite imperfect. There are a number of itinerant f systems, including all the heavy fermion materials, found in that regime. That should be expected because the interaction of the f orbital with other "ligand" orbitals does not require close proximity of the f orbital atoms. Thus, we began to use the Hill plot presentation of the systematics to pick out those materials where the mechanism driving f itinerancy was definitely *not* the f-f interaction which suggested the plots in the first place. It is the smallness of the interactions of the f orbitals with orbitals of other character that is the origin of mixed valent and heavy fermion behaviour and we were able to focus on these interactions by this mechanism.

The first success of this identification (coupled to the prior interest in $LaSn_3$ at Northwestern) came in the observation of de Haas- van Alphen signals[16] in $CeSn_3$ and the successful calculation of their frequency by standard band structure techniques[17]. Most assuredly Freeman then held true to the principal of first exploiting the simple explanation when he successfully calculated[18] the frequencies for the heavy fermion material UPt_3 in spite of considerable opinion to the contary! There remained the need for a systematic explanation of the tremendous mass enhancements of these materials (7 for $CeSn_3$ and 20 for UPt_3). This M.R.Norman was able to do by extracting the interacting susceptibility from inelastic neutron scattering and using it in the self energy[19]. An interesting historical footnote is that Norman came to a postdoctoral position at Argonne as a part of a package to induce Freeman to stay at Northwestern.

BEYOND STANDARD BANDS ...

Norman's discussion of the mass enhancements is one example of the practice of taking what one can from standard band formalism and then extending on that base. The clasic example is the treatment of the localized f systems such as Gd, or in our view CeSb. In this case, the variational freedom of the formalism underlying density functional theory has been restricted to reflect the known physics not presetn in the approximate functionals utilized. This technique is mentioned as more familiar and comfortable to the reader. This restricted variation scheme proved an excellent way to probe the relaxation effects in the photoemission from Ce materials. The famous two f-peak structure was taken as evidence that a band description was irrelevant in spite of admonishments that that structure should not appear in the band density of states. That structure results not directly from the ground state but from two channels leading to different excited states. If the f-orbital hole is very localized, then a Ce d orbital will be filled to partially screen it. If not, then it will be possible for the f character to be refilled to screen the hole. The latter case has a lower energy than the approximate f-->d transition so that the partially screened hole will be shifted down by roughly 2 eV. The well-screened hole will appear very nearly in the same position as would the direct band structure calculation because the system has "replaced" the f-charge. The energetics , but not the transition probabilities, of this simple model are calculatable by considering total energy changes. This proved quite successful[20]. Similar techniques have successfully yielded both Δ_+ and Δ_- as well as the Hubbard U parameter across the entire rare earth series[21]. The situation becomes more murky in the actinides. The 5f orbital is more itinerant so that the poorly screened orbital becomes both far more difficult to detect[22] and more difficult to model. The restricted-freedom approach is less appropriate because one does not have as well defined a prescription for the restriction. The cuprate superconductors share this difficulty and are driving renewed interest in developing Wannier functions.

Another such case of using the standard rare-earth style treatment of the 4f is a model for the deHaas-vanAlphen frequencies of CeSb[23]. If one assumes that the f-orbital is essentially localized and exists in a definite magnetic state in the magnetic field, the field resulting from that anisotropic charge density will affect the conduction electrons breaking cubic symmetry. As the moment flops with a rotation of field, the resultant dHvA frequencies will also flop. The calculations are reasonably successful in light of their omission of the hybridization effects which drive the rich magnetic phase diagram.

OUTSTANDING PROBLEMS

This is not a memorium! By no means should one believe that all problems -- or even the majority -- are solved. In fact, we are just now getting to the Slater's (1966) program. What are some of the interesting problems from the area of localizing orbitals? One is, of course, the desire to relate calculated results to the parameters appearing in the many body model Hamiltonians. Such thinking underlied the efforts on the two-peak structure in the Ce photoemission. A good deal of progress is being made in this area and there is a long way to go and the cuprate superconductors have done much to spur the effort. The benefit will be a considerably greater understanding of the models used. Another problem will be the calculations of response functions to examine their poles and to use them in GW or self energy calculations. Progress is being made on that front as well and we can look forward to some very interesting developements over the next few years. Simulation techniques are also beginning to be used and these are going to give us insight into dynamical effects not previously accessible. These are broad issues. What are some specifics? Let me offer three.

°UPt_3 and URu_2Si_2 exhibit very small moments of hundredths of a Bohr magneton which nonetheless behave more like local moments. The band calculations[24] give a large moment comparable to that seen when the material is doped reminicent of $TiBe_2$. The mechanism of this moment suppression offers a very interesting puzzle.

°The alloy properties of the actinides also offer some very interesting puzzles. The Hill critical separation for U and Pu is about 3.4 Angstrom whereas for Np it is about 3.25 Angstrom. One might argue that this apparent violation of an actinide contraction is a consequence of creating a zero moment shell in Pu. But would one then be able to explain the observation that many 50-50 U-Pu alloys do mimic Np? An example of this occurs in the dialuminides where both the U and Pu compounds exhibit fluctuation phenomena whereas both Np and the 50-50 U-Pu compound exhibit moment behaviour. Another puzzle occurs in the $UPd_{3-x}Pt_x$ alloy system where a second f-orbital photoemission peak appears very strong only in a very narrow concentration range around 50-50 mixture.

°Magnetic field effects are strong enough to be seen at even modest fields. One example is the appearance of induced polarization[25] very close to the Ge atom in UGe_3. A credible explanation for this effect assumes it is much like a transferred hyperfine splitting where the U f-orbital responds directly to the applied field but that the Ge ion is more influenced by the f-orbital modifications than directly by the field. Perhaps a similar set of logic can be applied to the excess e_g d character observed[26] in $CeSn_3$. But then one must understand why the Fermi surfacecalculated for zero field matches the dHvA frequencies which are actually taken at higher fields. The case of $CeAl_2$ which the author is currently studying in collaboration with members of the MTG provides an even stronger case. $CeAl_2$ is truly very close to the border of localized f character. At zero applied field, it is antiferromagnetic which is correctly discribed by band calculations[27]. However, a very modest magnetic field flips the system into a ferromagnetic configuration where one can see from the band calculation that the f-orbitals will be far more local in character. DeHaas-vanAlphen measurements are made at fields such that $CeAl_2$ is in this induced ferromagnetic configuration. One factor making $CeAl_2$ challenging is that, within the local f model, the Fermi energy falls in a hybridization induced anti-crossing of the underlying transition metal like band structure. This significantly enhances the sensitivity of the results to the f orbital behaviour. Some properties of the Fermi surface are driven by that underlying band behaviour (thus the crude similarity to the $LaAl_2$ Fermi surface) and others from the interaction of the f orbitals. Another factor complicating interpretation is that one starts with four huge Fermi surface pieces that almost fill the entire Brillouin zone. Then, as the model is changed, the larger surfaces contact the zone surface and break up. Thus, one is not dealing with modest variations of surface size but qualitative changes in surface topology. A systematic approach to modelling this material starts by probing the effects of hybridization using the f-band model compared to the local f model and then probes exchange interactions using spin and moment polarized calculations. This is the part of the program nearing completion. Thereafter, one should explore orbital couplings and anisotropic effects such as applied to CeSb. Clearly $CeAl_2$ is a material that will occupy our attention for some time to come.

To close, what is going to happen in the area of techniques in the 1990's? Our band technology has come a long way over the 35 of so first years of Freeman's career. The advent of massively parallel computers and the introduction of concepts of non-linear optimization are going to change our thinking and open up new opportunities. A great deal of effort is going into representing electronic structure in terms of those local orbitals of Slater's discussion. And simulation techniques are going to open up our ability to ask detailed questions about the effects of interactions and fluctuations. There should be plenty of exciting problems for Prof. Freeman and his MTG in the 1990's -- and for all the rest of us as well!

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