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BAND STRUCTURE STUDIES OF ACTINIDE SYSTEMS

D. D. Koelling

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## BAND STRUCTURE STUDIES OF ACTINIDE SYSTEMS\*

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### ABSTRACT

The nature of the f-orbitals in an actinide system plays a crucial role in determining the electronic properties. It has long been realized that when the actinide separation is small enough for the f-orbitals to interact directly, the system will exhibit itinerant electron properties: an absence of local moment due to the f-orbitals and sometimes even superconductivity. However, a number of systems with the larger actinide separation that should imply local moment behavior also exhibit itinerant properties. We have been examining such systems (URh<sub>3</sub>, UIr<sub>3</sub>, UGe<sub>3</sub>, UC) to learn something about the other f-interactions.

A preliminary observation we have made is that there is apparently a very large and anisotropic mass enhancement in these systems. There is very good reason to believe that this is not solely due to large electron-electron correlations but to a large electron-phonon interaction as well. These features of the "non-magnetic", large actinide separation systems will be discussed in light of our results to date. Finally, the results of some recent molecular calculations on actinide hexafluorides will be used to illustrate the shielding effects on the intra-atomic Coulomb term  $U_{f-f}$  which would appear in any attempt to study the formation of local moments. As one becomes interested in materials for which a band structure is no longer an adequate model, this screened  $U_{ff}$  is the significant parameter and efforts must be made to evaluate it in solid state systems.

### I. INTRODUCTION

The major factor controlling the electronic properties of actinide materials is the nature of the f-orbitals: whether the incomplete f-shell of the atoms gives rise to states of a localized or itinerant nature [1]. The nature of the states arising from the f-orbitals will depend on the relative importance of the intra-atomic Coulomb correlation and such bandwidth producing effects as: (1) the direct f-f overlap and interaction, (2) hybridization and/or bonding with other orbitals. Those systems where the actinides are sufficiently close to have direct f-f interactions always exhibit itinerant character. This is the basis for the Hill plots [2] which correlate local moment behavior (ferromagnetic and antiferromagnetic transition temperatures) and itinerancy (Pauli paramagnetism and superconducting transition temperatures) with actinide separation. One sees there that for actinide separations below a critical distance (which is dependent on the actinide considered), the material always exhibits itinerant character. It is significant that this critical separation is fairly sharp as it indicates the dominance of the direct f-f interaction. One very interesting set of materials for examining this effect are the Np cubic Laves phase compounds. There, by varying the B element, one can move the Np separation across this critical separation and thus see the effect directly [3]. This effect was also found to be dominant in the metals. See the article by A. J. Freeman and D. D. Koelling in Ref. [1]. (Time and space limitations will not permit the inclusion of the metal results here so we will focus on our more current interests.)

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The direct f-f interaction is not, however, the only bandwidth producing effect as can be seen by examining the region of large actinide separation in the Hill plots: there are itinerant systems also to be found in this region. We have been studying these systems as a way to examine some of the other bandwidth producing mechanisms. Progress in this direction has been greatly aided-- and even motivated--by the successful observation of the de Haas-van Alphen effect in three of these systems [4,5]. The de Haas-van Alphen effect has the advantage over other more readily available experimental data that it requires far less effort to compare with experiment once one has the electronic structure dispersion relations. Indeed most other experiments also require a knowledge of the wave-functions. The de Haas-van Alphen data will be discussed in the following paper by A. J. Arko. Here we will merely use selected results without further discussion.

The calculated results to be presented here are still somewhat preliminary as we are continuing the process of extending our calculational capabilities to fulfill the stringent requirements of these systems which are more demanding than the metals we have already studied. However, we are confident that several features we have observed will remain when we perform the improved calculations. These we will present in Sec. III after a very brief discussion of the techniques we are currently using in Sec. II. This discussion will focus on the accuracy to be expected in our calculations. Finally in Sec. IV, we will discuss briefly some results of interest concerning the intra-atomic Coulomb interaction. These arose from some molecular calculations we performed on the actinide hexafluorides [6].

## II. CALCULATIONAL TECHNIQUES: ANALYSIS OF ERROR BARS

The calculation of electronic band structure can be separated into two more or less distinct parts: the representation of the complex interactions of the system by an approximate one-electron potential and the solution of the resultant quantum mechanical equations involving this potential. For actinide systems the quantum mechanical equations must be based on the four-component Dirac equation as the electrons are moving very rapidly in the vicinity of the nucleus. Nonetheless, it is easier to assay the precision of the techniques used to solve the single particle equation than the accuracy inherent in the potential. Thus we will first discuss these techniques and then briefly consider the potential used. Somewhat more discussion of the band structure technique will be given here than might otherwise be dictated because the technique is not a standard one and has been developed for these actinide compound systems. (The details will not be given in the oral presentation.) Like any description of "experimental apparatus", this can be skipped by the disinterested reader.

Almost all band structure techniques are based on obtaining a variational solution to the problem. Thus a full description of the technique consists of describing the basis functions to be used, how to set up the matrix equations, and how to solve them. Here, I will spend some time describing the basis functions, merely give the results for the matrix elements and briefly touch on a few features of their solution. The insight is, after all, in the basis functions with the rest being merely (crucial) engineering details of the calculation.

To set up the basis functions, we approximate the potential by a muffin tin: a potential which is spherical within non-overlapping spheres about each ion and constant (flat) in the remaining interstitial region. Although this approximation to the potential is used to set up the basis functions, it need not be-- and, in fact, is not--used in the final calculation of the electronic structure. However, some care should be taken in its construction as the more closely it approximates the potential the better will be the basis functions. That one does indeed want to include the more general shape is indicated by the fact that the rms error of the optional constant in the interstitial region is roughly 0.25 Rydberg for most of the systems we are discussing. For these cubic systems, this is the major correction so we have retained the spherical averaging about each ion.

The basis set is now constructed by taking Dirac plane waves in the interstitial region

$$\phi(k, s) = \frac{1}{\sqrt{N\Omega}} \exp i\mathbf{k} \cdot \mathbf{r} \begin{bmatrix} \chi^s \\ \frac{c\mathbf{k} \cdot \boldsymbol{\sigma}}{p + mc^2} \chi^s \end{bmatrix}$$

$$p = [c^2 k^2 + m^2 c^4]^{1/2}$$

and augmenting them with a set of functions in the interiors of the muffin-tin spheres through a generalization of the Rayleigh expansion. It is the form of this augmentation which makes this method different from the standard relativistic APW method [7]. Note that we have not included all the normalizing factors in the plane wave as after augmentation it will require renormalization anyway. The notation used is:  $N$  - number of unit cells;  $\Omega$  - volume of the unit cell; and  $\chi^s$  - a two component Pauli spinor (up or down).

To augment this plane wave, we will use two functions for each  $\kappa$  angular component. ( $\kappa$  is the standard relativistic quantum number that gives both  $l$  and  $j$ .) This will allow us to make both function and derivative continuous for the large component but leave us with a discontinuous function for the small component for the basis functions. (The fully converged variational solution will not have this non-physical property.) By adding additional functions, one could, of course, make the small component of the basis function continuous but actual testing shows that this yields little reward for considerable additional effort (expense). However, the use of two functions eliminates a problem which occurs in the standard APW method when the one function used vanishes at the matching radius. The singularities that this produces would be much more numerous and devastating in the actinide compounds. Thus we are forced to use this second function whereas we were able to do quite well with the standard APW method for the metals.

We can now complete the specification of the basis functions by stating that the two radial functions to be used are the solution of the spherical potential at an energy parameter  $\epsilon$  and its energy derivative at that energy. The parameter  $\epsilon$  thus becomes a non-linear variational parameter which can be handled in a variety of ways [8]. In the calculations to be presented here, it has merely been set equal to the Fermi energy since we are primarily interested in

Fermi surface properties. The use of the energy derivative was suggested some time ago by Marcus [9]. However, it was O. K. Andersen [10] who really performed the first analysis suggesting the great range over which the linear expansion is useful. Our own experiments [11] confirmed this to a surprising degree.

The energy derivative is easily obtained for if one has the radial solution  $U_{\kappa}$

$$U_{\kappa} = \begin{bmatrix} g_{\kappa} \\ f_{\kappa} \end{bmatrix}$$

$$(h_{\kappa} - \epsilon)U_{\kappa} = 0$$

$$h_{\kappa} \equiv \begin{bmatrix} V(r) & c\left(\frac{\kappa - 1}{r} - \frac{d}{dr}\right) \\ c\left(\frac{\kappa + 1}{r} + \frac{d}{dr}\right) & (V(r) - 2mc^2) \end{bmatrix}$$

The equation for the energy derivative  $\dot{U}_{\kappa}$  is obtained by straightforward differentiation

$$(h_{\kappa} - G)\dot{U}_{\kappa} = U_{\kappa}$$

and is the inhomogeneous equation with  $U_{\kappa}$  as the inhomogeneous part. By requiring  $U_{\kappa}$  to be normalized within the spheres and differentiating this condition, we find that  $U_{\kappa}$  and  $\dot{U}_{\kappa}$  must be orthogonal. Thus the indeterminacy of the solution is removed except for an overall constant. This is also assigned from the requirement that  $U_{\kappa}$  be normalized in the sphere via a relation obtained from Gauss' theorem. However, one result of this is that

$$N_{\kappa} \equiv \int_{r < R} d^3r \dot{U}_{\kappa} \dot{U}_{\kappa} \neq 1$$

but that

$$U_{\kappa}(\epsilon) = U_{\kappa}(\epsilon_0) + (\epsilon - \epsilon_0)\dot{U}_{\kappa}(\epsilon_0) + \dots$$

Putting these basis functions together into variational calculation yields the secular equation

$$\underline{H} \underline{C} = \underline{E} \underline{S} \underline{e}$$

$$H_{qr} = \langle \chi^{s_q} | f_{qr} | \chi^{s_r} \rangle [P_r - m_c^2] U(k_q - k_r) + V(k_q - k_r) \\ + \frac{4\pi}{\Omega} \sum_n S_n(\kappa) \sum_{\kappa} \langle \chi^{s_q} | D_{\kappa}(\hat{k}_q, \hat{k}_r) | \chi^{s_r} \rangle \{ \epsilon t_{\kappa}^n(q, r) + a_{\kappa}^n(q) b_{\kappa}^n(r) \}$$

$$S_{qr} = \langle \chi^{s_q} | f_{qr} | \chi^{s_r} \rangle U(k_q - k_r) \\ + \frac{4\pi}{\Omega} \sum_n S_n(\kappa) \sum_{\kappa} \langle \chi^{s_q} | D_{\kappa}(\hat{k}_q, \hat{k}_r) | \chi^{s_r} \rangle t_{\kappa}^n(q, r)$$

$$f_{qr} = 1 + \left[ \frac{c^2}{(p_q + m_c^2)(p_r + m_c^2)} \right] [k_q \cdot k_r + i k_q \times k_r \cdot g]$$

$$D_{\kappa}(\hat{k}_q, \hat{k}_r) = |\kappa| P_{\ell}(\hat{k}_q \cdot \hat{k}_r) + i \frac{\kappa}{|\kappa|} (\hat{k}_q \times \hat{k}_r) \cdot g P'_{\ell}(\hat{k}_q \cdot \hat{k}_r)$$

$$t_{\kappa}^n = a_{\kappa}^n(q) a_{\kappa}^n(r) + b_{\kappa}^n(q) b_{\kappa}^n(r) N_{\kappa}^n$$

$$a_{\kappa}^n(q) = R_n^2 \left\{ \frac{c k_q \kappa}{(p_q + m_c^2) |\kappa|} j_{\ell}^{-}(k_q R_n) g_{\kappa n}^{\cdot}(R_n) - j_{\ell}^{\cdot}(k_q R_n) f_{\kappa n}^{\cdot}(R_n) \right\}$$

$$b_{\kappa}^n(q) = R_n^2 \left\{ \frac{-c k_q \kappa}{(p_q + m_c^2) |\kappa|} j_{\ell}^{-}(k_q R_n) g_{\kappa n}^{\cdot}(R_n) - j_{\ell}^{\cdot}(k_q R_n) f_{\kappa}^{\cdot}(R_n) \right\}$$

In these expressions:  $S_n(\kappa)$  is a structure factor for each atom type  $n$ ;  $P_{\ell}$  is a Legendre polynomial and  $P'$  its derivative;  $j_{\ell}$  is a spherical Bessel function;  $\ell$  is the  $\ell$ -value to be associated with the small component of the  $\kappa$  decomposition of the Dirac plane wave;  $V(\kappa)$  is the Fourier analysis of the interstitial potential; and  $U(\kappa)$  is the Fourier component of a step function which is one in the interstitial region and zero-inside the muffin tin spheres,

$$U(\kappa) = \delta_{\kappa, 0} - \int \left( \frac{4\pi R_n^3}{\Omega} \right) \frac{j_1(\kappa R_n)}{(\kappa R_n)} S_n(\kappa)$$

$$S_n(\kappa) = \int_j e^{i\kappa \cdot r_j}$$

Those terms involving  $U$  all arise from the interstitial region. Those involving a  $D_K$  arise from within the muffin tin. The  $a_K^n$  and  $b_K^n$  are actually expansion coefficients for the  $K$ -function and  $K$ -energy derivative function. Probably the only important thing to note from these expressions is that we have obtained a secular equation in standard form. Because of their size and near singular properties, they require some special handling [12] but are otherwise in the classical secular-equations format.

At this point the reader can see that there are really two points to consider concerning the precision of the solutions obtained: (1) Are enough basis functions (RAPW's) included? and (2) Over what range is the energy variation of the radial solutions adequately described by the linear Taylor series expansion. We have performed all these calculations with adequate RAPW's to insure 0.01 eV convergence. This requires 150-200 reciprocal lattice vectors (300-400 RAPW's) for the  $Cu_3Au$  structured materials and about 75 for the rock salt structured UC. The linear expansion appears to be good to the same precision for  $\pm 2$  eV about the Fermi energy for the  $Cu_3Au$  structure of materials. It is even much better than that for the UC. We tested the rock salt structure version of the codes on NbC against a standard APW calculation. Over a range of more than 10 eV, the only discernible difference was attributable to our slightly better basis-functions convergence. (It should be noted that NbC is a slightly more favorable case—but so is UC.)

Some precision is lost by the necessity of fitting our ab initio points to perform further calculations. We have fitted our calculated points to a Fourier series making maximal use of symmetry. These fits ranged in quality from 0.01 eV rms error up to 0.2 eV rms error. Clearly, for the system with the larger errors, we are definitely looking for a better way. However, even for these systems (notably  $UCe_3$ ), we are able to determine some gross features.

Finally, we should consider the question of how good our potentials are. We are not yet ready to address the fundamental question of how well a local single particle potential can represent our systems—although they were carefully chosen to maximize its success. We do have one advantage though: because of the high atomic number, the electronic density is high. Thus the exchange correlation potential is well represented by the simple Kohn-Sham-Gaspár [13] form—which has been used in all calculations to be discussed here.

We are still struggling to build something comparable to the best potentials obtained for transition metals (which are quite good). These calculations have been performed using the overlapping charge density model. In this model, one uses the results of SCF atomic calculations which are then overlapped to form the approximation to the charge density. The potential is then obtained from this charge density in a straightforward fashion. There is a considerable art in choosing the configuration to be used in the atomic calculation such that one obtains a good potential. Here again the actinide compounds prove more difficult than the metals in that the number of parameters involved goes up drastically. Thus, where we could easily use good "rules of thumb" to adjust the potential for the metals, it is just not as tractable in the compounds and only for favorable cases are we going to be successful. At present we are currently engaged in some numerical experiments to see if the configuration can be chosen variationally [14]. If successful, they will allow us to use this simple model potential construction as a close approximation to the results of a full SCF calculation (at a considerable reduction in effort!).



For now, however, we have simply chosen the atomic configurations according to experience and then checked to see how sensitive the results were to that choice. The one exception is UC--which we will discuss later.

There are definitely improvements which we would like to make in our calculations (primarily in the construction of the potential) but we believe that they are adequate to reveal some of the gross features that will be a primary focus of our future actinide research.

### III. BAND STRUCTURE RESULTS FOR SELECTED ACTINIDE COMPOUNDS

Historically, the first actinide compound we examined was URh<sub>3</sub> [4]. This was based on the twin facts that URh<sub>3</sub> is a congruent melter such that good samples could be prepared and that it is a favorable system in which to observe an f-d bond. Experiencing some initial success in this systems, we chose to also look at UIr<sub>3</sub> with the expectation that it would show great similarities to URh<sub>3</sub> much as Pt is quite similar to Pd. Indeed this is the case as the dominant feature of the Fermi surface is produced by a band dipping down at the point M ( $k = \frac{\pi}{a}(110)$ ) in the Brillouin zone. This is clearly seen in Fig. 1 which shows the band structure in the immediate region of the Fermi energy resulting from our best potential for UIr<sub>3</sub>. The Fermi

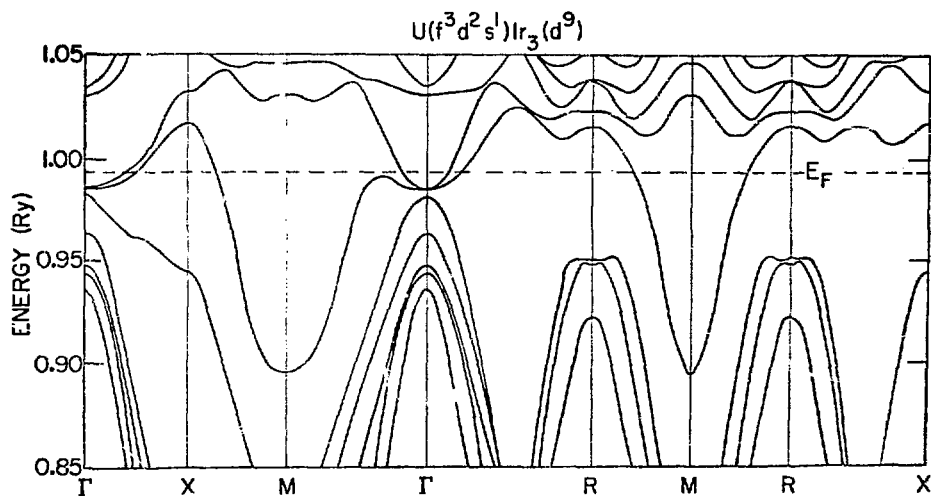


Fig. 1: Band structure of UIr<sub>3</sub> in the immediate region of the Fermi energy. Note the expanded energy state (which is in Rydberg units). The most significant feature is the band dipping below the Fermi energy about the point M.

surface that results is shown in Fig. 2. This piece of Fermi structure gives remarkably good agreement with the observed de Haas-van Alphen areas (see next paper by A. J. Arko). The one exception is that one must draw a fence around one small area of the surface and not permit those orbits which require the electrons to traverse that area. The area in question is the protrusion seen along the cube edge as one goes up from the point M to the cube corner.

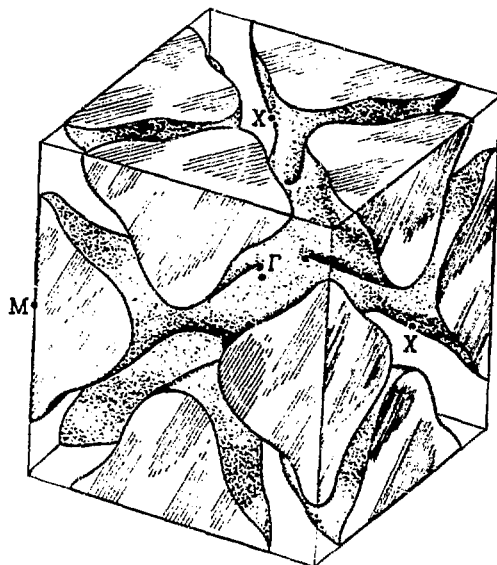


Fig. 2: Structure of the predominant piece of Fermi surface due to the band noted in Fig. 1.

This is also the region most sensitive to our choice of potential so it would be tempting to suggest the formation of necks. This, however, would not be consistent with the experiment as there does not appear to be any turn-up in the frequencies as they approach extinction. On the other hand, there is also no increase in mass as one would expect if the problem was that the mass were increasing beyond what could be observed. Nonetheless, one feels that we do have a fairly good knowledge of this Fermi surface structure since not only did it correctly give (1) the  $\beta$  frequencies near 0.20 atomic units, and (2) the neck frequencies  $\xi$  in the 0.015 atomic unit range, but it also was able to predict (a) the  $\mu$  frequency near 0.10 atomic units due to an orbit centered on the point X; and (b) the  $\eta$  frequency which exists for a short distance about the (111) direction at about 0.08 atomic units. This  $\eta$  orbit involves traversing three of the necks that join into the  $\Gamma$  centered part of this structure. This part of the Fermi surface is believed to be a result of the U(f)-Ir(d) bonding and is fairly insensitive to the potential used. The remaining Fermi surface structures are not so convenient, unfortunately, and we cannot give a definitive statement as to where they come from. We can make several guesses, however. The  $\alpha$  frequency, which is extremely strong, may come from some small spherical electron pockets observed along the line  $\Lambda$  ( $\Gamma$ -R) in a calculation performed with a different potential. The  $\gamma$  frequency has the same shape but one fourth the size of a  $\Gamma$ -centered piece generally observed for all potentials we have studied. Thus one can make this tentative identification.

We were initially very enthused [4] by our results for URh<sub>3</sub> even though we were only able at that time to do calculations on symmetry lines and points-- and thus only able to guess at the Fermi surface implied by the calculation. With our new calculational power, we re-examined briefly one of the potentials and find a somewhat disturbing feature: Although we again correctly predict that the major Fermi surface piece should be centered at M, the dip in the bands along  $\Lambda$  which corresponds to a neck structure similar (but not identical) to UIr<sub>3</sub> is lower than the one along S (X-R). We currently believe that the experimental data would be more consistent with the necks along the zone face than in the interior. This is most likely a somewhat sensitive feature of the potential and will require further investigation.

In URh<sub>3</sub> and UIr<sub>3</sub>, we have the formation of a strong f-d bond which is quite helpful as it makes our result less potential dependent. We will see a dramatic example of this when we consider UC. Since the Ge in UGe<sub>3</sub> [5] does not have any occupied d-states in the conduction band, one can correctly anticipate that we have far more difficulties with this system. The situation is that most of the band structure is fairly potential insensitive except for one band which moves dramatically. One feature which does appear which is relatively potential insensitive is a large peak in the density of states very near the Fermi energy. It is very tempting to speculate that this peak may be closely related to the weak many-body effects in UGe<sub>3</sub>.

The most interesting feature in all the above systems is found when we compare the calculated and measured mass values: many of these orbits have large mass enhancements. This can be anticipated by comparing the measured specific heat to the density of states at the Fermi energy to get an enhancement factor. It is found to be roughly two in all three cases. This enhancement varies widely from orbit to orbit: it is 2.1 for the  $\beta$  orbits in the (110) direction in UIr<sub>3</sub> but one (i.e., no enhancement) for the  $\mu$  orbit centered around the X-point. There does seem to be some inverse correlation of the enhancement to the band mass for the dominant features: i.e., the larger the band mass the smaller the enhancement. This is a very tentative empirical observation which is usually violated by the very small low mass pieces. These large mass enhancements may, however, be a result of having an intermetallic compound rather than an actinide system as recent data on Pt<sub>3</sub>Sn also appears to show these large enhancements [15].

Finally we consider UC: the one compound system which we have looked at for which there is no de Haas-van Alphen data. (Nor is there likely to be as the mono-carbides are notorious defect systems.) Aside from its possible technological significance, UC is an interesting system to examine because: (1) it should exhibit a very strong p-f bond; and (2) it is a rock-salt structured material with no local magnetic moment related to UN, US, UP, etc., which are very interesting magnetic systems studied using the nonrelativistic KKR technique by Davis [16]. Our initial approach to UC was to perform a molecular cluster calculation for the fictitious system UC<sub>6</sub> from which we chose the configuration to be used in setting up our potential. This resulted in the energy bands shown in Fig. 3. When the density of states at the Fermi energy was compared to the observed specific heat, we found an enhancement factor of nearly 5! Our initial reaction to this was based on a famous maxim in computational physics: "Nothing resembles a new effect like a mistake". We thus did two things:

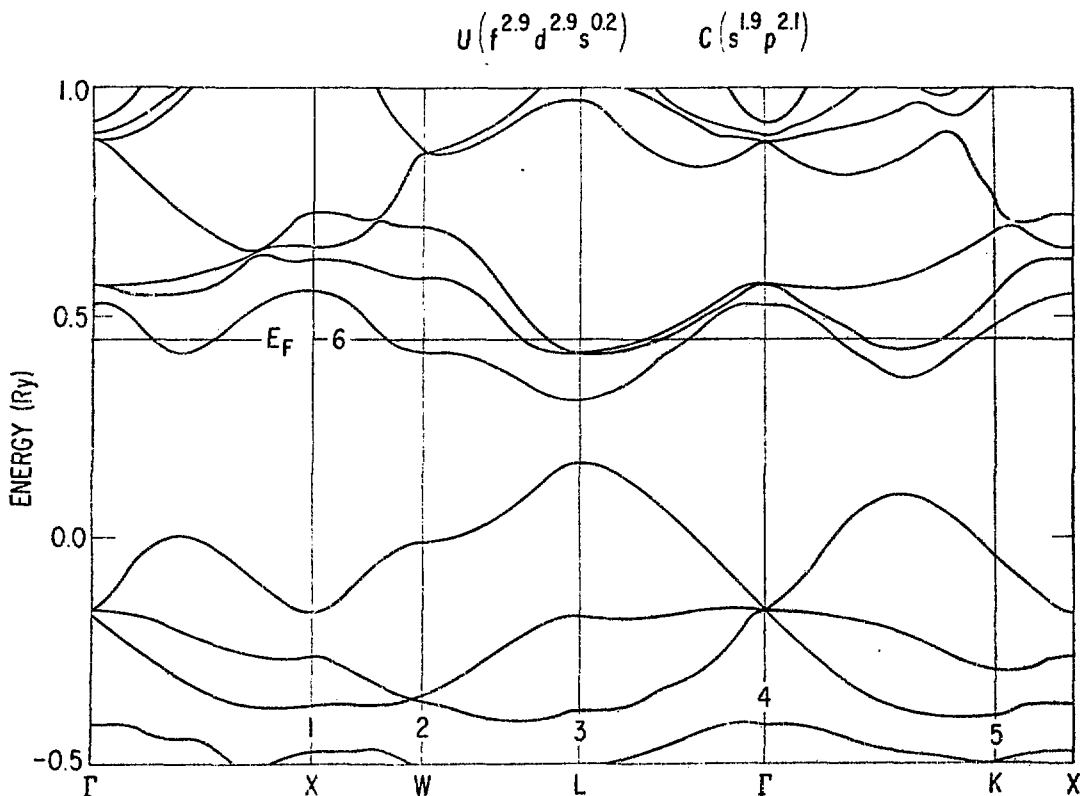


Fig. 3: Band structure of UC.

(a) we checked out the computer code by performing calculations on NbC where we had the results of another calculation for comparison; and (2) we tried two different additional potentials constructed with very different uranium configurations. We found that the computer codes were working very well and that the bands from the two other potentials were nearly identical to those of Fig. 3--more so than the variations were in URh<sub>3</sub> or UIr<sub>3</sub>, for example. Thus we are left with strong evidence that there really is an enhancement factor of 5. One is somewhat reassured that this might be possible as enhancement factors of 3 are reported for UN and US [16].

It is interesting to examine the UC bands in Fig. 3. The normal interpretation of the three bands at the bottom of the figure is that they are the C p-bands. However, we can be quite sure that the  $\Gamma_{15}$  type f-orbitals are quite strongly admixed into these bands. Estimates based on the molecular cluster calculations would have these bands nearly a 50-50 mixture of U-f and C-p orbitals. The next bands above the gap are also f-p bands as they have negative parity at  $\Gamma$ . Only when we go to the bands at the top of this figure do we find the uranium spin-orbit split  $t_{2g}$  d-bands lying quite close to the f-band of xyz symmetry. The wavefunctions have been stored on magnetic tape and further analysis will be performed on them. It should also be quite interesting to see what will happen when we look at UN. In this system the

molecular cluster calculations indicate much less covalent and more ionic bonding. In this regard, the phonon data [17] suggest a great deal of covalent bonding in UC if one uses the following argument. The optical phonons of UC are dramatically lower in frequency than those of the heavy transition metal carbides. As the ionic interatomic interactions are very stiff, this must mean that the ionic character is much reduced in UC which can only occur if the C p-bands are strongly hybridized or bonded. Consistent with this interpretation we may note that ThC, which will not exhibit the f-p bonds, melts almost 200 degrees higher in temperature.

#### IV. MOLECULAR CALCULATIONS AND THE INTRA-ATOMIC COULOMB INTERACTIONS

We have recently performed calculations [6] in the hexafluoride molecules  $UF_6$ ,  $NpF_6$ , and  $PuF_6$  using a Dirac-Slater molecular orbital technique [18]. These calculations were done in an effort to understand the optical spectra using the transition state approach which approximates the relaxation effects by performing a single SCF calculation with the initial and final state each half occupied. The ground state results of the calculations are summarized in Fig. 4 where we give the Mulliken orbital decomposition of the various molecular orbitals. One should note that the seven (unoccupied in  $UF_6$ ) "f-states" are not purely f-orbitals but a mixture with the F-p orbitals.

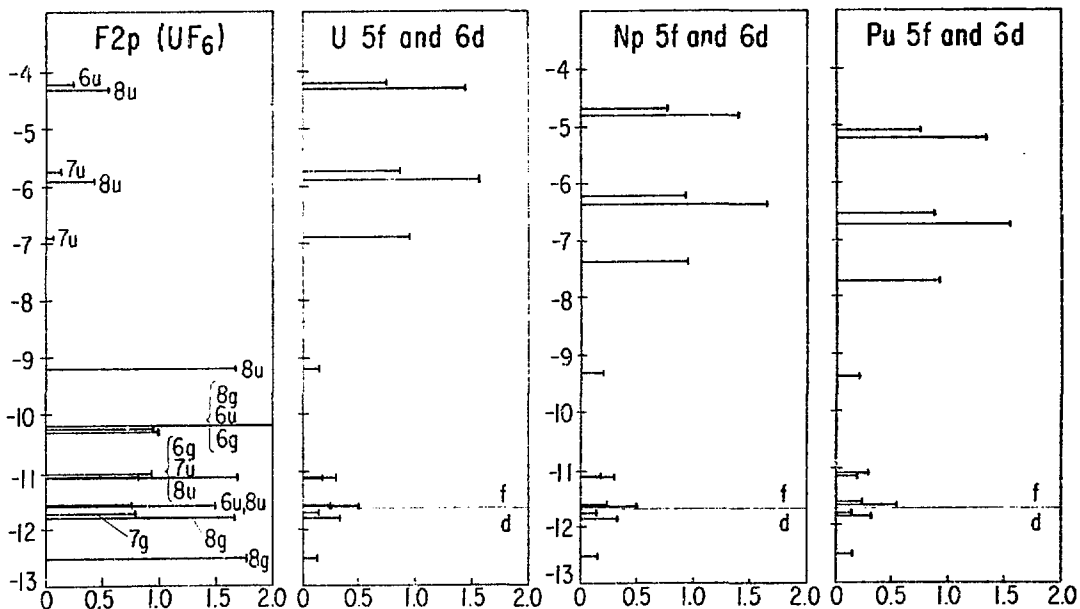


Fig. 4: Energy levels and orbital decomposition of the actinide hexafluoride ground states. A degeneracy factor has been included such that this is much like a decomposed density of states. The energy scale is in electron volts.

The remaining f-orbital contribution is found among the bonding states and amounts to a total of 2.75 electrons in  $UF_6$ , 3.85 in  $NpF_6$ , and 4.93 in  $PuF_6$ . A very similar thing seems to be happening in  $URh_3$ ,  $UIr_3$ , and  $UGe_3$  where the density of states shows seven large unoccupied peaks and a strong admixture at and below the Fermi energy. Although the density of states for UC have not been carried to high enough energy, this feature appears not to persist under the stronger bonding.

The main reason for mentioning these molecular calculations, however, is to illustrate some features of the intra-atomic Coulomb interaction. In attempting to apply a Hubbard type model calculation, it is necessary that the intra-atomic Coulomb interaction parameter  $U_{5f-5f}$  include corrections for screening (i.e., relaxation of the system) which reduce its magnitude by a factor greater than three for the 3d transition metals. As this  $U_{5f-5f}$  is basically a competing factor which makes the application of a band theory less tractable with its increased size, we would like to see what happens as it is screened. A useful illustrative example can be found in our  $NpF_6 \uparrow \uparrow \gamma_{8g} \rightarrow \gamma_{7g}$  calculation. If we identify U (dropping the 5f subscripts for convenience) as the difference in energy found using the transition state and the ground state

$$U \approx \Delta\epsilon_{T.S.} - \Delta\epsilon_{G.S.}$$

then we can perform the transition state with "frozen orbitals" obtained from the ground state calculation and then allow the calculation to become self-consistent. The "frozen orbital" calculation yields  $U_0 = 5.1$  eV whereas the screened result was  $U = 0.4$  eV or a reduction by a factor of eight! The actual calculation of this Coulomb correlation term in a solid is basically a complicated impurity problem which can be seen to demand the inclusion of screening effects as a very crucial element.

## V. CONCLUSIONS

Throughout this paper the basic idea which we have wanted to convey is that although the problem of band structure calculation in actinide compounds is far from solved, we are making good progress. We have been able to apply, with some success, our calculational tools to a number of systems where the direct f-f interaction is not dominating. And although there are some improvements to be made in our ability to solve the one-electron potential problem, these are not crucial (i.e., they are cost-efficiency matters). Rather, we now must concern ourselves with generation of better potentials. This is, of course, a much more satisfying situation as that is where the physics is to be found.

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