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The band theory approach for actinides (*)

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Résumé. — Nous considérons l'application de la théorie des bandes aux actinides. On étudie les aspects fondamentaux pour définir les limites de validité. Nous examinons ensuite les méthodes approchées les plus pratiques afin de mettre en évidence les hypothèses de base et définir leur limite d'application. Les exemples sont tirés principalement de notre travail sur Th, α-U et UGe

Abstract. — We examine the application of band theory to actinide systems. The fundamental aspects are considered to define the limits of applicability. We then consider the more practical approximate applications to demonstrate their underlying assumptions and range of applicability. Examples are drawn primarily from our own work on Th, α-U and UGe.

1. Introduction. — Although there has been a fairly steady effort applying band theory to actinide systems for roughly ten years, these studies are still in their early stages — i.e., not as precise or as detailed as those for the transition metals. This is due primarily to the fact that the actinides are at the limit of applicability of band theory. It is also a result of additional complications which arise from the tendency of the actinides to crystallize in lower symmetry structures and the need for treating them with relativistic kinematics. We consider these problems in the next two sections and then discuss the directions future research might take.

2. Band theory formalism for actinides. — The essence of band theory lies in the assumption that one can write the total density of the system as a sum of single electron contributions and that these contributions can be obtained by solving single-particle equations which involve some form of effective potential. The density functional formalism of Hohenberg, Kohn, and Sham [1, 2] assures one that this can be done for any non-degenerate ground state of a spin-less system. Von Barth and Hedin [3] have extended this formalism to include spin but the requirement of a non-degenerate ground state persists. There exists an extensive analysis based on this formalism. We need here only the result that we are to solve a set of single-particle equations

\[(K + V_c(r) + V_{xc}) \phi = \epsilon \phi \]  
(1)

where \(K\) is the non-interacting kinetic energy operator \(c \alpha \cdot \mathbf{p}\), \(V_c(r)\) is the Coulomb potential, and \(V_{xc}(r)\) is the exchange correlation contribution which is normally obtained from homogeneous electron gas results and is treated as a local operator. Although this is an approximate form of the formalism, it is adequate for our considerations here. This local form is inherently a high density approximation as it is important that \(k_F = (3 \pi^2 \rho)^{1/3}\) be large compared to the Fourier components of the density, i.e. the Fermi wavelength should be short compared to the variation in density. Actinides actually satisfy this criterion better than any other materials. It is easy to show that high density actually helps in another way as well: namely, it tends to diminish the relative importance of the electron gas correlations. Thus if one writes the exchange correlation as

\[V_{xc} = \alpha(\rho) \frac{2}{\pi} k_F = 3 \alpha(\rho) \left(\frac{3}{\pi} \rho\right)^{1/3} \]  
(2)

and plots two evaluations [3, 4] of \(\alpha(\rho)\) as in figure 1, one sees that they both approach \(\alpha = 2/3\) for large \(\rho(r_s \rightarrow 0)\) as do the \(X_a\) prescriptions [5]. Hence, the uncertainties in exchange correlation

\[\alpha(r_s)\] Comparison

Fig. 1. — Two determinations [3, 4] of the scaling parameter multiplying Slater \(\rho^{1/3}\) exchange. To compress the density scale, the ordinate is \(r_s = (3/4 \pi \rho)^{1/3}\) the radius of the volume/electron.

(*) Work performed under the auspices of the Department of Energy.
potential have minimal effect for the actinides. Relativistic effects for this functional are not significant in the valence and conduction bands [6, 7]. So for the non-degenerate ground state of the paramagnetic system, the formalism is reasonably well developed.

However, local density functional theory considers only the total energy and density of the ground state. It does not define a meaning for the single particle eigenvalues or eigenfunctions nor does it discuss the excited states. One can proceed, however, by identifying the single particle eigenvalues with the occupation number derivative of the total energy [8]:

\[ \epsilon_n = \frac{dE_T}{dn_n} \]

Thus, for those cases where the change in eigenvalue with the change in occupation number is negligible, the use of the band energies is appropriate. Otherwise one must use the transition state [8] which is prohibitively expensive for most solid state problems. The problem of the occupation number dependence of the eigenvalues occurs when one is dealing with spatially localized solutions such as those for core electrons. When the occupation of one of these orbitals is changed, the large intra-atomic Coulomb interaction is greatly modified. The 5f orbitals are intermediate between the localization of a core electron and the delocalization of a s-p like valence or conduction electron. This is the crucial point in applying band theory to the actinides. The band eigenvalues will be directly applicable if \( \xi = fU/W < 1 \) (where \( f \) is the fractional f-orbital occupation and \( W \) is the width of the band) which has been shown to be the case for the light actinide systems [10]. We here consider a few examples.

Consider for the case of a free atom [11] two configurations of importance for \( \alpha \)-U: \( U(f^6 d^s s^0) \) and \( U(f^{2.5} d^{3.2} s^1) \). We write the derivative expression for the eigenvalues

\[
\begin{align*}
\delta \epsilon_s &= U_s \delta n_s + X_{sd} \delta n_d \\
\delta \epsilon_d &= U_d \delta n_d + X_{sd} \delta n_s
\end{align*}
\]

in the same fashion as Cox and Lloyd [12] have used or the rare earths. For simplicity, we average out the spin-orbit effects throughout our discussions. Because the d-orbitals are quite extended, we can assume \( U_d \approx 0 \). Then one finds \( X_{sd} \approx 0.7 \) eV and \( U_s \approx 3.4 \) eV. Note that this result depends on the ionic state. For \( U^{3+}(f^6 \rightarrow f^{2.5} d^{3.2}) \) this same analysis gives \( U_s \approx 25.6 \) eV! The principle cause of this difference is that in \( U^{3+} \) all orbitals have been drastically contracted relative to the neutral configurations. This shows the significance of the spatial extent of the orbitals.

When the atoms are put together to form a solid, one significant change is that the atom is now constrained to a finite volume. This is the basis of the renormalized atom approximation [13]. The major effect of this renormalization will be to increase the density of the outer non-f orbitals near the nucleus and to cause the f-orbitals to expand. Bonding will induce further expansion thereby reducing the size of \( U_f \) to roughly 1-1.3 eV (note that the \( U \) defined here is half the energy to form a polar state) [14, 15]. The other significant feature is that this bonding will also reduce \( f \). In \( \alpha \)-U, the bands at the Fermi energy have \( f \approx 0.8 \) and \( W \approx 2.5 \) eV so \( \xi \approx 0.4 \). \( \gamma \)-U is a less favorable case [16] for a band treatment as the near-neighbour separation is larger and the f-f interaction is reduced. From table I of reference [14], considering \( (f^6 d^s s^0 \rightarrow f^6 d^s s^0) \) gives \( W_{sf} \approx 0.2 \) eV and \( U_s \approx 1.4 \) eV. When one considers \( (f^6 d^s s^0 \rightarrow f^6 d^s s^0) \), one gets roughly half this value due, again, to the expansion of the f-orbitals. In fact, in the \( f^6 d^s s^0 \) case the atomic f orbitals do not even bind without the application of an external potential. Lacking the occupation number decomposition, we set \( f = 1 \) and obtain \( \xi < 0.5 \).

For the very ionic systems, \( U_f \) can be quite large. But it need not be if the f-orbitals bond with other orbitals. In our study [17] of UGe, we found that our best potential was generated with a \( U^{3+} \) ion density in the configuration \( f^{2.5} d^{3.2} \). Yet by comparing the band results to those from an assumed \( f^{2.5} d^{3.2} \) configuration, we find that \( U_f \) should be slightly less than 2 eV giving \( \xi \approx 1 \) consistent with UGe, being a spin-fluctuation system [18, 19]. This reduction in \( U_f \) from 25 eV can be attributed to the formation of a p-f bond with the effect that the f-character is expanded by 20% relative to the ionic orbital (cf. figure 2 which compares the f-component density to that of the atomic case). The d-orbitals do show the ionic contraction.

![Graphical representation of radial density](image)

**Fig. 2.** Comparison of the radial density of the f-orbital at the Fermi energy in UGe, to that of an atomic f-orbital (broken line).

### 3. Actinide band theory in current practice.

A formally correct application of band theory would involve performing a self-consistent field (SCF) calculation for the electronic structure in which no assumptions are made about the shapes of the solutions or potentials involved. Because the actinides have a large atomic number, their electrons experience a deep potential well near the nucleus and move at relativistic speeds. Thus the correct calcula-
tion must include relativistic kinematics. Clearly, since such an SCF calculation is a difficult task, it is often necessary to extract the physics with an approximate calculation. As the approximations made reflect assumptions about the system and, of course, affect the precision of the results, it is important to understand them.

We first briefly consider the approximations to the kinematics. The simplest of these is the non-relativistic approximation. We have discussed this previously [14] and concluded that it was too coarse for our purposes although empirical tests do indicate that one can get the gross features in this manner [20]. Since one can, for the same effort, perform calculations in which the mass-velocity and Darwin terms are included but only the spin-orbit coupling (SOC) is omitted, the fully non-relativistic approximation is difficult to justify. There are various schemes for omitting the SOC. For brevity we consider here only our own scheme [21]. It is designed to retain a definite spin for inclusion of magnetic interactions (which is not true of all schemes) and is a specific form of the elimination method [22].

For the Dirac Hamiltonian

\[ \mathcal{H} = \beta mc^2 + c \alpha \cdot \mathbf{p} + V \]

and solution \( \psi \) with eigenvalue \((mc^2 + E)\), one can write

\[ \left( \beta mc^2 + C \alpha \cdot \mathbf{p} \left[ mc^2 (1 - \beta) + E - V \right]^{-1} C \alpha \cdot \mathbf{p} + V \right) \psi = \left( mc^2 + E \right) \psi \quad (4) \]

where now the large and small components are decoupled. Near the nucleus where the relativistic effects are significant, the potential is spherical and one can separate completely the SOC term for the large component. This is then ignored to do a spin-orbitless calculation.

The omission of SOC is a great computational aid as it reduces the size of the secular equation by a factor of two. Even if SOC must finally be included, it can still be used to facilitate self-consistent calculations: one can perform iterations without SOC until only the final one or two iterations. In many cases, it probably is unnecessary to include SOC except for the final determination of the Fermi surface dependent properties. To understand this, one should note that SOC does not make large changes in the valence or conduction band wavefunctions; its primary effect is to modify energies (mostly near high symmetry points and lines) and thereby the occupation or non-occupation of a particular wavefunction. Thus SOC can affect the charge density only if

\[ \Delta E_{\infty} / \left| \frac{dE}{dK} \right| \]

is comparable to the size of the mesh used in sampling the Brillouin zone. As these meshes are usually fairly coarse, this criterion is often very well satisfied as was verified in the case of Th.

In Th the f-orbitals are just beginning to affect the properties. It would appear that one is only able to account for the Fermi surface by including the f-orbitals into the calculation [23]. On the other hand, the pressure dependence of the Fermi surface is mainly influenced by changes in the s-d hybridization [24]. We have performed a self-consistent calculation for Th making no potential shape approximations (to be discussed below) but omitting SOC in the LAPW method [25, 26]. The resulting potential was then used for a fully relativistic calculation to redetermine the charge density and potential. It was found that density calculated with SOC differed by 2% from that calculated without SOC in the outer regions of the unit cell. This resulted in 0.05 eV changes in the dispersion of the band structure. Figure 3 shows the cubic harmonic decomposition of the density about the Th site; one sees from the \( L = 6 \) (chain-dashed) component \( \sigma_6 \) that the f-orbitals are already making a contribution to the occupied conduction bands. Similar calculations for the noble and platinum group fcc metals show \( \sigma_6 \) zeros to about 1.5 Bohr and then steadily decreasing out to the half near neighbour distance—precisely what one would expect from overlapping spherical charges. In Th \( \sigma_6 \) becomes positive with peaks at the maxima of the 5f orbitals. This can only occur because the 5f orbitals contribute to the occupied bands and move charge from the [110] directions to the [010] and [111] directions.

![Fig. 3. The radial density in a.u. for the spherical (solid curve with scale at left) and \( L = 4 \) (chain-dot) and \( L = 6 \) (chain-dash) cubic harmonic components (scale at right). The reader's attention is called to the \( L = 6 \) component which reflects the presence of f-orbital contribution to the charge density.](image)

We next turn to a second broad category of approximations which can be characterized as shape approximations. Here we will emphasize the great importance of symmetry to the calculations. One of
the most significant shape approximations utilized in band theory is the spherical approximation to the potential and density about the nuclear site. Comparing the scale for $\sigma_n$ (on the left) to that for $\sigma_2$ and $\sigma_4$ (on the right) in figure 3 should convince the reader that it can be a reasonable approximation. Further, when one has cubic symmetry, only the $L = 4, 6, 8$, etc. terms enter. The $L = 4$ term can at worst provide site diagonal d-d or p-f coupling. But this is site symmetry dependent. For example, in UGe$_3$ the Ge atoms are in sites of $D_{3d}$ symmetry. The $L = 2$ term is no longer excluded and so s-d and p-p couplings can also occur. If the site symmetry is even lower, more couplings enter and one can only appeal to the smallness of the aspherical potentials when making this type of approximation.

Nonetheless a spherical approximation can give a great deal of useful insight since, as mentioned previously, one of the most significant features in forming the solid from a collection of atoms is that they are constrained to a finite volume. Most of the gross properties of the solid will be determined by the nature of the atoms involved but modified by this compression. This is the basis for the success of the Engels-Brewer [27] type or Miedema [28] type analysis. One of the earliest formulated band structure techniques is the Wigner-Seitz spherical cell-method in which the unit cell is replaced by a sphere of equal volume and the potential is assumed spherical within it. The principal difficulty with the method is the specification of the boundary conditions. The atomic sphere-approximation [29] (ASA) utilizes the Green's function method to specify these boundary conditions and is the ultimate logical extension of the method. This method omits a great deal of structure and thus is most sensibly applied to the simpler crystal structures. When one does this, one is able to provide a useful demonstration that the f-orbitals are contributing to the bonding of the light actinide metals by obtaining very reasonable results for the atomic volumes of these systems [30].

A widely known and often used related approximation is the muffin-tin (MT) approximation in which one assumes spherical symmetry only within non-interpenetrating spheres and a constant in the remaining interstitial region. It works very well in close packed structures with cubic symmetry but when the symmetry is lowered or the structure is more open the approximation is subject to question. The more suspect part of this approximation is usually the use of a constant potential in the interstitial region since within the MT spheres the atomic core dominates while the interstitial region is affected by multiple centres. Consider the case of $\alpha$-U where half of the unit cell volume is interstitial. Here a much better treatment is the warped muffin-tin (WMT) approximation which utilizes the actual potential in the interstitial region but retains the spherical averaging about each atomic site. Because the augmented plane waves (APW) are plane waves in the interstitial region, the additional matrix element required is a Fourier component of the potential and is easily included in the calculations. In principle, the non-spherical components inside the spheres are also easily included because this involves only a series of Clebsch-Gordan coefficient and radial integrals. In practice, however, this must be done for every matrix element (i.e. $10^{10}$ - $10^{14}$ times) so that it must be greatly optimized to be economically feasible. At present, we have done this only for cubic symmetry.

The WMT approximation can give quite reasonable results even in the case of low symmetry as can be seen from our results for $\alpha$-U (see paper by Freeman, Koelling, and Watson-Yang at this conference). The site symmetry in $\alpha$-U is $C_{nv}$ so the group is of order 4. From the full rotation group compatibility tables, we find that there will be a dipole ($L = 1$) term in the potential, two terms each from $L = 2$, $L = 3$ and $L = 5$, three terms from $L = 4$, and four from $L = 6$. These introduce many additional couplings in the system. Figure 4 shows the resulting 6th band Fermi surface of $\alpha$-U obtained assuming these terms to be negligible. Arko and Schirber [31] have obtained de Haas-van Alphen data for $\alpha$-U by using pressure to avoid the phase transitions at 40 K. As discussed by them at this conference, the calculated Fermi surface correlates well with their data. Also at this conference, Veal will discuss the photoemission and Freeman, Koelling and Watson-Yang will discuss the induced neutron form factor. The model is found to do reasonably well. However, the lowered symmetry has greatly increased the computational effort. In a cubic crystal, convergence is obtained with 50-75 APW’s (we will not count the spin doubling as we handle it in a different way); for $\alpha$-U, using almost 200 APW’s gives results which are not as well converged. Because of the lowered symmetry, one must do calculations throughout an irreducible octant of the Brillouin zone (BZ) rather than an irreducible 1/48th BZ in cubic systems. So we found it necessary to calculate nearly 250 k-points (rather than 50-80) to determine the band structure. Since the cost per k-point rises at a rate between the square and the cube of the number of APW’s, the calculation costs about 25 times that for a bcc or fcc metal. Further because of the extensive hybridization of bands, a Fourier series for the dependence of $e(k)$ is not rapidly convergent. The Fermi surface of figure 4 was determined from such an expansion which had rms errors of 0.1 eV. To check the surface we determined a number of points directly. The error bars on these points in figure 4 are our estimates of the interpolation errors. They show that the Fermi surface obtained is faithful except in the outer regions of the Brillouin zone where there is much structure.
The $\alpha$-U calculation was not carried to self-consistency as this would be a very expensive process. Instead, the potential was created from an overlapping charge density (OCD) model which is again based on the observation that most of the crystal potential will primarily be a result of the atomic structure. The model is constructed by performing an SCF atomic calculation and then rigidly placing the atomic density at each site to obtain a model charge density. The potential resulting from such a density is readily obtained and is used for the band calculation. Note that because the exchange potential involves the one third power of $p$, the OCD model is not the same as overlapping atomic potentials. Although the OCD model is often used with the muffin-tin shape approximation, it is actually a distinct aspect of the treatment. In the lighter materials, the SCF relaxation is compensated for by increasing the strength of the exchange potential but in the case of the actinides, this has not been necessary or desirable. The model has an uncertainty (or parametrization) involved in the choice of configuration. This can be determined self-consistently or by experience. For $\alpha$-U we used $t' d' s'$. By analysing our results and using models, one might suggest that a better choice would involve a shift of 1/4 to 1/2 electron from the f to the d states. This should not drastically affect our results. However, comparison with the induced neutron form factor results suggest that we have too little bonding — a limitation of the OCD model.

Although for monoatomic systems one can select the configuration reasonably well, the situation is much more difficult for compounds. Because charge transfer can occur with dramatic Madelung type effects, the configuration parameter set is greatly expanded. For example, in UGe$_3$, one has U(d$^6$ f$^3$ $s^2$) and Ge(s$^4$ p$^4$) with only a constraint on the total number of electrons. From the one or two free parameters for the monoatomic metals, we have gone to four. In the case of URh$_3$ and UIr$_3$, we were able only to determine $[32, 33]$ the dominant pieces of Fermi surface based on the f-d bonding properties. For UGe$_3$, we utilized a pseudo self-consistent model motivated by the renormalized atom and ASA approaches and did extremely well. We were able to sort out all pieces of the Fermi surface $[17]$. However, there is a crucial feature of the procedure requiring one to choose a Wigner-Seitz radius for each atom; this will affect the results beyond acceptable limits. (There is some indication that they should be chosen nearly equal for all systems; this has interesting metallurgical implications.) We feel that the success of the procedure depends too heavily on the intuition and skill of the researcher and have now begun full self-consistent calculations.

4. Future research: magnetic actinide systems. — Although we have thus far dealt only with systems which do not order magnetically, it is important to also consider those that do since they are, after all, in the majority. Although SCF calculations have
been performed for the 3d transition metals [34] and the rare earth Gd in the ferromagnetic state [35], little has been done for the actinide systems. Initially at least, the band structure approach will be most usefully applied to those systems with small moments which behave most anomalously in a crystal field analysis. Materials with the rock salt structure fit well into this category. In addition, they are cubic and so the number of possible interactions is restricted by symmetry — a great aid, as previously discussed. Thus they are a clear first choice for study — especially the type I antiferromagnets.

There is a serious problem in these systems. As any soothsayer knows, it is best not to be too detailed in ones predictions. We can with some confidence, however, predict that developments in this area will continue be quite interesting.

References

[11] Because we are using a spherical potential approximation, we omit the important Hund's rule coupling where the electrons orbit in such a way as to maximally avoid each other.
DISCUSSION

Dr. J. E. SCHIRBER. — Let me play the shill and ask which of the results which you did not have time to discuss have the most bearing on the localized-itinerant question we were discussing last night.

D. D. KOELLING. — The UGe, consideration are the most useful as one has a system close to the borderline. On the Hill plots, it appears well into the localized regime yet behaves in an itinerate fashion.


Dr. G. H. LANDER. — To what extent are you neglecting the orbital character of the 5f electrons in these systems? My reason for asking is that in a neutron measurement we must account for this effect before being able to compare with your spatial wave functions.

D. D. KOELLING. — The first thing to do is a spin-only form factor assuming the orbital contribution negligible. Then one can try doing the single site atomic calculations as worked out for Cr. Finally, if that is inadequate, one will consider doing a full orbital calculation but it will be expensive.

COMMENT BY Pr. A. J. FREEMAN. — I believe that your concern centres about the fact that neutron magnetic scattering is from both the spin and orbital contributions to the magnetization density. The band calculations yield magnetic field induced spin densities derived from fully relativistic Dirac calculations (no neglect of spin-orbit coupling). The calculation of the orbital magnetization is rather complicated and has been done only in one case that of Cr metal. One can use a simplified atomic model following the work of Trammel and Blume as has been done in the case of the rare-earths and transition metals. If, however, as in the case of α-U, our spin only factor is found to agree with experiment this may give important information about the quenching of the angular momentum of the f-electrons. Here it would be greatly helpful to have a measurement of the g value for this metal to see if indeed Δg is small.

Dr. JOHANSSON. — In your talk you sort of gave the impression that the localized vs. delocalized f-states question was not of importance for the ground state properties. However, having metallic f-states, they contribute significantly to the bonding, which shows up in the measured cohesive energy, lattice constant, bulk modulus, crystal structure, etc.

D. D. KOELLING. — My statement was, I believe, that the question of localization would be most easily seen in discussing the excitation spectrum. That was an observation on the pedagogy more than the physics.

Pr. BERTAUT. — I am a crystallographer. Assume Th had a predominantly f character: I would believe it if Th was dhcp. But it is fcc. Thus I would prefer to call it a d-metal. Can you comment on this?

D. D. KOELLING. — The f character in Th is very small — probably in the 0.1-0.2 level. Further, it is much more extended than in the rare earths. (This would correlate with the dhcp only occurring at Am, Bk, Cm.) Could this not be involved in the fact that La is dhcp and Th not? La is fcc under pressure.