PHYSICAL REVIEW B VOLUME 14, NUMBER 8 15 OCTOBER 1976

# Coulomb term $U$ and $5f$ electron excitation energies for the metals actinium to berkelium

J. F. Herbst*†
*National Bureau of Standards, Washington, D. C. 20234*

R. E. Watson
*Brookhaven National Laboratory,‡ Upton, New York 11973*

I. Lindgren
*Department of Physics, Chalmers University of Technology, Göteborg, Sweden*

(Received 30 June 1976)

Relativistic Hartree-Fock-Wigner-Seitz band calculations have been performed for the actinide metals Ac through Bk in order to estimate the Coulomb term $U$ and $5f$ electron excitation energies. Our calculations predict that the tetravalent state (four $6d$-$7s$ conduction electrons) is stable relative to the trivalent state for the lighter elements and that near uranium relative stabilization of the trivalent state occurs. We find that $U$ increases from 2–3 eV for Th to 4–5 eV for the heavier elements considered. $5f$ level widths $W$ are estimated and found to decrease from 2 to 1/2 eV; together with the results for $U$ this points to progressive localization of the $5f$ states. The ratio $U/W$, which is most indicative of localization, takes on values intermediate between those for $3d$ and $4f$ electrons.

## I. INTRODUCTION

The $5f$ electrons of the actinide metals are less localized than the $4f$ electrons of the rare-earth series while more localized than transition-metal $3d$ electrons. As a consequence, the magnetic properties of the actinides are in the interesting regime between the itinerant magnetism of transition metals and the local-moment behavior of the rare earths. The Coulomb term $U$, the energy required for a $5f$ electron to hop from one atomic site to another, is a quantity of particular relevance to magnetic behavior. In this paper we estimate[1] $U$ for the metals Ac through Bk. We find that $U$ increases, i.e., hopping is progressively impeded, across the series. This is consistent with the general view[2] that the $5f$ states become increasingly more localized with increasing atomic number. Our calculations suggest that a crossover region occurs in the vicinity of Am, the heavier elements Cm and Bk exhibiting behavior approaching that of the rare earths, while the $U$'s of the lighter elements are more characteristic of transition metals. In addition we estimate the $5f$ level width $W$, which is also important to magnetic behavior. We find that $W$ decreases from $2\frac{1}{2}$ eV for Ac to $\frac{1}{2}$ eV for Bk while remaining, even at $\frac{1}{2}$ eV, significantly greater than the $4f$ level width of the corresponding rare-earth metal.

Our results for $U$ are based upon estimates of $5f$-electron excitation energies which are of interest in themselves. The computational scheme we employ has been very successful[3,4] in predicting $4f$ excitation energies in the rare-earth metals as measured by x-ray photoemission (XPS), and one of our aims is to assess the applicability of the method to the actinides. There are recent experimental data[5] for thorium and uranium metals, and we will compare these with our results. Further experimental progress will allow a more detailed comparison.

In Sec. II we describe the method through which the $5f$ excitation energies, $U$, and level widths are obtained. Section III deals with the use of spectroscopic data to estimate correlation effects, and results are given in Sec. IV.

## II. CALCULATIONAL SCHEME

A central aspect of this investigation is the neglect of hybridization between the $5f$ and the $6d$-$7s$ conduction electrons. Of course, the $5f$ states of the lighter actinides are degenerate with the conduction bands, and hybridization is significant in these metals.[2] Our goal, however, is to estimate the excitation energy of a single $5f$ electron as a function of $5f$ occupation number, and for this purpose it is essential to keep the $5f$'s distinct from the conduction electrons by setting hybridization equal to zero.

### A. Band calculations

Our approach is based upon the renormalized atom method.[6] In analogy with our calculations[3,4] for the rare earths, the initial atomic configuration $5f^n 6d^{m-1} 7s$ is assumed appropriate to the metal, and we perform calculations for varying $5f$ occupancy $n$ (with a concomitant change in the valence $m$ to preserve charge neutrality). $n$ is confined to integral values so that atomic spectral data may be used to estimate correlation effects. Relativistic Hartree-Fock (RHF) free-atom solutions are obtained for the configurations of interest through the use of the average of *LS* configuration scheme[7] which involves averaging over the $L$, $S$, $M_L$, and $M_S$ quantum numbers of the open shells. The lighter metals (i.e., through americium) have negligible paramagnetic moments, and our use of the *LS* average RHF scheme is consistent with the absence of a moment. For Cm and Bk we will make use of multiplet theory to place the 5*f* electrons of the metals in Hund's rule states to approximate the observed paramagnetic behavior. The free-atom wave functions are truncated at $r_{WS}$, the Wigner-Seitz radius of the metal, and normalized to unity within the Wigner-Seitz sphere; Table I lists the values of $r_{WS}$ used in this work. Initial band-structure potentials are then constructed with the truncated wave functions. The extrema of the 6*d* and 7*s* bands are determined by imposing Wigner-Seitz-type[1,3,4,6] boundary conditions at $r_{WS}$ on the large components of the wave functions obtained from integration of the Dirac-Fock equations.[7,8] Specifically, the potential for either a 6*d* or 7*s* electron is used in the Dirac-Fock equations, which are integrated to yield wave functions over a range of energies $\epsilon$. The value of $\epsilon$ for which the large component of the wave function has zero derivative at $r_{WS}$ specifies the bottom of the appropriate band; the $\epsilon$ for which the large component of the 6*d* wave function is zero at $r_{WS}$ determines the energy maximum of the *d* band. These criteria were found[6] to determine band extrema at high symmetry points in the Brillouin zone to within 0.1 eV for the transition metals.

Allowing the 6*d* and 7*s* occupancies to be nonintegral, the band calculations are iterated to crude self-consistency in the following manner. The Fermi level $\epsilon_F$ is determined by assuming a rectangular *d*-band and a parabolic *s*-band density of states. Admittedly this is a great oversimplification, but it suffices for our present purposes since the *d* bands of concern here are almost unfilled; we ultimately desire *differences* between total band energies per cell [see, for example, Eq. (1)], and we believe the resultant error is small compared to those introduced by the other approximations. Wave functions for the 6*d* and 7*s* electrons are found at average energies in the occupied bands, and 6*d* and 7*s* contributions to the band potentials are estimated by reconstructing the potentials with these average wave functions. Band extrema are again determined and the procedure repeated until $\epsilon_{\Gamma_1}$ and the *d*-band extrema have converged to within 0.005 eV. In accordance with our neglect of hybridization, the 5*f* wave function and occupation numbers are fixed during this process. The total Hartree-Fock band energy $E_{\text{band}}$ and one-electron energies $\epsilon_i$ are then evaluated. These quantities are given by the standard expressions[8] but are computed with the renormalized wave functions, including the self-consistent average 6*d* and 7*s* wave functions and occupation numbers. It is to be emphasized that $E_{\text{band}}$ is the total RHF energy of *all* the electrons in a Wigner-Seitz sphere of the metal. Calculations using other approximations for the shape of the density of states and other choices for the average 6*d* and 7*s* band energies suggest an uncertainty of less than $\frac{1}{2}$ eV in $E_{\text{band}}$ and less than 1 eV in $\epsilon_F - \epsilon_{5f}$, the 5*f* one-electron energy measured with respect to the Fermi level.

TABLE I. Wigner-Seitz radii $r_{WS}$ used in this work.

| Element | $r_{WS}$ (a.u.) |
|---|---|
| Ac | 3.92 |
| Th | 3.75 |
| Pa | 3.43 |
| U | 3.22 |
| Np | 3.28 |
| Pu | 3.43 |
| Am | 3.61 |
| Cm | 3.64 |
| Bk | 3.56 |

### B. 5*f* excitation energies

In estimating the excitation energy of a 5*f* electron we make the assumption, invoked[3,4] in analogous calculations for the rare earths, that the hole created by the removal of an *f* electron (either in a photoemission event or when the *f* electron hops to an adjacent site) will be completely screened, i.e., that the screening response of the conduction electrons is such that the final state of the atomic cell is electrically neutral. We estimate the energy of the final state through a band calculation for a metal with one fewer 5*f* electron and one more conduction electron than the initial state. This description of the final state is crude but has the virtue of being well defined and computationally tractable. Identifying $\Delta_-$ as the energy necessary to so excite a 5*f* electron into the conduction bands, we have

$$\Delta_-(f^n \rightarrow f^{n-1}) = E_{\text{metal}}[f^{n-1}(ds)^{m+1}] - E_{\text{metal}}[f^n(ds)^m] , \qquad (1)$$

where $E_{\text{metal}}$ represents the total energy per cell of the metal. $\Delta_-(f^n \rightarrow f^{n-1})$ is to be interpreted as the 5*f* electron excitation energy relative to $\epsilon_F$ for a metal having $n$ 5*f* electrons per site.

Since we are not able to directly calculate correlation effects in the metallic state, we make use of the correlation energy difference $\xi$ between the two free-atom configurations appropriate to the metallic excitation:

$$\begin{aligned}\xi \equiv\ & E_{\text{corr}}(f^{n-1}d^{m}s)-E_{\text{corr}}(f^{n}d^{m-1}s)\\ =\ & [E(f^{n-1}d^{m}s)_{\text{expt}}-E^{\text{RHF}}_{\text{gnd}}(f^{n-1}d^{m}s)]\\ & -[E(f^{n}d^{m-1}s)_{\text{expt}}-E^{\text{RHF}}_{\text{gnd}}(f^{n}d^{m-1}s)]\\ =\ & [E(f^{n-1}d^{m}s)-E(f^{n}d^{m-1}s)]_{\text{expt}}\\ & -[E^{\text{RHF}}_{\text{gnd}}(f^{n-1}d^{m}s)-E^{\text{RHF}}_{\text{gnd}}(f^{n}d^{m-1}s)]\ . \qquad (2)\end{aligned}$$

The first bracket in the last line of Eq. (2) is supplied by experimental spectral data[9] for atomic configurations most closely corresponding to the band results; the second bracket is obtained from our free-atom RHF calculations. The calculations involve the average of $LS$ configuration scheme, and we correct the total energy to correspond to the proper atomic ground state (specifically, the $LS$ state most accurately describing the true ground state) through the use of multiplet theory; $E^{\text{RHF}}_{\text{gnd}}$ denotes the corrected total energy. The correction is exactly analogous to that described in the Appendix of Ref. 4. This adjustment can equally well be viewed as a modification of the spectroscopic energy difference to make it correspond to the calculated $LS$ average total energy difference; unscreened Slater integrals are used in the multiplet theory expressions.

Under the assumption that the free-atom $\xi$ is a good approximation for correlation effects in the metal and with the use of our RHF results for the total band energies, $E_{\text{band}}$, Eq. (1) becomes

$$\begin{aligned}\Delta_{-}(f^{n}\rightarrow f^{n-1}) =\ & \xi+E_{\text{band}}[f^{n-1}(ds)^{m+1}]\\ & -E_{\text{band}}[f^{n}(ds)^{m}]\ . \qquad (3)\end{aligned}$$

This may be rewritten to display the purely atomic contribution to the excitation energy:

$$\begin{aligned}\Delta_{-}(f^{n}\rightarrow f^{n-1}) =\ & \xi+[E(f^{n-1}d^{m}s)-E(f^{n}d^{m-1}s)]^{\text{RHF}}_{LS\,\text{av}}\\ & +(\{E_{\text{band}}[f^{n-1}(ds)^{m+1}]-E^{\text{RHF}}_{LS\,\text{av}}(f^{n-1}d^{m}s)\}-\{E_{\text{band}}[f^{n}(ds)^{m}]-E^{\text{RHF}}_{LS\,\text{av}}(f^{n}d^{m-1}s)\})\\ \equiv\ & \xi+\delta E(\text{atom})+\delta E(\text{atom}\rightarrow\text{metal}). \qquad (3\text{a})\end{aligned}$$

Equation (2) defines the free-atom correlation energy difference $\xi$; the first term in brackets [$\delta E$(atom)] is the difference between the initial- and final-state total energies from our average of $LS$ configuration atomic calculations, and the second bracketed term, $\delta E$(atom→metal), is the difference in excitation energy between our free-atom and self-consistent band calculations.

### C. Hund's rule effects for Cm and Bk

As mentioned previously, the metals Ac through Am have miniscule paramagnetic moments, and use of the average of $LS$ configuration scheme corresponds to assuming zero moment. On the other hand, magnetic measurements[10] for metallic curium indicate an effective moment $\mu_{\text{eff}} \sim 8\mu_B$, a value consistent with a $5f^7$ configuration, while the moment for trivalent Bk is only slightly smaller than that expected for a $5f^8$ configuration in the Hund's rule $LS$ ground state. To take the existence of these moments into account we employ multiplet theory to correct the total band energies so that the $5f^n$ shell of each configuration is in the Hund's rule ground state; that is, we add

$$\begin{aligned}\delta E(\text{Hund}) =\ & \Delta E(f^{n-1};\ LS\ \text{av}\rightarrow\text{g.s.})\\ & -\Delta E(f^{n};\ LS\ \text{av}\rightarrow\text{g.s.}) \qquad (4)\end{aligned}$$

to Eq. (3a). For Cm and Bk we then have

$$\begin{aligned}\Delta_{-}(f^{n}\rightarrow f^{n-1}) =\ & \xi+\delta E(\text{atom})+\delta E(\text{Hund})\\ & +\delta E(\text{atom}\rightarrow\text{metal}). \qquad (3\text{b})\end{aligned}$$

### D. Single-particle estimate of excitation energies

The $\Delta_{-}(f^{n}\rightarrow f^{n-1})$ described above are multielectron estimates of the $5f$ excitation energies. Since a self-consistent calculation is performed for the final state, readjustment of the wave functions in the presence of the $5f$ hole, intra-atomic relaxation, is implicitly taken into account; and because the final state incorporates one more conduction electron to insure charge neutrality of the Wigner-Seitz cell, extra-atomic screening effects are also included in a straightforward manner. In addition, the $\Delta_{-}$ include atomic estimates of correlation effects. It is useful to contrast $\Delta_{-}$ with the single-particle estimate of the $5f$ excitation energy which is simply $\epsilon_F - \epsilon_{5f}$, the initial-state $5f$ one-electron energy measured with respect to the Fermi level.

### E. Coulomb term $U$

The term $U$ is the energy necessary for a $5f$ electron to hop from one atomic site to an adjacent one. Beginning with ions having a $5f^n$ ground-state configuration, the hopping of one $5f$ electron leads to one $5f^{n+1}$ and one $5f^{n-1}$ site. In the simplest, unscreened, single-particle picture $U$ is approximated by the $F^0(5f, 5f)$ Slater integral. Under the complete screening approximation we have assumed here, in which the $6d-7s$ electrons respond to keep each cell electrically neutral, we have

$$U=\Delta_-(f^n\rightarrow f^{n-1})-\Delta_-(f^{n+1}\rightarrow f^n)\,. \qquad (5)$$

In our scheme the negative of $\Delta_-(f^{n+1}\rightarrow f^n)$ is to be interpreted as the energy above $\epsilon_F$ of an unoccupied $5f$ level, $f^n$ denoting the initial-state configuration; hence $U$ can also be described as the energy difference between the occupied and unoccupied $f$ levels for the $f^n$ ground state. $U$ may alternatively be estimated in terms of the one-electron energies considered in Sec. II D

$$U=[\epsilon_F(f^n)-\epsilon_{5f}(f^n)]-[\epsilon_F(f^{n+1})-\epsilon_{5f}(f^{n+1})]\,; \qquad (6)$$

the inner parentheses indicate the configuration for which the quantities are calculated.

### F. 5f level widths

Another measure of the degree of localization of the $5f$ electrons and an indication of whether, in fact, energy band theory is applicable to them, is their intrinsic level width. Specifically, we mean the width obtained from a band description in which hybridization between the $5f$ states and the $6d-7s$ bands is turned off. Our procedure allows a simple measure of this quantity, namely, the difference between the energies at which the large component of a $5f$ wave function has zero value or zero derivative at $r_{WS}$:

$$W=\epsilon_{5f}(\text{zero value})-\epsilon_{5f}(\text{zero derivative})\,. \qquad (7)$$

Given the crystal potential acting upon the $5f$ electrons these energies are straightforwardly calculated by integration of the appropriate Dirac-Fock equations; from experience with $d$ bands the result for the width is known to be quite accurate. The one-electron energies of Eq. (7) are evaluated for the $5f_{5/2}$ and $5f_{7/2}$ states separately since the spin-orbit splitting is significant in comparison to $W$.

## III. CORRELATION EFFECTS AND SPECTROSCOPIC DATA

The components of $\Delta_-$ are presented in Table II, and it is evident that the atomic correlation energy difference $\xi$ changes with the $5f$ occupation number. With the exception of Ac, to which we will return shortly, the $\xi$ values are positive. This indicates [see Eq. (2)] that correlation is greater in the initial state, which has one more $5f$ and one fewer $6d$ electron than the final atomic state. Since the $5f$ electrons are spatially more compact than the $6d$ electrons, this comes as no surprise. Table II also shows that $\xi$ increases with increasing $5f$ count, a quite plausible relationship that is consonant with earlier results[4,6] for the iron and lanthanide series.

As specified by Eq. (2), the $\xi$'s are obtained by comparing the difference between two RHF free-atom total energies with the spectroscopically observed energy difference. Although uncertain in many instances, spectroscopic data exist[9] for all but the tetravalent ($6d^3 7s$) configurations of Cm and Bk. For those elements we resort to an expedient employed in our calculations[3,4] for the rare earths, for which no reliable atomic data for the $5d^3 6s$ configurations are available. We assume that the $5f$ occupation number is the primary factor determining $\xi$ and use the $\xi$ values for the $f^7\rightarrow f^6$ transition in Am and the $f^8\rightarrow f^7$ transition in Cm for the corresponding transitions in Cm and Bk. Comparison of the other $\xi(f^n\rightarrow f^{n-1})$ pairs in Table II suggests that this assumption[11] yields results accurate to $\sim\frac{1}{2}$ eV, an accuracy greater than that of the atomic data upon which some of the $\xi$ values depend.

As noted earlier, the $\xi$ entry for actinium in Table II is conspicuous because it is negative, implying that correlation effects are greater in the configuration with no, as opposed to one, $5f$ electron. There is an explanation for this in our RHF results. The $5f$ orbital calculated for a free actinium atom ($5f6d7s$ configuration) is markedly distinct from the $5f$ orbitals of Th and the other actinides; most of its density is *outside* the $f$-electron centripetal barrier and the $6d$ and $7s$ shells. Since the orbital is quite diffuse,[12] little correlation is associated with the $5f$ electron, and $\xi$ reverses sign. It is our intention to discuss other implications of this barrier-penetration behavior elsewhere.

Finally, the fact that the tetravalent ($d^3s$) levels of Cm, Bk, and the rare earths are too high in energy to be identified spectroscopically provides information in itself, even though the lack of atomic data is inconvenient for estimating $\xi$. If it is energetically costly to produce tetravalent atoms of these elements, then $U$ must be large. This experimental fact alone, without recourse to detailed calculation, suggests that Cm and Bk are rare-earth-like, whereas the lighter actinides are not.

TABLE II. Components of $\Delta_-(f^n \to f^{n-1})$. See Eqs. (2)–(4) for definition of these terms; all energies in eV.

| Element | $\Delta_-$ | $\xi$ | $\delta E$ (atom) | $\delta E$ (atom → metal) | $\delta E$ (Hund) | $\Delta_-$ |
|---|---|---|---|---|---|---|
| Ac | $\Delta_-(f^1 \to f^0)$ | −0.8 | −2.6 | −0.9 | ··· | −4.3 |
| Th | $\Delta_-(f^2 \to f^1)$ | 0.7 | −3.8 | −2.3 | ··· | −5.4 |
|  | $\Delta_-(f^1 \to f^0)$ | 0.6 | −1.9 | −1.7 | ··· | −3.1 |
| Pa | $\Delta_-(f^3 \to f^2)$ | 1.2 | −3.0 | −2.0 | ··· | −3.8 |
|  | $\Delta_-(f^2 \to f^1)$ | 0.4 | −0.9 | −1.6 | ··· | −2.1 |
| U | $\Delta_-(f^4 \to f^3)$ | 1.6 | −2.3 | −2.0 | ··· | −2.7 |
|  | $\Delta_-(f^3 \to f^2)$ | 0.4 | 0.1 | −1.3 | ··· | −0.8 |
| Np | $\Delta_-(f^5 \to f^4)$ | 2.1 | −1.5 | −2.0 | ··· | −1.4 |
|  | $\Delta_-(f^4 \to f^3)$ | 1.2 | 1.1 | −1.7 | ··· | 0.6 |
| Pu | $\Delta_-(f^6 \to f^5)$ | 1.8 | −0.7 | −2.7 | ··· | −1.6 |
|  | $\Delta_-(f^5 \to f^4)$ | 2.3 | 2.1 | −1.6 | ··· | 2.8 |
| Am | $\Delta_-(f^7 \to f^6)$ | 2.0 | 0.0 | −2.7 | ··· | −0.7 |
|  | $\Delta_-(f^6 \to f^5)$ | 2.2 | 3.0 | −2.0 | ··· | 3.2 |
| Cm | $\Delta_-(f^8 \to f^7)$ | 2.8 | 0.7 | −2.7 | −2.5 | −1.6 |
|  | $\Delta_-(f^7 \to f^6)$ | 2.0 | 3.9 | −2.0 | 1.5 | 5.4 |
| Bk | $\Delta_-(f^9 \to f^8)$ | 2.0 | 1.5 | −2.8 | −1.6 | −0.9 |
|  | $\Delta_-(f^8 \to f^7)$ | 2.8 | 4.8 | −2.4 | −2.6 | 2.7 |

## IV. RESULTS AND DISCUSSION

### A. 5$f$ excitation energies

Our results for the 5$f$ excitation energies, $\Delta_-(f^n \to f^{n-1})$, are shown in Fig. 1 for both divalent and trivalent initial states. The uncertainties of the spectroscopic data[9] affect the reliability of the $\xi$ and $\Delta_-$ values, as Fig. 1 specifies; for the tetravalent states the data are too poor for $\Delta_-$ estimates. A negative $\Delta_-$ means [see, for example, Eq. (1)] that the $f^{n-1}$ state is stable with respect to the $f^n$ state. A particularly prominent aspect of the figure is that $\Delta_-$ for trivalent initial states changes sign from negative to positive between uranium and neptunium, implying that the tetravalent metallic state is stable relative to the trivalent from thorium to uranium and that thereafter the trivalent state is favored. The stabilization of the tetravalent state in the lighter elements implies that the first actinide metal having any 5$f$ electrons is protactinium; in contrast, the lightest rare earths are trivalent, and the 4$f$ shell is progressively filled from Ce onward into the series. Experimental studies[2,5] and the band-structure calculations[2] of Freeman and co-workers indicate that there is little or no 5$f$ character in Th metal, and our results are consistent with those findings.

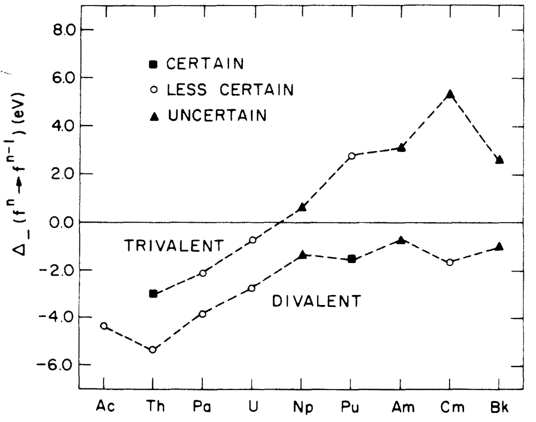

FIG. 1. Values of $\Delta_-(f^n \to f^{n-1})$ for the divalent $[(ds)^2]$ and trivalent $[(ds)^3]$ configurations of the actinide metals. Reliability of the spectral information entering the $\Delta_-$ estimates is indicated by the different symbols.

$\Delta_-$ for divalent initial states remains negative throughout the range from actinium to berkelium, and inspection of Table II reveals that the Hund's rule term, associated with the onset of magnetic moments in Cm and Bk, is responsible for the stabilization of the trivalent state with respect to the divalent in those metals. The signs of the $\delta E$(Hund) entries for Cm and Bk in Table II conform to the general observation that Hund's rule effects produce an energy lowering which is greater for the state of greater spin. That is, $\Delta_-$ is reduced in value when the final state has greater spin multiplicity and is enhanced when the initial state has larger spin. Since the trivalent states of Cm ($f^7$) and Bk ($f^8$) have greater spin multiplicity than their divalent ($f^8$ and $f^9$) counterparts, the divalent $\Delta_-$ curve is depressed; on the other hand, the peak in the trivalent $\Delta_-$ curve at Cm stems from the fact that the trivalent state is $f^7$ while the tetravalent state is $f^6$.

Returning to Table II, we see that all components of $\Delta_-$ are significant. The *experimental free-atom* energy difference analogous to $\Delta_-$ is essentially given by $[\xi + \delta E(\text{atom}) + \delta E(\text{Hund})]$. It displays the same qualitative shape as $\Delta_-$ but is generally larger; in particular, it is positive from Np onward for the divalent initial states, whereas $\Delta_-$ remains negative in that range. The *calculated free-atom* energy difference, which is the sum $[\delta E(\text{atom}) + \delta E(\text{Hund})]$ of the atomic RHF terms, reproduces the trend and magnitude of the $\Delta_-$ values rather well, especially for the heavier elements. We found[4] this to be the case for the 4*f* excitation energies in the rare earths as well; correlation effects ($\xi$) and band effects $[\delta E(\text{atom} \rightarrow \text{band})]$ balance each other to some extent, though both are on the order of $\Delta_-$.

Since $\Delta_-$ is obtained from total energy calculations and is thus inherently a multielectron quantity, it is of interest to compare $\Delta_-$ with the one-electron prediction for the 5*f* excitation energy. The dashed lines of Fig. 2 connect the $\Delta_-$ results, and the solid lines represent the mean of the $5f_{5/2}$ and $5f_{7/2}$ one-electron energies (computed with the self-consistent 6*d* – 7*s* band wave functions and occupation numbers) relative to $\epsilon_F$,[13]

$$\epsilon_F - \epsilon_{5f} \equiv \epsilon_F - \left(\tfrac{6}{14}\epsilon_{5f5/2} + \tfrac{8}{14}\epsilon_{5f7/2}\right). \qquad (8)$$

From Fig. 2 it is clear that the one-electron and multielectron estimates yield rather similar results for the 5*f* excitation energy. This is in marked contrast to the situation[4] in the lanthanides, for which the single-particle estimate consistently overestimates the 4*f* excitation energy, while $\Delta_-$ is in excellent accord with XPS measurements. The failure of single-particle theory for the 4*f* states is primarily due to the greater influence of final-state screening effects, which reduce $\Delta_-$ by lowering the energy of the final state, relative to correlation energy contributions, which increase $\Delta_-$. We estimated[4] screening energies of 4–6 eV for the rare earths while $\xi$ ranges from 1 to 4 eV. Although we have not investigated screening in as much detail for the actinides, there is apparently a closer balance of the two effects for the 5*f* states.

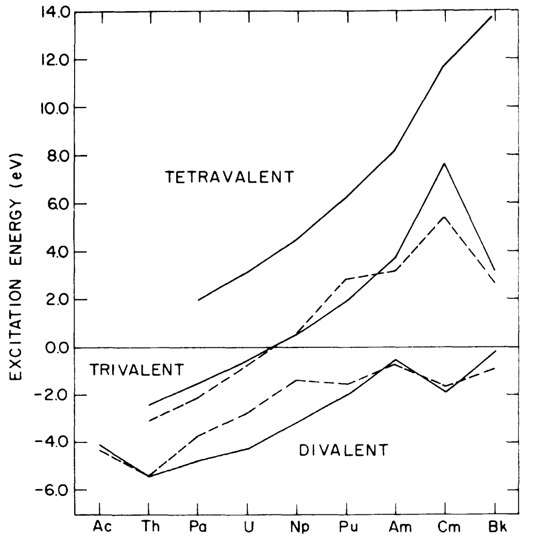

FIG. 2. Values of $\epsilon_F - \epsilon_{5f}$ [defined by Eq. (8)] for the divalent, trivalent, and tetravalent configurations of the actinide metals are given by the solid lines. The dashed lines show the $\Delta_-$ estimates of Fig. 1 for comparison.

It is to be kept in mind, however, that spectral data which are uncertain in several instances have been incorporated into $\Delta_-$. We surmise that more reliable atomic information may reduce the discrepancy between $\Delta_-$ and $\epsilon_F - \epsilon_{5f}$ for the divalent case in Pa, U, and Np. Furthermore, since we expect the 5*f* states to exhibit more rare-earth 4*f* character near the middle of the row, better spectroscopic data may lead to a larger disparity between the one-electron and multielectron results for Am, Cm, and Bk, that is, in the direction of our findings for the lanthanides.

XPS spectra[5] for metallic uranium show a structure 0–1 eV below $\epsilon_F$ which probably arises from 5*f* emission. Our Fig. 2 results predict the $5f^2$ (tetravalent) state to be energetically more favorable than the $5f^3$ (trivalent) state in uranium; $\epsilon_F - \epsilon_{5f} \sim 3$ eV for the former and $\sim -0.5$ eV for the latter. It must be remembered that hybridization of the 5*f* states with the 6*d*-7*s* bands has not been included in our calculations. Simple interpolation of the Fig. 2 values indicates that a 5*f* occupancy of $2\frac{1}{2}$ to $2\frac{3}{4}$ electrons would yield an excitation energy in the observed range. We consequently believe that uranium metal has a 5*f* occupancy of 2–3 electrons; in considering cohesive energies, on the other hand, Johansson and Rosengren[14] have concluded that one or two 5*f* electrons are present in uranium metal.

### B. Coulomb term *U*

We turn now to estimates of the Coulomb term *U*. As we have described in Sec. II E, our present calculations afford both multielectron [Eq. (5)] and one-electron [Eq. (6)] predictions. These are given in Fig. 3; the solid line denotes the one-electron energy differences and the dashed line the total energy differences. In obtaining $U$ from Eqs. (5) and (6) the value of $n$ corresponding to the trivalent state has been used for all the metals except Pa and U, for which tetravalent initial states were assumed so as to be in accord with our $\Delta_-$ predictions. With the exception of Cm and Bk, the choice of initial states does not affect $U$ by more than a few tenths of an eV. The spike at Cm is a consequence of the previously discussed Hund's rule effects; the $f^7$ configuration is particularly stable, and this is reflected in the large $U$ value for it.

The spectral data[9] alone provide another estimate[15] of $U$:

$$U_{\text{atomic}} = E(f^{n-1}d^3s) + E(f^{n+1}ds) - 2E(f^n d^2 s). \quad (9)$$

This is simply the energy cost for a $5f$ electron to hop from one *atom* to another while maintaining charge neutrality. Values of $U_{\text{atomic}}$ are presented in Fig. 3; sufficient atomic information does not exist for Cm and Bk. Johannson[16] has also estimated $U_{\text{atomic}}$, and his results are in overall agreement with ours. All three of our estimates show a general increase in $U$ from Th to Am. Herring exploited atomic data to estimate[15] $U \sim 1.8$ eV for Ni, and from XPS data Hüfner and Wertheim have found[17] $U \sim 2$ eV for $3d$ electrons. From $\Delta_-$ calculations we estimated $U \sim 5$–6 eV for the rare earths, in overall agreement with experiment.[17,18] Therefore, our results for $U$ support the view that the $5f$ electrons of the lightest actinides are similar to the itinerant $3d$ electrons of the transition metals, while at Am the local character of the rare-earth $4f$ states is approached. For the sake of completeness we note that the $F^0(5f, 5f)$ Slater integral, the unscreened one-particle estimate for $U$, ranges from about 13 eV for Th to approximately 22 eV for Bk; the screening and relaxation effects included in our $\Delta_-$ predictions lower this simplest result by about a factor of 7 to the 2–4 eV values of Fig. 3.

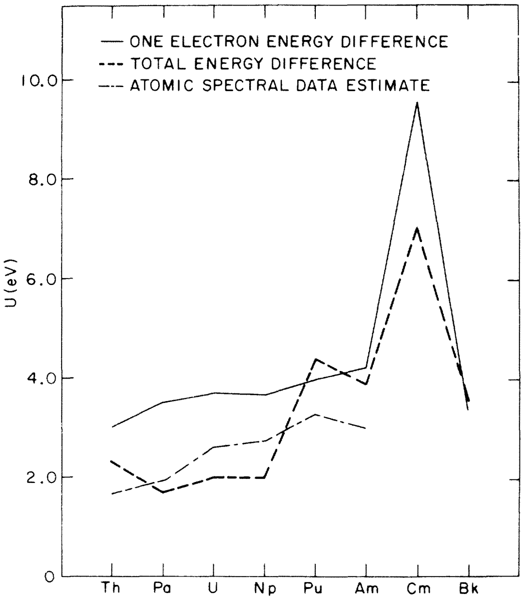

FIG. 3. Values for the Coulomb term $U$. $U_{\text{atomic}}$ is obtained from atomic spectral data. Estimates of $U$ for the metals are obtained from Fig. 2 and are based on the $\Delta_-$ results or their one-electron analogs, $\epsilon_F - \epsilon_{5f}$, as described in the text.

### C. $5f$ level widths

Table III lists the energies at which the $5f$ wave functions have zero value or zero derivative at the Wigner-Seitz radius $r_{\text{WS}}$ and the level widths to which they lead. The results are based on the tetravalent initial state for Pa and U and on the trivalent state for the other metals. (As a consequence of our method of potential construction, the energies are calculated with respect to the crystal zero, the electrostatic potential at the boundary of a Wigner-Seitz sphere in the bulk of the metal.) The widths decrease from ~2 eV for Pa and U to ~0.5 eV for Cm and Bk; the corresponding range for the rare earths is ~0.4–~0.07 eV. From the table we see that the two spin-orbit components overlap until plutonium, after which they no longer do so. By itself the decrease in the widths furnishes evidence for increasing localization of the $5f$ states, but the quantity particularly indicative of localization is the ratio $U/W$. Figure 3 and Table III show $U/W$ to increase from approximately 1 for Th to about 7 for Bk. In contrast, this ratio is at most 2 for the $3d$ transition metals and increases from roughly 20 to about 100 across the lanthanide series. Even though $U$ approaches rare-earth-like values at the middle of the actinide row, the $f$-level width keeps $U/W$ somewhat smaller than its value for the rare-earth analog.

In conclusion, the results of this work show that the $5f$ electrons of the actinide metals do indeed exhibit properties intermediate between those of the $3d$ and $4f$ states. The growth of the Coulomb term $U$ through the first half of the series and the reduction of the $f$-level widths signal increasing localization of the $5f$ states. Through berkelium, however, the widths $W$ and $U/W$ have not reached values comparable to those we have estimated for the $4f$ states of the rare earths, and the departure of the one-electron from the multielectron results for the excitation energies is noticeably less than

TABLE III. Energies at which $5f$ wave functions have zero derivative or zero value at $r_{\mathrm{WS}}$ and associated level widths. All values are in eV.

| Element | $\epsilon_{5f_{5/2}}\left(\begin{matrix}\text{zero}\\ \text{deriv.}\end{matrix}\right)$ | $\epsilon_{5f_{5/2}}\left(\begin{matrix}\text{zero}\\ \text{val.}\end{matrix}\right)$ | $W_{5f_{5/2}}$ | $\epsilon_{5f_{7/2}}\left(\begin{matrix}\text{zero}\\ \text{deriv.}\end{matrix}\right)$ | $\epsilon_{5f_{7/2}}\left(\begin{matrix}\text{zero}\\ \text{val.}\end{matrix}\right)$ | $W_{5f_{7/2}}$ |
|---|---|---|---|---|---|---|
| Pa | − 5.0 | −2.9 | 2.1 | −4.5 | −2.2 | 2.3 |
| U | − 5.0 | −2.5 | 2.5 | −4.4 | −1.7 | 2.7 |
| Np | − 3.3 | −0.9 | 2.3 | −2.6 | 0.1 | 2.7 |
| Pu | − 5.6 | −4.2 | 1.3 | −4.8 | −3.2 | 1.6 |
| Am | − 8.1 | −7.4 | 0.7 | −7.0 | −6.2 | 0.8 |
| Cm | − 9.6 | −9.1 | 0.5 | −8.3 | −7.7 | 0.6 |
| Bk | −10.4 | −9.9 | 0.5 | −8.9 | −8.3 | 0.6 |

for the lanthanides (although improved spectral data may alter the situation somewhat). Since our calculations indicate the presence of unoccupied $f$ levels rather near $\epsilon_F$ for uranium onward into the series, we expect that valence changes and fluctuations of the type observed in many rare-earth compounds can also occur for the actinides, perhaps with even greater likelihood.

---

*Work supported by National Research Council–National Bureau of Standards Postdoctoral Research Associateship.

†Part of work done while guest of Brookhaven National Laboratory.

‡Work supported by the U. S. Energy Research and Development Administration.

[1] Preliminary results for Ac through Am were reported previously: J. F. Herbst and R. E. Watson, Phys. Rev. Lett. 34, 1395 (1975).

[2] For an excellent review, see *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), Vols. I and II.

[3] J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972).

[4] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 13, 1439 (1976).

[5] J. Verbist *et al.*, J. Electron. Spectrosc. Related Phenomena 5, 193 (1974); B. W. Veal and D. J. Lam, Phys. Rev. B 10, 4902 (1974), and references therein.

[6] R. E. Watson, H. Ehrenreich, and L. Hodges, Phys. Rev. Lett. 24, 829 (1970); L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972).

[7] I. Lindgren and A. Rosén, Case Studies in Atomic Physics 4, 93 (1974).

[8] I. P. Grant, Adv. Phys. 19, 747 (1970).

[9] Summarized by L. Brewer, J. Opt. Soc. Am. 61, 1101 (1971).

[10] Cornelius Keller, *The Chemistry of the Transuranium Elements* (Verlag Chemie, Weinheim, 1971), p. 90.

[11] Given the interplay between Hund's rule and correlation effects and the fact that we have assumed Hund's rule ground $5f$ states for Cm and Bk (as for the $4f$ shells of the rare earths), the assumption that $\xi$ depends chiefly on $f$ occupancy becomes compelling.

[12] We might note that the assumption that the free-atom $\xi$ is appropriate to the metal is questionable in such a case.

[13] The weighted result averages the effect of the $5f$ spin-orbit splitting, which ranges from 0.01 to 1.1 eV for the configurations treated here and is not significant on the scale necessary for qualitative comparison. For Cm and Bk multiplet theory has been employed to correct the average of $LS$ configuration $\epsilon_{5f}$'s so that they correspond to excitation of the least tightly bound electron in the Hund's rule ground $5f$ multiplet; this is done in order that $\Delta_-$ for these elements can be compared with the appropriate single-particle analog.

[14] B. Johansson and A. Rosengren, Phys. Rev. B 11, 1367 (1975).

[15] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. IV, Chap. IX.

[16] B. Johansson, Phys. Rev. B 11, 2740 (1975).

[17] S. Hüfner and G. K. Wertheim, Phys. Rev. B 7, 5086 (1973).

[18] M. Campagna, G. K. Wertheim, and E. Bucher, in *Magnetism and Magnetic Materials*, edited by C. D. Graham, Jr. and J. J. Rhyne, AIP Conf. Proc. No. 24 (American Institute of Physics, New York, 1974).