Localization in f-shell metals

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Anderson's theory of local moments is applied to the f-shell metals with the use of parameters for the electronic structure given earlier. A criterion for localization (abrupt in this theory) of Z_f levels per atom is that the resonance width be less than $2U \sin^2(\pi Z_f/14)$, with U the intra-atomic repulsion associated with s-f transfer. Americium and the heavier actinides satisfy this criterion, as do all the rare earths except cerium; plutonium is borderline. The traditional term "localized state" is used here though "correlated state" would be more appropriate. For the cases considered the localized states are found to have net spin (or moment) but that is not a necessary condition. They are found to contribute to the f-band pressure on the crystal, but reduced by a factor of about $W_f/3U$, equal to 0.09 for americium, where W_f is the itinerant f-band width. The localized f levels may themselves be thought to form bands, but with reduced width, and they may even have Fermi surface, though that was not found for the systems considered. A comparison of this state with band ferromagnetism is made. An approximate calculation of the total energy of the localized and delocalized states as a function of volume correctly predicted the large volume and localization for americium.

I. LIMITATIONS OF DENSITY-FUNCTIONAL THEORY

Rigorous density-functional theory[1] provides a formulation of the total ground-state energy of atoms and solids. The density itself is written in terms of one-electron wave functions, and a variational argument leads to one-electron eigenvalues; the ground state is necessarily specified in terms of occupation of these levels consecutively in energy. If the exact density functional could be used, this would lead to the exact ground-state energy; the local-density approximation ordinarily gives quite good values for the ground-state energy.

The eigenvalues themselves are not directly meaningful, though in many systems they are approximately equal to a removal energy for the corresponding state, thus they are frequently thought of as one-electron energies. This view is quite inappropriate in the rare earths where the f-like states are generally thought of as localized or atomlike. A few volts may be required to transfer an electron from an f state to the Fermi energy, and a few volts may also be required to take an electron at the Fermi energy and add it to an f shell. Thus two energies are required for the f shell, one for adding electrons and one for subtracting them. Density-functional theory gives only one energy for each orbital, and the eigenvalues representing the partially filled f shell must come at the Fermi energy. This narrow f band would *suggest* a high density of states at the Fermi energy and a correspondingly large electronic specific heat which will in fact not be observed. This is not an error of density-functional theory, since that theory is only guaranteed to give the ground-state energy. However, it is a serious limitation in density-functional theory in not suggesting the nature of the state as reflected in its excited states. A representation of the electronic structure which

does suggest the nature of the state is much preferred.

The missing characteristic here is localization of the electron. The simplest case of such a localization is that associated with the Heitler-London transition; it is desirable to describe that phenomenon since it is based upon the same physics which we will analyze here, but is simpler and can be solved exactly. Consider a single atomic orbital on each of two identical atoms. The corresponding states, with spin up or down, are written $|1\pm\rangle$ and $|2\pm\rangle$. If the two states of the same spin are coupled by V, an eigenstate for a single electron of that spin can be written $\cos\gamma|1\pm\rangle + \sin\gamma|2\pm\rangle$, where we have written the coefficients as a sine and a cosine to assure normalization. Let this be the lowest-energy one-electron state of that spin, for example, $\cos\gamma = \sin\gamma = 1/\sqrt{2}$. Now we seek the ground state with two electrons present if the Hamiltonian contains, in addition to the coupling V, a repulsive interaction U which increases the energy of the system by an energy U if both electrons are on the same atom. This is no longer a one-electron problem, but the basis contains only six states (e.g., one electron of spin up on the first atom and one of spin down on the second) and it can be solved exactly giving an energy relative to that of uncoupled atoms with one electron on each. The ground-state energy is $U/2 - [(U/2)^2 + 4V^2]^{1/2}$. When V is large in comparison to U the corresponding state is close to that of each electron occupying a symmetric bond orbital as described above. These are also the one-electron states which would be obtained in density-functional theory, since density-functional theory would lead to a symmetric Hamiltonian. However, as V becomes small the exact state becomes predominantly a combination of the localized state with one electron on the first atom and the other on the second (with opposite spin).

This localization occurs continuously in the exact solu-

tion, but is not apparent in the states arising from density-functional theory even if the exact density functional, leading to the exact energy, is used. For the more complicated problems we shall treat, only an approximate solution of the problem can be made in any case, and we seek an approximate ground state which contains this localization. We may do this by approximating the repulsive term in the Hamiltonian as in mean-field theory. We write that term as the probability (e.g., $\cos^2\gamma$) of one electron being on an atom multiplied by the probability for the other on that atom multiplied by U. The corresponding ground state will consist of an electron in a state such as given above (with a value of γ to be determined) with one spin, and an electron in the mirror-image state with the opposite spin. The energy, relative to two atomic energies, is

$$4V\sin\gamma\cos\gamma + 2U\sin^2\gamma\cos^2\gamma \ .$$

These two terms and their sum are plotted in Fig. 1(a) for negative V. If $-V$ is greater than $U/2$ there is a single minimum ($2V + U/2$ relative to isolated atoms) corresponding to a doubly occupied symmetric bonding state.
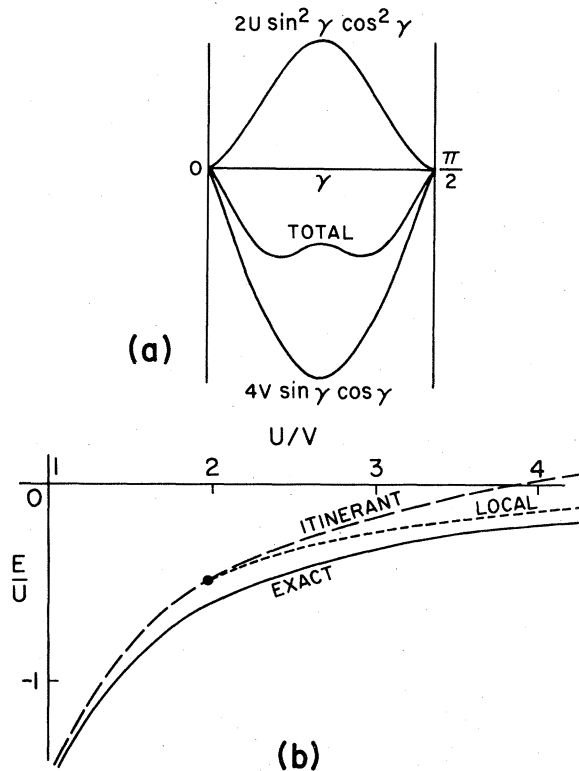

(a)

(b)

FIG. 1. Localization for two electrons in a pair of coupled levels. γ specifies the form of the one-electron states in mean-field theory and is midway, at $\pi/4$, for a symmetric bond state. The upper curve in (a) is the Coulomb energy from the intra-atomic U, the lower curve is the energy gain from the interaction between levels, and the middle curve is the total, showing two minima corresponding to partial localization. (b) Shows the total energy as a function of U/V, corresponding to simple bonds—or itinerant electrons—at small values of U (dashed line) with a second-order transition to localized states (dotted line) at large U. The solid curve is the exact energy with no sharp transition.

On the other hand, if $-V$ is less than $U/2$, there are two equivalent solutions (with spins flipped) ($-2V^2/U$) in which each electron resides predominantly on one atom and can be said to be localized as in the exact solution.

In this mean-field approximation there is an abrupt transition to a localized state, rather than the continuous transition of the exact solution. Furthermore, the energy obtained for the localized solution is $-2V^2/U$ while the exact solution approaches $-4V^2/U$ when V is small. It is nevertheless a significant improvement upon density-functional theory as ordinarily carried out. In Fig. 1(b) we have plotted the exact energy, along with the mean-field energy. Also shown is the continuation of the delocalized solution to small V which would correspond to an approximate solution of the density-functional theory (corresponding to the local-density approximation). In comparison to the latter we have improved upon the energy and have also incorporated localization in the state. This introduces an abrupt transition, which does not occur in the exact solution, but there is no discontinuity in the slope at the transition so that the transition to delocalization under pressure is only of second order and the error is not serious even near the transition.

Also, it provides the satisfying view that on the itinerant side of the transition the ordinary band theory, with no correction, is appropriate, but on the other side a partially localized solution is to be preferred. The physics of the localization obtained here is essentially the same as that in the Mott insulators discussed by Brandow[2] and in the f-shell metals which are described here.

The Anderson Hamiltonian and Anderson's solution[3] accomplished this localization in a metal. The Hamiltonian contained a d state of spin up and one of spin down; both were coupled to a series of free-electron states so that they became resonant d states. In addition, there was a term in the Hamiltonian adding an energy U if both states were occupied; thus a state could be constructed (if U was large enough) with the spin-down state occupied (below the Fermi energy) and the spin-up state empty (above the Fermi energy). The two were separated by approximately U due to the occupation of one. Another state of the system was found with both states partially occupied at the Fermi energy, but that state of the system was of higher energy.

The new state obtained is closely analogous to the Heitler-London state discussed above and was referred to as a "local moment," since the spin of the state could be reoriented at no cost in energy, just as in an isolated free atom. However, the electronic state is a resonance whether or not the local moment is formed, and the spacial extent is not significantly different in the two cases. T. V. Ramakrishnan (private communication) has suggested to us that for this reason it would be preferable to refer to a "correlated" rather than a "localized" state. We agree, but retain the traditional terminology in the present study.

In Anderson's solution the transition is abrupt, but in the exact solution it is continuous.[3] The essential feature which has been added is the possibility of different potentials being seen by different electrons as in the approximate treatment of the Heitler-London transition given above.

Here we directly extend this concept to f-shell metals for which we have a relatively simple understanding of the electron structure.[4,5] The f shell has 14 states on each atom. We shall consider the possibility that some Z_f of these may be resonances below the Fermi energy and $14-Z_f$ may be resonances above the Fermi energy. We shall in fact need to check in each case to see if such a state exists, and if it is more stable than the state with all 14 resonances at the same energy, near the Fermi energy. The U which enters is associated with the energy for transferring an additional electron from the sd shells to the f shell, not the energy U_x associated with aligning or misaligning a fixed number of f electrons, so the essential question is not one of moment formation or ferromagnetism, but of localization; we may in fact expect localized spins to align in accord with Hund's rule, but that is not the central point. We shall also generalize the Anderson model to include an f shell on every atom and the corresponding formation of bands. As long as the bands formed from the occupied resonances and those associated with the empty resonances do not cross the Fermi energy, this makes only a minor difference in the arguments, but when a crossing occurs the formation of the local state itself will be seen to be impeded.

II. FORMULATION

A phase shift may be associated with each of the 14 resonances for each atom, depending upon energy. The interesting value is that at the Fermi energy $\delta^-(\xi)$ for the occupied resonances and $\delta^+(\xi)$ for the empty resonances; we shall suppress the Fermi energy ξ at which the evaluation is made, since only these values enter. From the Friedel sum rule[6] it is known that each resonance accumulates an integrated electron density $\delta^\pm/\pi$ at the scattering center. Thus it is convenient to define an effective f-state occupation for the atom

$$Z_f^* = Z_f \delta^- /\pi + (14-Z_f)\delta^+ /\pi , \qquad (1)$$

which will be approximately equal to Z_f in all cases. Now if we are to increase the occupation of some resonance, the energy at which we add electron density depends upon the occupation of the other states—as in Anderson's analysis. The energy will contain a term $Z_f^* U$, but reduced by the contribution of the state itself. We write those energies as

$$\epsilon_f^- = \epsilon_f^0 + (Z_f^* - \delta^- /\pi)U, \quad \epsilon_f^+ = \epsilon_f^0 + (Z_f^* - \delta^+ /\pi)U . \qquad (2)$$

This gives the different resonant energies for the two types of states. The phase shifts themselves depend upon a resonance width Γ, which will be the same for all; these phase shifts are given approximately by

$$\tan\delta^\pm = \frac{\Gamma/2}{\epsilon_f^\pm - \xi} . \qquad (3)$$

Equations (1) and (3) may be used to convert Eq. (2) into the two relations between δ^+ and δ^- to be given in Sec. IV, and the allowed solutions are the intersections of the two. There will always be a solution with $\delta^+ = \delta^-$ which we write as δ^0. It is the itinerant or delocalized state and the state described by traditional band theory.

There may also be solutions with $\delta^+ \neq \delta^-$, which are what may be called localized states. We shall return in Sec. VIII to the total energy and see that these localized states, if they exist, have lower energy. In this mean-field theory the distinction is sharp, as in the approximate curve in Fig. 1(b), whereas we presume that in an exact solution the transition is continuous.

III. PARAMETERS FOR THE f-SHELL METALS

Most of the needed parameters are available from a recent paper on the electronic structure of f-shell metals[4] and are collected in Table I. The appropriate Z_f is an integer which was given for both rare earths and actinides, as was r_0. U, obtained from Herbst, Watson, and Lindgren,[7] was listed for the actinides and the corresponding values for the lanthanides were obtained from Hüfner and Wertheim.[8] U_x had been given for the actinides, but was corrected here for a factor-of-2 error; corresponding correct values for the lanthanides were obtained from the same source.[9]

Bandwidths provided by Skriver[10] had been given for the actinides and are included in Table I. The corresponding values for the lanthanides are not available, except for lanthanum and cerium given by Glötzel and Fritsche.[11] We have extrapolated these to the other lanthanides using a known form,[4] $W_f = 182\hbar^2 r_f^5 /mr_0^7$. We deduced a value of $r_f = 0.58$ Å for cerium from the bandwidth for γ-cerium computed by Glötzel and Fritsche and obtained the corresponding bandwidth for α-cerium corrected for the change in r_0. We then assumed that the ratio of r_f for each lanthanide to that of cerium was the same as that of the corresponding actinide to that of thorium; the resulting values for W_f are listed in Table I. The value for lanthanum obtained in this way was 1.55 eV, but we listed the value 1.20 eV obtained by Glötzel and Fritsche;[11] the discrepancy provides some kind of estimate of the reliability of the extrapolation.

The resonance width Γ in Eq. (3) may be related to the bandwidth using a condition for the band minimum and band maximum in the atomic sphere approximation.[12] This can be evaluated by expanding the spherical Neumann and Bessel functions for small arguments to give

$$\Gamma = 2(k_f r_0)^7 W_f /3675 , \qquad (4)$$

where W_f is the f bandwidth, k_f is the electron wave number at which the resonance occurs, and r_0 is the atomic sphere radius. k_f in our case may be taken equal to the Fermi wave number. For all of the actinides and almost all of the rare earths, there are three free electrons per atom so $k_f r_0 = (27\pi/4)^{1/3}$, and we obtain

$$\Gamma = 0.677 W_f . \qquad (5)$$

Values for the ϵ_f^0 could be obtained following Froyen's procedure[13] for the transition metals. He obtained values for the s-state and d-state terms from free-atom calculations, and used a tight-binding formula to relate the s-band minimum to the s-state energy, and then a free-electron formula to obtain the Fermi energy ξ. The values for ϵ_d^0 depended significantly upon whether or not Hartree-Fock or Herman-Skillman term values were used,

TABLE I. Parameters for the f-shell metals, mostly from Ref. 4.

	Z_f	r_0 (Å)	W_f (eV)[a]	U (eV)[b]	U_x[c]	r_0^{loc} (Å)	r_0^{ferro} (Å)
La	0	2.08	1.20				
Ce	1	2.02	0.65	5.6		2.30	
Pr	2	2.02	0.37	6.7	0.39	1.71	1.52
Nd	3	2.01	0.26	7.1	0.41	1.45	1.43
Pm	4		0.23		0.42		
Sm	5	1.99	0.20	6.0	0.47	1.27	1.33
Eu	7	2.27	0.08	5.0	0.48	1.27	1.33
Gd	7	1.99	0.20	12.0	0.49	1.12	1.33
Tb	8	1.95	0.23	6.9	0.52	1.22	1.31
Dy	9	1.96	0.22	7.3	0.53	1.24	1.31
Ho	10	1.95	0.23	7.7	0.55	1.28	1.30
Er	11	1.94	0.24	7.8	0.58	1.36	1.30
Tm	12	1.93	0.25	7.6	0.61	1.52	1.29
Yb	14	1.99	0.20	5.1			
Lu	14	1.92	0.25				
Ac	0	2.10	7.08				
Th	1	1.99	3.58	2.3		3.29	
Pa	2	1.81	3.71	1.7	0.22	2.59	2.05
U	3	1.70	4.24	1.9	0.27	2.20	1.91
Np	4	1.66	3.93	2.0	0.29	1.98	1.82
Pu	5	1.68	3.10	4.4	0.32	1.66	1.76
Am	6	1.91	1.26	3.9	0.36	1.65	1.73
Cm	7	2.03		7.0	0.40		

[a]From Ref. 10 for the actinides and extrapolated from Refs. 11 and 10 for the rare earths.
[b]From Refs. 7 and 8; in hindsight we would prefer actinide values from Ref. 18.
[c]Reduced from Ref. 9; an error of a factor of 2 in Ref. 4 has been corrected.

but the final self-consistent energies were quite independent of that. It will be adequate here to require that as the resonances become very narrow (δ^- approaches π and δ^+ approaches zero), Z_f^* approaches Z_f and the Fermi energy lies midway between the two resonances. This gives, from Eq. (2),

$$\epsilon_f^0 - \xi = -(Z_f - \tfrac{1}{2})U .$$ (6)

This gives us explicit values for all parameters needed to determine for each case whether or not localization occurs and what the energies of the resonances are.

However, we should recognize that these resonant states are still coupled to each other, as when bands formed in the light actinides,[4] and we should ascertain in each case whether these bands cross the Fermi energy. In Ref. 4 we replaced the true density of f-band states by the Friedel model,[14] a constant density of states (14 states per atom) of width W_f, where W_f was obtained by requiring that this model reproduce the second moment of the f band. (These are the values listed in Table I.) The relation was

$$W_f^2 = \frac{12n}{7}(V_{ff\sigma}^2 + 2V_{ff\pi}^2 + 2V_{ff\delta}^2 + 2V_{ff\phi}^2) .$$ (7)

(Here we neglect spin-orbit coupling which made only a small contribution.) n is the number of nearest-neighbor atoms, taken as 12. We wish to make the same approximation here, but note that the sum over couplings for the occupied resonances is reduced by the restriction to only occupied resonances. If Z_f is 7 and we assume, by Hund's rule, that if localization has occurred all Z_f states will

have parallel spin, the occupied resonance W_f from the earlier analysis will be reduced by a factor $(Z_f/7)^{1/2}$. Among the empty resonances, all of one spin will be present, so W_f remains appropriate. This is a very crude treatment of the bands, but an improvement requires specifying just which orbitals are occupied and a calculation of the resulting bands.

There is also coupling between empty and full resonances, which will be included in Sec. V using perturbation theory. This crude description of the bands will be sufficient to indicate when crossing is expected and what the effect will be when it does.

IV. SOLUTION FOR AMERICIUM

By substituting Eqs. (1), (3), and (6) into Eq. (2), we may solve one for δ^- and the other for δ^+ in exact analogy with the local-moment problem.[3] We obtain

$$\delta^- = \frac{\pi}{Z_f}\left[\frac{\Gamma}{2U\tan\delta^+} - (14 - Z_f)\frac{\delta^+}{\pi} + \frac{\delta^+}{\pi} + (Z_f - \tfrac{1}{2})\right] ,$$

$$\delta^+ = \frac{\pi}{14 - Z_f}\left[\frac{\Gamma}{2U\tan\delta^-} - Z_f\frac{\delta^-}{\pi} + \frac{\delta^-}{\pi} + (Z_f - \tfrac{1}{2})\right] .$$ (8)

Taking parameters for americium from Table I, we plot these two curves in Fig. 2 (we have also iterated these numerically to obtain the values we quote). We see that there are three intersections. The interesting one at $\delta^- = 2.85$ corresponds to six localized states at $\epsilon_f^- = 1.44$
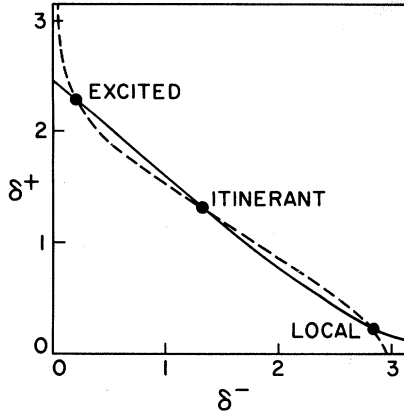
FIG. 2. Separation of the 14 f states per atom into upper resonances, with phase shifts δ^+ at the Fermi energy, and lower resonances, with phase shifts δ^- at the Fermi energy, is allowed. Each is written in terms of the other and with parameters for americium three self-consistent solutions are obtained. Middle solution is the itinerant, band-structure-like solution. To the right is a localized solution, of lower energy, with six resonances below the Fermi energy. Solution on the left has higher energy; it corresponds to an excited state with eight resonances below the Fermi energy; all three have effective f-state occupation Z_f^* close to 6.

eV below the Fermi energy; the eightfold ϵ_f^+ states lie 1.81 eV above the Fermi energy. With an americium bandwidth of 1.26 eV neither set of f bands overlaps the Fermi energy.

The solution at $\delta^- = \delta^+ = 1.34$ may be called the itinerant state. It corresponds to all 14 resonances lying 0.10 eV above the Fermi energy. This state is of higher energy than the localized state, as we shall see in Sec. VIII. The bands in this case would extend well below the Fermi energy, giving f bands corresponding to itinerant f electrons very similar to the d electrons of transition metals; however, this is not the low-energy state and we have predicted localization. The third solution at $\delta^- = 0.20$ is also interesting. The eight δ^+ resonances lie below the Fermi energy at -0.35 eV, and the six δ^- resonances lie above at 2.26 eV. We would have obtained the same solution had we assumed $Z_f = 8$, rather than 6 at the outset. We expect this to be of higher energy than the state with 6 below, and indeed the procedure used to obtain the total energy in Sec. VIII confirms this. Thus this state is a screened excited configuration. One should presumably compare all different occupation values for each case to see which has lowest energy, but we have not done that.

It is interesting that the Z_f^* obtained from the localized ground-state solution is 6.04; that for the itinerant state is 5.97. Both are close to the free-atom value of 6, and are close to each other. Even the excited configuration gives $Z_f = 6.14$. It would appear that a density-functional description would see little difference between the three solutions.

V. STRUCTURE OF THE STATES

Having established that the localized state is the appropriate description, we may ask which set of f states are

expected to be filled. The exchange energy will of course favor an alignment of the spins, according to Hund's rule. That energy is $-Z_f(Z_f - 1)U_x/2$ for all Z_f spins aligned, as opposed to $-2(Z_f/2)(Z_f/2 - 1)U_x/2$ for half of the spins up and half of the spins down. For americium, with U_x given in Table I, this difference is $9U_x = 3.24$ eV.

Spin-orbit coupling of this $S = 3$ state will tend to orient it antiparallel to the $L = 3$ orbital state to give a $J = 0$ state. The increase in energy in going to the $J = 1$ state would be $2V_{so} = 0.66$ eV, taking the value of V_{so} from Ref. 4.

Opposing this tendency is an orbital energy associated with the coupling between resonances on neighboring atoms. If all f orbitals could be occupied on one site and all orbitals empty on the neighboring site, we could estimate the total lowering in energy of all of the occupied orbitals from this interaction in perturbation theory as

$$2(V_{ff\sigma}^2 + 2V_{ff\pi}^2 + 2V_{ff\delta}^2 + 2V_{ff\phi}^2)/(\epsilon_f^- - \epsilon_f^+) \ ,$$

with the factor of 2 for spin. If we randomly occupied Z_f spin-up and spin-down states on the two atoms, this would be reduced by a factor $(14 - Z_f)/14$ for the reduced number of empty states and $Z_f/14$ for the reduced number of filled states. Finally, we may multiply by the number of neighbors n to obtain the energy gain per atom as

$$E_{band} = nZ_f(14 - Z_f)(V_{ff\sigma}^2 + 2V_{ff\pi}^2$$
$$+ 2V_{ff\delta}^2 + 2V_{ff\phi}^2)/98(\epsilon_f^- - \epsilon_f^+)$$
$$= -Z_f(14 - Z_f)W_f^2/168U \ , \qquad (9)$$

where we have used Eq. (7) to obtain the final form, and approximated $\epsilon_f^- - \epsilon_f^+$ by $-U$. For americium, E_{band} is only 0.12 eV. This could be enhanced by decoupling the spin and orbital motion and suitably picking spin orientations, but the band energy would appear to be too small to cause that. These considerations confirm the picture given, for example, by Skriver, Andersen, and Johannson,[15] of a localized, $J = 0$ state for americium.

For itinerant electrons, the corresponding energy is[4] $E_{band} = -Z_f(14 - Z_f)W_f/28$. For the localized case this is replaced by Eq. (9), a reduction of the energy by a factor of $W_f/6U$ and the volume derivative of the energy by a factor of $W_f/3U$, equal to 0.09 for americium. This is, of course, part of the cause of the large atomic volume of americium. There is also a large expansive contribution from the localization energy to be calculated in Sec. VIII.

It is interesting that the localization reduces the compressive effect of the f electrons, but does not eliminate it. There could be cases where the splitting between full and empty resonances is not nearly so large and a sizable compressive effect remains. There may also be cases where different terms dominate in the determination of the nature of the localized state—instead of localization of a Hund's-rule state, $Z_f/2$ specific orbitals, with both spins occupied, could be occupied because of a lifting of the orbital degeneracy by the crystalline environment.

VI. CONDITION FOR LOCALIZATION

It is very useful to derive a criterion for localization (analogous to the $U > |2V|$ for the Heitler-London case of

Sec. I) from the two conditions, Eq. (8), which were plotted in Fig. 2. The second equation, that for δ^+, is the one which diverges as δ^- goes to zero. The condition for having three solutions, and therefore localization, can then be seen from the figure to be that the magnitude of the slope of the second curve, evaluated at the itinerant solution $(\delta^+ = \delta^- = \delta^0)$, be less than that of the first curve. We evaluate the slopes of both the second curve and the first curve, respectively, as follows:

$$\frac{\partial \delta^+}{\partial \delta^-} = \frac{1}{14 - Z_f} \left[-\frac{\Gamma \pi}{2U \sin^2 \delta^-} - Z_f + 1 \right] ,$$

$$\frac{\partial \delta^+}{\partial \delta^-} = Z_f \left[-\frac{\Gamma \pi}{2U \sin^2 \delta^+} - (14 - Z_f) + 1 \right]^{-1} . \tag{10}$$

Both are negative. Note that they are equal if $\Gamma \pi / (2U \sin^2 \delta)$ is equal to one. The condition for localization becomes

$$\Gamma \pi / 2U \sin^2 \delta^0 < 1 . \tag{11}$$

We may use Eq. (1) and the approximate equality of Z_f^* and Z_f to rewrite the condition as

$$\Gamma \lesssim (2U / \pi) \sin^2 (Z_f \pi / 14) . \tag{12}$$

The condition for the Anderson Hamiltonian, with only a single level, does not contain the $\sin^2$ factor, which is a major difference. That factor drops to 0.05 at the beginning and end of the series making it more difficult to localize. It is striking that this same factor appears in the theory of the photoemission of cerium by Gunnarsson and Schönhammer.[16]

All of the necessary parameters appear in Table I. A convenient way to present the result is to evaluate the critical Γ from Eq. (12), and the critical W_f from this Γ using Eq. (5), and then obtain the critical atomic sphere radius (from the W_f given in Table I and dependence $W_f \sim r_0^{-7}$). The resulting values are listed in Table I as r_0^{loc}.

When the observed r_0, also given in Table I, is less than r_0^{loc}, the states are regarded as delocalized and bandlike. We see that this is true for the actinides up to plutonium. For plutonium the condition is so close that we must see if the bands overlap the Fermi energy. Using just the procedure carried out for americium in Sec. IV, we find, for plutonium (with $Z_f = 5$), the resonances ϵ_f^+ at 1.47 eV above the Fermi energy and ϵ_f^- at -0.49 eV below the Fermi energy. (Z_f^*, incidentally, is found to be 5.04.) From the W_f in Table I we see that both bands overlap the Fermi energy and each other. When a band overlaps the Fermi energy the electrons redistribute, reducing the energy shift in the equations such as Eq. (2). This has the same effect as reducing U and suppresses localization. It seems clear that this more complete analysis would predict plutonium to be itinerant, and a preliminary estimate using a Friedel model for the density of states confirmed this.

We saw in Sec. IV that americium was predicted to be localized with no bands overlapping the Fermi energy, and this would clearly be true for the heavier actinides. Thus the theory can be said to be completely in accord with experiment for the actinides. On the other hand, this is not

really a prediction of localization. The principal difference in the parameters for americium and the heavier actinides as opposed to the lighter actinides is the difference in the experimental r_0. If americium were compressed to the r_0 value of plutonium it would be predicted to be itinerant, and that prediction is presumably correct. A real prediction of localization requires the prediction that the total energy of the large-r_0, localized state is lower than the small-r_0, itinerant state. We shall attempt this in Sec. VIII, where we consider the total energy.

In the rare earths, we correctly predict localization for all of the elements except for cerium. The observed r_0 which appears in Table I for cerium is for the room-temperature γ phase which is thought to have localized electrons. For our $T = 0$ theory we predict delocalization and the consequent contraction of the volume, consistent with the observed low-volume α phase at low temperature. We have not included temperature to see if the transformation to γ at higher temperature would be predicted. It is principally the factor $\sin^2 Z_f \pi / 14$ which makes the delocalization condition so easy to satisfy in cerium; it is satisfied though U is nearly 10 times the f bandwidth.

VII. FERROMAGNETISM: ITINERANT AND LOCALIZED

We found that when localization occurs an alignment of the spins in each atom is expected. In the solid these might then form a paramagnetic state, an antiferromagnetic state, a ferromagnetic state, or even a spin-glass. If it forms a ferromagnetic state and the localized states form into bands, as we have indicated that they do, we might ask what distinguishes the state from the usual band ferromagnetism. The distinction is clear in our analysis. First, the driving force is U, not U_x. Furthermore, the Z_f levels lowered are just those occupied, and not all levels of the same spin. On the other hand, given the final set of bands (in the ferromagnetic case), it is not clear that there is an objective distinguishing characteristic. It may still be valid to distinguish the state in real systems, as we distinguish ordinary liquids and gases, although it is possible to go smoothly from one to another around a critical point.

It is therefore interesting to discuss, in the context of our analysis, the itinerant ferromagnetic state. Skriver, Andersen, and Johansson[15] had in fact found that in the itinerant description of americium a spontaneous spin polarization, the itinerant ferromagnetic state, was favored. In Ref. 4 we made the corresponding analysis for the simplified electronic structure, finding a criterion for spin polarization of $U_x > W_f / 7$. Our failure to predict spin polarization for americium arose from an error of a factor of 2 in obtaining the value of U_x from the data given by Nugent.[9] We have corrected that error in Table I where we see that the criterion predicts spin polarization for americium, but not for the other actinide metals. This is again a result of the large experimental atomic volume for americium, not from the differences in f-state radius r_f, and U_x, which are very much the same for plutonium and americium. Skriver, Andersen, and Johansson[15] were in fact using the ferromagnetism as a way of modeling the

true localization which the present analysis indicates occurs in americium, since the f-electron pressure which produces the small atomic volumes in the itinerant actinides is also greatly reduced in the ferromagnetic state of americium: The pressure deriving from the $-Z_f(14-Z_f)W_f/28$ term in the energy is reduced by a factor of 4 by placing all six electrons in states of one spin, compared to the reduction by a factor of 11, about which we found for localization.

We may tabulate the criterion for itinerant ferromagnetism in the same form we used for localization. We simply use the condition $W_f < 7U_x$ to find the atomic sphere radius r_0 at which ferromagnetism occurs; the results are listed in Table I. It seems astonishing that the criteria are so nearly the same, perhaps within the uncertainties of the parameters, since they depend upon the fundamentally different atomic parameters U and U_x. It helps justify the use of ferromagnetism as a model of localization, at least for half-filled bands.

However, we should remember that the states themselves are quite different in this case. We anticipate that the localized state gives no density of states at the Fermi energy as the band model does. Furthermore, if localization is favored, as we find for americium, the alignment of spins gains all of the energy which ferromagnetism does and the localized ferromagnetic state should be favored over the itinerant one.

In a system such as praseodymium, where we find r_0^{ferro} greater than r_0^{loc}, we would predict that under pressure the localized electrons (with spins aligned) should first delocalize into an itinerant ferromagnetic state, and then into an itinerant nonmagnetic state. This prediction could be questioned since there is a continuous path between the first two states, but this fact does not preclude a first-order transition to the itinerant state.

VIII. TOTAL ENERGY

We may also discuss the total energy of the system as a function of volume. For a real criterion for localization this is necessary since we must compare the energy of the

localized state (at the corresponding large equilibrium volume) and that of the itinerant state (at the corresponding reduced volume). In Ref. 4 we obtained the volume-dependent terms in the energy; they were the kinetic energy of the sd electrons (three per atom), the exchange energy for those electrons, their pseudopotential repulsion (in terms of an empty-core pseudopotential radius), the Madelung energy (for ions of charge 3), the band energy associated with the partial filling of an f band, and the f-f repulsion energy. These terms describe the crystal with itinerant f electrons, and gave a good account of the light actinides though there were significant errors in the predicted bulk modulus due to small errors in large canceling terms. All parameters are given there, and we may use the forms given there for the itinerant state. The corresponding plot for americium is shown in Fig. 3.

In the localized state, the band energy is reduced to the value given in Eq. (9). In addition, there is a lowering of the energy which we call the *localization energy* due to the splitting into two resonances and the occupation of only the lower resonance. In Fig. 4 we show the energies of the two resonances for americium as a function of atomic sphere radius r_0. As the splitting occurs with increasing r_0, there are 14 levels per atom at the center of the resonance at ϵ_f^{itin} which split into Z_f levels per atom dropping in energy and $14-Z_f$ levels rising in energy. In addition, the energy of all other levels coupled to this resonance are shifted in energy. The two effects are of opposite sign and of comparable magnitude so we must include both.

The first contribution to the localization energy is the gain from dropping Z_f electrons per atom from ϵ_f^{itin} to ϵ_f^-. The second may be obtained by summing the shifts in energy over the states from the bottom of the free-electron band ($\epsilon=0$) to the Fermi energy ($\epsilon=\xi$). If there are Z_r resonant states, at ϵ_r this value is[17]

$$\sum \delta\epsilon = Z_r \int_0^\xi d\epsilon\, \delta_l(\epsilon)/\pi$$

$$= Z_r \frac{\Gamma}{2\pi} \int_0^\xi \frac{d\epsilon}{\epsilon-\epsilon_r} = \frac{Z_r\Gamma}{2\pi} \ln\left|\frac{\xi-\epsilon_r}{-\epsilon_r}\right| , \qquad (13)$$
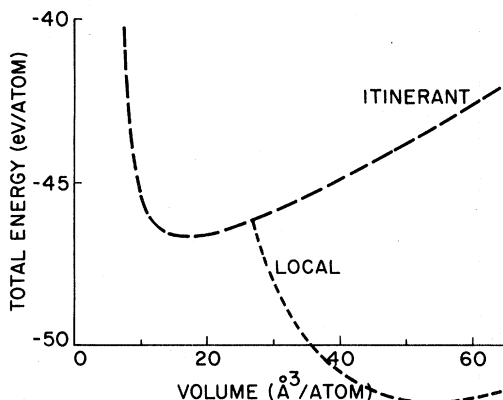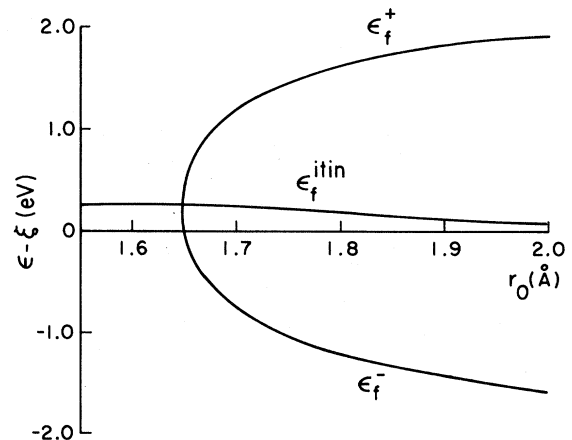

FIG. 3. Total energy for americium as a function of volume. The dashed curve is for the itinerant bandlike state, based upon parameters from Ref. 4. The dotted curve is the energy of the localized state. This predicts a localized ground state at a volume considerably larger than the observed 30 Å^3.

FIG. 4. Energy ϵ_f^+ of the upper resonance, that of the lower ϵ_f^-, and that of the itinerant state ϵ_f^{itin}, as a function of the atomic sphere radius r_0 in americium. The localized state is predicted to occur at r_0 greater than 1.65 Å.

where in the second step we used Eq. (3) for the phase shift, taking the small argument form for the tangent; this should be suitable if the resonance is not too near the Fermi energy. Principal values were taken in the integration

across the singularity. The contribution to the localization energy is such a contribution from Z_f resonances at ϵ_f^- plus the effect of $14 - Z_f$ at ϵ_f^+ minus the effect of 14 resonances at ϵ_f^{itin},

$$
\begin{aligned}
\delta E_{\text{loc}} &= \frac{\Gamma}{2\pi} \left[Z_f \ln \left| \frac{\epsilon_f^- - \xi}{\epsilon_f^-} \right| + (14 - Z_f) \ln \left| \frac{\epsilon_f^+ - \xi}{\epsilon_f^+} \right| - 14 \ln \left| \frac{\epsilon_f^{\text{itin}} - \xi}{\epsilon_f^{\text{itin}}} \right| \right] \\
&= \frac{\Gamma}{2\pi} \left[Z_f \ln \left| \frac{\epsilon_f^- - \xi}{\epsilon_f^+ - \xi} \frac{\epsilon_f^+}{\epsilon_f^-} \right| + 14 \ln \left| \frac{\epsilon_f^+ - \xi}{\epsilon_f^{\text{itin}} - \xi} \frac{\epsilon_f^{\text{itin}}}{\epsilon_f^+} \right| \right] .
\end{aligned}
\tag{14}
$$

We take the different ϵ_f to have similar values, measured from the free-electron band minimum, and set the final factor in each logarithm equal to one. Numerical estimates confirm this as a good approximation. Then we use Eq. (3) and add the transfer term to obtain the total localization energy,

$$
E_{\text{loc}} = Z_f (\epsilon_f^- - \epsilon_f^{\text{itin}})
$$

$$
+ \frac{\Gamma}{2\pi} \left[Z_f \ln \left| \frac{\tan\delta^+}{\tan\delta^-} \right| + 14 \ln \left| \frac{\tan\delta^0}{\tan\delta^+} \right| \right] .
\tag{15}
$$

This is the form we shall use in calculating the total energy, but it is helpful first to simplify it somewhat in order to see more clearly what it means. We may look in particular at the weak-localization limit where $\delta^+ = \delta^0 - \Delta$ and $\delta^- = \delta^0 + \Delta$, with Δ small and positive. Then the tangents and the logarithms may be expanded to give

$$
E_{\text{loc}} \approx -\frac{Z_f \Gamma \Delta}{2 \sin^2 \delta^0} + \frac{(14 - 2Z_f) \Gamma \Delta}{2\pi \sin\delta^0 \cos\delta^0} .
\tag{16}
$$

The first term is from the first term in Eq. (15) and is always negative—a gain in energy due to localization. The second term will generally be positive; when Z_f exceeds seven so the numerator is negative, the resonance will lie below the Fermi energy and $\cos\delta^0$ will also become negative. Evaluation of this as a function of Z_f (taking $\delta^0 = Z_f \pi / 14$) indicates that the first term is always larger in magnitude, so we may generally expect localization to occur if the criterion, Eq. (12), is satisfied and if neither resonance produces bands which cross the Fermi energy.

In this weak-localization limit, with only a small splitting between the two resonances, only a small portion of the $E_{\text{band}} = Z_f (14 - Z_f) W_f / 28$ is lost; an approximate calculation of E_{band} which varies smoothly between this form and Eq. (9) would be appropriate. However, in the weak-localization limit the bands will cross the Fermi energy so other refinements are also necessary. For our purposes it will be sufficient to use Eq. (9) which is appropriate for strong localization, and in fact the resulting energy is small enough that we may neglect it altogether. We thus add E_{loc} from Eq. (15) to all terms in the f-shell—metal energy from Ref. 4 (except the E_{band} term) to obtain the total energy labeled "local" in Fig. 3.

Before discussing this curve we may note that the same evaluation of Eq. (15) may be made for the second local-

ized solution from Fig. 2, that with eight resonances, rather than six, below the Fermi energy. This yields a *positive* localization energy of 0.175 eV, rather than the -3.87 eV for the $Z_f = 6$ solution, confirming that it is an excited state.

The behavior of the localized curve is qualitatively correct. It reaches a minimum at larger volume than the itinerant curve, and the energy at the minimum is considerably less than at the itinerant minimum. However, we appear to have considerably overestimated the gain in energy due to localization. The minimum occurs at a volume considerably larger than 30 Å^3, at which americium is observed.

In Ref. 4, the pseudopotential core radius was actually adjusted to yield the correct equilibrium spacing for americium, assuming that with localization there was no band energy, but also that there was no localization energy; the discrepancy has come because we have now added the localization energy from Eq. (15). We might therefore readjust the pseudopotential core radius to bring the equilibrium volume into agreement with experiment, requiring an r_c of 0.28 Å, rather than 0.80 Å. This, however, seems too small in comparison to the core radii obtained from the free-atom ionization potential for the f-shell metals. We presume therefore that the discrepancy comes not from an inappropriate pseudopotential, but from inaccuracy in our estimate of the localization energy from Eq. (15), in analogy with the factor-of-2 error in the energy of the localized Heitler-London state (compared to the exact value) which we noted in Sec. I. We may also note that the discrepancy may not be excessively large in comparison to discrepancies we found in Ref. 4, and as large as a factor of 3 in the predicted bulk modulus for two of the actinides.

For the lighter actinides the condition for localization becomes more difficult to satisfy. First, U tends to decrease as we move to the left in the table (except for Pu, which from Herbst's values[7] is larger than Am; Johansson[18] did not find this reversal and perhaps his numbers are to be preferred). In addition, the $\sin^2$ factor in Eq. (12) drops from 0.95 to 0.81 in going from Am to Pu and continues to drop. Both Am and Pu have the same W_f at the same volume, but W_f and Γ increase as we go further to the left. Thus the general trend is correct. However, it is clear that the same calculation which predicted localization for Am would predict locali-

zation also for Pu, since localization is expected very near the Pu equilibrium spacing (see Table I) and the similarity with Fig. 3 makes it clear that the prediction will be similar. A more accurate treatment of the localization energy, and perhaps other terms is clearly needed if these predictions are to be numerically accurate.

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