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Corrections to an exact solution of a two-electron problem for correlation in *f*-shell metals

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The generalization to *f*-shell metals of an exact solution of a two-electron problem is explored, based upon existing parameters. Using a simplified energy-band framework, it yields elementary predictions of specific heats and paramagnetic susceptibilities in quite good accord with experiment for the light actinides, through plutonium, but with large corrections to local density approximation theory. For americium and beyond, and for the rare earths, an approach beginning with atomic multiplets becomes appropriate, leading to Curie-Weiss behavior. It leads, however, to the same band picture when applied to the lighter actinides. For americium, it is important to go beyond an **L**·**S**-coupling approximation for the multiplets.

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I. INTRODUCTION

It is a familiar fact that many *f*-shell metals do not fit the description in terms of energy bands which has been so successful in all other metals. They are called strongly correlated metals, and the *f* states retain much of the character which we associate with isolated atoms. We sought to understand[1,2] the bonding properties of these metals, with some success, by building on a simple strongly correlated system which we can understand quite completely. Our goal here is to extend that understanding to the electronic properties of the *f* shell metals.

The simple system considered is a Li_2 molecule, a system with a single important valence *s* orbital of energy ε_s and a single electron on each atom. These two orbitals are coupled by some matrix element $-V$ and there is an extra energy U if both electrons are at any moment on the same atom. In the context of this limited basis there are only six two-electron states, and with the reflection symmetry of the molecule we can solve for the electronic states exactly. The ground-state energy in particular is given by[1,2]

$$E_{\text{TOT}}=2\varepsilon_s+\frac{U}{2}-\sqrt{\left(\frac{U}{2}\right)^2+(2V)^2}. \tag{1}$$

The two limiting cases of this solution are very familiar. When the Coulomb repulsion is small compared to the coupling, $U\ll V$, we may expand the square root in U/V to obtain $2\varepsilon_s+U/2-2V$, which corresponds to the standard local-density approximation (LDA) to the ground state, the band approximation in the case of solids. The two electrons are placed in bond states, each at energy $-V$, which produces the cohesion of the molecule. There is also a 50% chance at any moment that the two electrons are on the same atom, adding $U/2$. In the other limit, $U\gg V$, we may expand the square root in V/U to obtain $2\varepsilon_s-4V^2/U$. The electrons have appropriately segregated onto separate atoms and there is a residual effect of the coupling which favors their spins being antiparallel. There is a widely used approximation[3] for *f*-shell metals which is called the unrestricted Hartree-Fock or Anderson impurity model,[4] the essential feature of which is the omission of the artificial self-interactions of the LDA. When applied to this two-level system it gives[1,2] a LDA solution as long as $V>U/2$, but then switches to $2\varepsilon_s-2V^2/U$ for $V>U/2$, the total energy and its first derivative with respect to V being continuous through the transition. The discontinuity in the second derivative and the factor of two error at small V are not present in the exact solution.

We wish to extend the exact solution to *f*-shell metals, but face five serious complications: there are many atoms, rather than two; there are seven orbitals per atom rather than one; there are some Z_f electrons per atom rather than one; there is an exchange interaction between electrons, which did not arise with two electrons of opposite spin; and there is spin-orbit coupling, $V_{\text{SO}}\sigma\cdot\ell$, which was not present for *s* states. We can nevertheless make the generalization if we simplify the effect of the coupling between neighboring orbitals to a single parameter, the *f*-band-width W_f, and if we then proceed from the two limits discussed above toward the center. This approach is a very considerable improvement upon the local-density approximation, and even upon the unrestricted Hartree-Fock approach, in the treatment of electron correlations, but it is at the expense of the reduced accuracy relative to the LDA for the effects of the coupling between neighboring atoms. For the *f*-shell metals, it would seem the appropriate choice. Further, there is a natural extension of this approach to LDA calculations, which may allow a more accurate treatment of the effects of interatomic coupling.

The simplification of the band structure which is employed here is the Friedel approximation,[5] in which the density of states due to the *f*-shell states is replaced by a constant density of states per atom of

$$n(\varepsilon)=14/W_f \tag{2}$$

over an energy range of W_f centered at an energy ε_f. Then the energy per atom gained by filling the lower states with Z_f electrons per atom is easily obtained as

$$\Delta E_{\text{TOT}}=-\frac{Z_f(14-Z_f)}{28}W_f, \tag{3}$$

and electronic properties which depend upon the density of states at the Fermi energy can be obtained using Eq. (2). These may be thought of as approximations to the LDA theory of these properties. Then the generalization of Eq. (1) to the effects of the *f* bands is, quite naturally,

TABLE I. Parameters for the actinides W_f values were from Skriver's LMTO calculations (Ref. 6). U_f was based upon experimental values from Brewer (Ref. 7). U_x is from Ref. 1. The spin-orbit coupling $V_{\rm SO}$ was obtained from Herbst, Watson and Lindgren (Ref. 8). $Z_f = Z - 3$ is the number of *f*-electrons per atom. Energies are in eV.

	Z_f	r_0 (Å)	W_f	U_f	ζ	U_x	$V_{\rm SO}$
Ac	0	2.10	12.90	3.00			
Th	1	1.99	5.56	3.20	0.87		
Pa	2	1.80	3.79	3.35	0.75	0.22	0.17
U	3	1.69	3.76	4.09	0.68	0.27	0.20
Np	4	1.66	3.09	3.90	0.62	0.29	0.24
Pu (α)	5	1.67	2.50	4.61	0.48	0.32	0.26
Pu (δ)	5	1.81	1.42	4.61	0.29	0.32	0.26
Am	6	1.91	0.98	4.96	0.19	0.36	0.33
Cm	7	2.03	0.82	5.10	0.16	0.40	0.36

$$\Delta E_{\rm TOT} = -\frac{Z_f(14-Z_f)}{28}\left(\sqrt{U_f^2+W_f^2}-U_f\right), \qquad (4)$$

chosen such that it gives the correct result in the LDA and strongly correlated limits. We shall take the band width W_f from the LDA linear muffin-tin orbital (LMTO) calculations of Skriver,[6] but will find it helpful to think of it as having been written in terms of the second moment of the bands when we incorporate spin-orbit coupling.

We may note that the attractive force, or pressure, which this energy contributes is proportional to the derivative of this energy with respect to spacing, or volume. Since only W_f varies with spacing, these are reduced by a factor

$$\zeta = \frac{W_f}{\sqrt{U_f^2+W_f^2}}. \qquad (5)$$

Similarly we may expect the variation of energy from state to state and the effective band width to be decreased by this same factor. It is true that the second moment for all states will be proportional to $\sqrt{U_f^2+W_f^2}$ and is increased, but that arises from the upward shift of the empty atomic states by U_f relative to those occupied and does not apply to electrons transferred from state to state. Thus the density of states of Eq. (2) is increased by a factor $1/\zeta$.

Using Eq. (4) we evaluated the total energy of the actinides as a function of volume,[2] calculating separately the contributions from the *f*-shells and from the remaining three free electrons per atom. This indeed seemed to account well for the reduced spacing of the elements neptunium and below, relative to those of americium and beyond, and of the tendency of plutonium to occur at two different densities. We turn now to the electronic properties using these same parameters.

II. FROM THE BAND LIMIT

All of the parameters needed have been listed in Ref. 2, and are repeated in Table I. We begin from the band limit, for which we correct the band width by the factor ζ of Eq. (5), also listed in Table I. We see that the corrections become very considerable by the time we reach plutonium.

The corresponding bands do not include the effects of spin-orbit coupling, which is given by a term in the Hamiltonian (e.g., Ref. 2, p. 199),

$$H_{\rm SO} = -V_{\rm SO}\sigma\cdot\ell. \qquad (6)$$

This introduces additional elements in the Hamiltonian matrix from which LDA bands would be obtained. In Ref. 2 (pp. 603ff) we equated the second moment of the bands, $M_2 = W_f^2/12$ in the Friedel model, to the second moment obtained from sums over the interatomic matrix elements. We similarly saw that spin-orbit coupling added $3V_{\rm SO}^2$ to the second moment. Like U_f it is an atomic property not depending upon spacing so that we could include its effect in ζ for the volume-dependent energy by adding $36V_{\rm SO}^2$ to U_f^2 in Eq. (5). Indeed $V_{\rm SO}$ is seen to be small enough from Table I that when squared its effect is quite small even when multiplied by 36. It is less clear whether it should increase or decrease the density of states and we neglect it here. The exchange energy U_x simply gives a constant shift in the energy of each state and does not affect the bands otherwise, unless there is a spontaneous formation of ferromagnetism. Such a state does not form in the actinides, so our results are not affected by exchange. Actually the parameters of Table I would indicate ferromagnetism in these systems according to a criterion given in Ref. 2 (p. 591), $U_x > 1/7(\sqrt{W_f^2+U_f^2}-U_f)$. However, it does not occur and we can proceed with the density of states, using Eq. (5), as

$$n(\varepsilon) = \frac{14\sqrt{U_f^2+W_f^2}}{W_f^2}. \qquad (7)$$

Two properties of metals which depend directly upon the density of states at the Fermi energy are shown schematically in Fig. 1 as dark lines. One is the low temperature specific heat, given by

$$C_v = \frac{\pi^2}{4}k_B^2 T n(\varepsilon_F). \qquad (8)$$

The slope is given by $C_v/T = (\pi k_B/2)^2 n(\varepsilon_f) = 1.768\ {\rm eV} \times n(\varepsilon_F)$ millijoules/mole K^2. We have $n(\varepsilon_F)$ in reciprocal eV, and multiplying that value by 1.768 gives the linear term in the customary units. The other property is the temperature-independent Pauli paramagnetic susceptibility,

$$\chi_p = \mu^2 n(\varepsilon_F)/\Omega_0. \qquad (9)$$

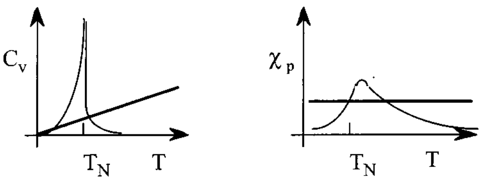

FIG. 1. A schematic representation of the temperature-dependence of the specific heat C_v and of the paramagnetic susceptibility χ_p for traditional metals as dark lines and for Curie-Weiss systems of coupled moments as light lines.

TABLE II. Properties of the actinides for the band limit, obtained from Eqs. (7), (8), and (9) using the parameters of Table I. Experimental electronic specific heats were from Brodsky (Ref. 9) except for more recent values for Pu from Hecker, Harbur, and Zocco (Ref. 10) and for Am from Smith, Stewart, Huang, and Haire (Ref. 11). Experimental susceptibilities are from Brodsky (Ref. 9).

	C_v/T, mJ/mol K^2		$\chi_p\times10^6$, cgs/gram atom	
	Eq. (8)	Expt.	Eq. (9)	Expt.
Th	5.1	4.3	93	80
Pa	8.7	-	159	270
U	9.7	9.1	178	390
Np	12.9	12.4	236	550
α-Pu	20.8	25	380	510
δ-Pu	59.2	53	1083	550
Am	130.3	2 ± 2	2383	780

The moment μ is the Bohr magneton $\mu_B=e\hbar/2mc$, and substituting that form we see that χ_p is dimensionless. It is however common to think of it as a magnetic-moment per unit volume, and to quote it instead as a magnetic moment per gram-atom (or per mole). To obtain those values we need to multiply the form in Eq. (9) by the volume (in cm^3) of one gram-atom (or mole) of the metal. Ω_0 is the volume per atom, or per an atomic weight of nucleons. Thus the atomic weight cancels and we obtain $\chi_p=32.3\text{ eV}\times n(\varepsilon_F)\times10^{-6}$ cgs units per gram atom, the customary units.

Equations (7) and (8) [or the reduced form given after Eq. (8)] together with the parameters of Table I give directly the predictions of specific heat which are compared with experiment in Table II. These predictions of C_v/T are remarkably close for all elements through plutonium, much closer than one could hope with a crude Friedel model of the density of states, and strongly support our picture. Note that the predictions corresponding to the LDA would be smaller by the factor ζ of each element from Table I. For americium, and presumably the heavier actinides, the prediction is quite wrong. For Am the observed specific heat is comparable to the expected contribution of 0.85 millijoules/mole K^2 for a free-electron gas of three electrons per atom. (Note that such a contribution could be added to each of the other predictions, but is not a significant contribution.)

We may similarly evaluate the paramagnetic susceptibility of Eq. (9), also compared with experiment in Table II. Again the comparison with experiment supports the band picture for all elements through plutonium. The agreement is not nearly so good as for the specific heat, which reflects more on the theory of the susceptibility which gives it as universal constants times the same density of states, just as is C_v/T. It is known, for example, that the coupling with phonons enhances the quasiparticle density of states which enters the specific heat, by as much as a factor of two, but does not enhance the density of states for moving the relative Fermi energies in spin-up and spin-down bands which enters the susceptibility (e.g., Ref. 12, p. 421). The exchange interaction, which can produce band ferromagnetism, reduces the energy required to flip spins in nonmagnetic metals and thus enhances the susceptibility, without having that effect on the specific heat. This is the Stoner enhancement factor $1/[1-n(\varepsilon_F)U_x/2]$ (Ref. 5, p. 383. In that expression $n(E_M)=n(\varepsilon_F)/2$ refers to only one spin). This factor more than makes up the discrepancies for χ_p in Table II. The factor even becomes negative for δ-Pu and beyond, corresponding to a ferromagnetic instability, which however does not in fact occur, as mentioned earlier. Our goal is to understand the electronic structure, not to refine the theory of properties such as the susceptibility. The prediction for Am cannot be meaningful in any case when the more direct measurement (C_v) of the density of states indicates such a small value.

III. FROM THE ATOMIC LIMIT

We turn next to the other limit, when U_f is large compared to the band width. Then each atom is taken to have Z_f occupied *f* states, well below the Fermi energy, and $14-Z_f$ at ε_f+U_f, well above the Fermi energy. The most familiar

TABLE III. The lowest values of the sum of the exchange and spin-orbit energies for Russell-Saunders states of the atom for different multiplets of a given Z_f. The degeneracy of each is $2J+1$. ζW_f is an estimate of the width of multiplet bands in the metal.

S	L	J	Energy per atom	Moment/μ_B
$Z_f=5(\text{Pu})\zeta W_f=1.10\text{ eV}(\alpha),\ 0.38\text{ eV }(\delta)$				
5/2	5	5/2	$-10U_x-5/2\ V_{\text{SO}}=-3.85$ eV	5/7
5/2	5	7/2	$-10U_x-23/12\ V_{\text{SO}}=-3.70$ eV	26/9
5/2	4	3/2	$-10U_x-2\ V_{\text{SO}}=-3.72$ eV	0
$Z_f=6(\text{Am})\zeta W_f=0.17$ eV				
3	3	0	$-15U_x-3/2\ V_{\text{SO}}=-5.90$ eV	0
3	3	1	$-15U_x-11/8\ V_{\text{SO}}=-5.85$ eV	3/2
2	2	0	$-10U_x-4\ V_{\text{SO}}=-4.92$ eV	0
$Z_f=7(\text{Cm})\zeta W_f=0.12$ eV				
7/2	0	7/2	$-21U_x=-8.40$ eV	7
5/2	0	5/2	$-15U_x-3\ V_{\text{SO}}=-7.08$ eV	5
3/2	0	3/2	$-11U_x-5\ V_{\text{SO}}=-6.20$ eV	3

approach for including exchange and spin-orbit coupling is the $\mathbf{L}\cdot\mathbf{S}$ coupling Approximation (or Russell-Saunders coupling), appropriate when V_{SO} is small. In this approach one initially ignores V_{SO} so that the spin angular momentum and orbital angular momentum are separately conserved and one may specify states by total spin quantum numbers S, and orbital quantum numbers L, and then distinguish states by the total angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$. The states are then held fixed and the expectation value of the spin-orbit interaction is calculated in terms of them. The expectation-value of the H_{SO} of Eq. (1) is customarily written as $\zeta(S,L)\mathbf{L}\cdot\mathbf{S}=[J(J+1)-L(L+1)-S(S+1)]\zeta(S,L)/2$. This is quite misleading (though seen to be valid, Ref. 13, p. 194) since it is the individual one-electron spin and orbit which are coupled, not the total spin $\mathbf{S}$ and total orbital angular momentum $\mathbf{L}$, and $\zeta(S,L)$ is considerably reduced from the one-electron values and strongly dependent upon S and L. This is the approach used by Wills and Eriksson[14] and it is useful to use it first, though we shall find that we must do better, particularly for Am.

For Pu, with $Z_f=5$, the lowest-energy multiplet is found by aligning all spins, so $S=5/2$, and minimizing $\mathbf{L}\cdot\mathbf{S}$ with $L=5$, and $J=5/2$, giving a sixfold-degenerate energy -3.85 eV as seen in Table III. Further, there are also eight-fold and four-fold states with similar energy, seen also in Table III, as well as many states at somewhat higher energy. We can also obtain the magnetic moment for each of these terms, given by $(1+[J(J+1)+S(S+1)-L(L+1)]/[2J(J+1)])J$ (Ref. 13, p. 187) equal to 5/7 Bohr magnetons for the ground state, also in Table III.

We should note here that the coupling between multiplets on neighboring atoms will broaden these levels into bands. Bands arising from coupled Z_f-electron states are different from one-electron bands and we should reconsider the question of width. It may be helpful to write the coupling between the orbitals on an atom numbered j and those on a neighboring atom i, at relative position $\mathbf{d}$, in terms of annihilation and creation operators,

$$H_{\mathrm{couple}}=\sum_{m,\sigma}(c^{\dagger}{}_{m\sigma i}c_{m\sigma j}+c^{\dagger}{}_{m\sigma j}c_{m\sigma i})V_{ffm}, \tag{10}$$

since this makes it explicit that the only couplings which enter are between occupied and empty states, differing in energy by a U_f. [For Eq. (10) the angular momentum of all of the orbitals has been quantized around $\mathbf{d}$ and σ is the spin quantum number for each orbital.] Then the coupling between neighboring occupied orbitals comes from second-order terms, V_{ffm}^2/U_f, reducing the spread in energies produced to an energy of the order of W_f^2/U_f, also the leading term in an expansion of ζW_f in W_f/U_f. Deriving a reduced bandwidth in detail, for example with a Friedel model based upon second moments, gives a factor (depending upon Z_f) of order 1. Since we need only an approximate magnitude it will be adequate to take this reduced band width to be simply ζW_f, listed in Table III. This is sufficient in plutonium that the bands arising from the lowest multiplets will cross each other, being therefore partially filled. This returns us to the bandlike behavior discussed in the preceding section so that the same essential picture of plutonium arises starting from either limit, and is in accord with experiment as we have seen.

For Am, with $Z_f=6$, the lowest-energy multiplet is again found with all spins aligned, with the maximum $L=3$ consistent with that, and with minimum $J=0$ as indicated in Table III. This result is problematic since this state is seen to have no moment, as indicated by Skriver, Andersen, and Johansson,[15] while we noted a large paramagnetic susceptibility for Am. The ζW_f band width listed would say that the lowest multiplet band would cross the next, as in Pu, which would give a temperature-independent susceptibility, but this is not consistent with the observed specific heat. We return to an improved treatment of Am shortly.

We first note that for Cm, with $Z_f=7$, spin alignment fills all orbitals, leading to $L=0$, and any change in state requires flipping a spin opposite to the remaining six, costing a large energy of $6U_x$, as seen in Table III. Thus we do not expect the band from the ground-state multiplet to cross other bands. The large moment of $7\mu_B$ can rotate, but the coupling between adjacent moments will favor some ordered state below a Néel temperature T_N. There will be no contribution to a linear term in the specific heat as there was for bands, but there will be a contribution due to disordering of the moments. This is classic Curie-Weiss behavior, illustrated in Fig. 1, and presumed to be correct for Cm and all heavier actinides.

IV. BEYOND L·S COUPLING

We return now to a more accurate determination of the multiplet states for Am. Because we include only V_{SO} and U_x, and not anisotropies in the potential nor variations of the parameters from orbital to orbital, we find it straightforward to proceed. We select a z axis, along which we shall later apply a magnetic field. Then we may distinguish the basis set of f-orbitals by the component of orbital angular momentum L_z along this axis, and the spin by the component $\sigma_z=\pm 1/2$ along the axis. Further we may rewrite the spin-orbit coupling in terms of raising and lowering operators (e.g., Ref. 13, p. 13):

$$H_{\mathrm{SO}}=-V_{\mathrm{SO}}[(\sigma^{+}\ell^{-}+\sigma^{-}\ell^{+})/2+\sigma_z\ell_z]. \tag{11}$$

We see that the final term shifts each diagonal energy in the 14×14 Hamiltonian matrix based upon these L_z, σ_z orbitals, and that the first two terms couple basis states by pairs of the same j_z, e.g., $\sigma_z=1/2$, $\ell_z=2$ and $\sigma_z=-1/2$, $\ell_z=3$ for $j_z=3/2$. They do not couple basis states of different j_z. Further U_x only shifts the diagonal energies, by an amount equal to U_x times the total occupation of other states of the same spin on the atom (we do not include artificial self-interactions). Thus the solution of the Hamiltonian matrix reduces to the solution of two-by-two matrices. We wrote a small program which writes the solution of this matrix in terms of the diagonal and off-diagonal ($-\sqrt{6}V_{\mathrm{SO}}/2$ for $j_z=3/2$) elements. That is, we obtain the coefficients u and v on the two basis states and the energy ε_{jz} for each of the two solutions for each j_z. From these we can sum the contributions and recalculate the exchange shifts for each state, and iterate till the solutions converge. The total energy obtained by adding the energies of the occupied solutions contains the exchange energy twice, once in the energy of each of two interacting electrons, so it must also be evaluated separately and subtracted once. This procedure can be redone with different choices of states occupied.

It is interesting that the procedure, applied for example to Am with $Z_f = 6$, gives the lowest energy with one electron in the lower state of each of $j_z = 5/2$, 3/2, 1/2, $-1/2$, $-3/2$, and $-5/2$. This would also be true of the ground state assumed in a *jj*-coupling scheme, but exchange causes the state to break symmetry and form a moment. Using the parameters of Table I, the total energy is found to be -6.82 eV, and the magnetic moment obtained by adding the appropriate squared coefficient times $(\ell_z + 2\sigma_z)\mu_B$ for the occupied states is $\pm 2.31\mu_B$, the sign depending upon whether states of predominantly spin-up or spin-down are chosen. By letting the states readjust this has gone well beyond the $\mathbf{L}\cdot\mathbf{S}$ coupling approximation, as well as the *jj*-coupling scheme, but the resulting many-electron states are not yet eigenstates. They remain coupled to each other, the most important coupling being between these two lowest-energy states with moments of $\mu_z = \pm 2.31\mu_B$. The j_z electronic state entering each six-electron state is made up of the same pair of one-electron states with coefficients $u\pm$ and $v\pm$ and contributes a coupling ($-\sqrt{6}V_{\mathrm{SO}}/2$ for $j_z = 3/2$) between the $+$ and $-$ one-electron states, with a factor $u_+v_- + v_+u_-$. Most importantly, there is also a factor $u_+u_- + v_+v_-$ for each of the other five pairs from integrating over all coordinates in the six-electron wave functions. The contributions of these products for each of the six pairs is added, giving in the case of Am an inter-multiplet coupling of $-0.273V_{\mathrm{SO}}$. This reduction of the matrix elements between states by the overlap between shifted and unshifted spectator states (e.g., Ref. 16, pp. 310ff.) can be important in many aspects of these strongly correlated systems. In this case the reduced coupling between the up-moment and down-moment states produces two atomic states, the lower being the sum of the two, with no net moment, and presumably $J = 0$. The other is the difference of the two, again with no moment and higher in energy by $\Delta\varepsilon = 2\times 0.273V_{\mathrm{SO}} = 0.18$ eV. This is approximately equal to our estimate of the multiplet bandwidths, 0.17 eV from Table III, but we presume that the two bands do not overlap since experimentally there is no large linear specific heat in Am.

These two states do give a temperature-independent contribution to the paramagnetic susceptibility (of the Van Vleck type from coupling between states, rather than of the Pauli type from repopulating states). A magnetic field along the z axis shifts the two contributing states by $\pm\mu H$, with μ equal to 2.31 Bohr magnetons (obtained above), giving a matrix elements between the two composite states of the same magnitude and a susceptibility of

$$\chi_p = \frac{2\mu^2}{\Omega_0 \Delta\varepsilon} = 1917\infty 10^{-6} \;\; \text{cgs/gram atom for Am.} \tag{12}$$

This is 2.5 times the experimental value listed in Table II, comparable agreement to that for actinides with bands listed in Table II. Thus it is fair to say that the observed properties of Am are not inconsistent with our picture, including the low specific heat and high temperature-independent susceptibility.

The more accurate calculation of the multiplets was essential in the case of americium. It produced the very closely spaced $J = 0$ multiplets, which with $\mathbf{L}\cdot\mathbf{S}$ coupling were separated by an electron volt (Table III). The same improved calculation of multiplets for Pu still gives multiplets very close in energy, depending upon which five of the low-energy j_z states are occupied, and overlapping bands are expected as with $\mathbf{L}\cdot\mathbf{S}$ coupling. This approach again gives a ground state for Cm some $6U_x$ lower than the first excited state, so the conclusions for the other heavy actinides are not modified.

V. RARE EARTHS

The parameters listed in Table I were also given in Ref. 2 (p. 605 except for V_{SO}) for the rare earths. The largest $\zeta = 0.03$ is for Ce, with $W_f = 0.21$ eV and $U_f = 7.2$ eV, leading to a band width of only 0.006 eV. With $Z_f = 1$ we expect a $j = 5/2$ ground state with a $j = 7/2$ excited multiplet. The experimental[17] V_{SO} for Ce is 0.08 eV, corresponding to a splitting between multiplets of $7V_{\mathrm{SO}}/2 = 0.28$ eV. This is so large compared to the band width that there can be no overlap of multiplet bands. A Curie-Weiss behavior is expected in Ce, and in all other rare earths, and indeed in most cases it is true, as summarized by Rocher.[18]

Cerium, however, has a sizable linear term in the specific heat, 42 mJ/mole K^2. Gunnarsson and Schonhammer[19] have indicated that the parameters are such that a Kondo state forms, a state in which the local moment combines with the free-electron states to form a peak in the density of states at the Fermi energy, and that this is consistent with the observed high specific heat and magnetic susceptibility of Ce at low temperatures. Also, europium is anomalous.[20] It is directly above Am in the periodic table, but is generally assumed to have taken an additional free electron into the f shell to form a $Z_f = 7$ state with a moment of 7/2 Bohr magnetons. Having only two remaining free electrons per atom explains why it has a volume much larger than its neighboring rare earths. It does form an antiferromagnetic state with a Néel temperature of 86 K, but Bozorth and Van Vleck[20] indicated that the particular ordering of the spins seemed inconsistent with the Friedel oscillations of a two-electron gas. Further, the susceptibility does not drop below the Néel temperature as in a Curie-Weiss system (Fig. 1) but begins to rise at lower temperature until it takes a high constant value below 18 K. One wonders if a Kondo state, as Gunnarsson and Schonhammer suggested for Ce, may have formed. Indeed, not only is the susceptibility large and temperature-independent, but the linear term in the experimental specific heat is elevated, at $C_v/T = 6$ mJ/mole K^2, significantly higher than a free-electron value of 1.23 mJ/mole K^2 for two electrons per atom at the europium density. We are not aware that this aspect of Eu has been explored quantitatively.

VI. CONCLUSION

These peculiarities of Ce and Eu are quite consistent with our conclusion that for all rare earths, as well as the heavier actinides, an atomic approach is appropriate. For the light actinides, through plutonium, a band approach is preferable, though there are increasingly important correlation corrections to the band width as we go along the series. It is remarkable that the direct generalization of these correlations from the two-level system, using previously tabulated parameters, has led to simple formulas which give such good quantitative estimates of the relevant properties.

In this study we have considerably simplified the band properties using a Friedel model. In the context of a tight-binding representation of the bands,[2] one could of course return to the full bands, simply reducing the interatomic couplings V_{ffm} by a factor ζ (and the hybridization between orthogonalized-plane-wave and f states $\langle \mathbf{k}|H|f\rangle$ by a factor $\sqrt{\zeta}$) in order to more accurately represent the electronic structure. Certainly, the same adjustment could be made for any other LDA band-structure technique, and in fact the making of some f orbitals corelike by Wills and Eriksson[14] had essentially this effect. The resulting deviations from the Friedel-model constant density of states are essential, for example, in determining the stable crystal structure. The possibility of perpendicular σ bonds between f states[21] favoring the near-90° angles between bonds characteristic of the α-Pu structure, and the zigzag structure of Np, can only be understood in the context of such a more complete description of the density of states.

The Kondo effect which may be playing a role in the atomic states in some rare earths is well beyond the scope of the present study. So also are the high-energy excited states which arise in optical absorption. Indeed the optical absorption energy for Li_2 as discussed in Sec. I is *increased* by the Coulomb U. These are appropriately described in terms of a spectral function, as for example by Gunnarsson and Schonhammer.[3,19] They are quite interesting and important in their own right, but only weakly reflect the fundamental structure of the ground state and low-lying excitations discussed here. It is the ground-state electronic structure, not the high-energy excitation, which bears on the many interesting bonding, structural, and alloying properties of these f shell metals.

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