PHYSICAL REVIEW B VOLUME 61, NUMBER 15 15 APRIL 2000-I

Variation of the LDA+U method appropriate to f-state localization: Application to magneto-optical properties

David L. Price
Department of Physics, University of Memphis, Memphis, Tennessee 38152-6670

B. R. Cooper
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

Say-Peng Lim
Department of Physics and Astronomy, California State University at Northridge, Northridge, California 91330-8268

Ibrahim Avgin
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

(Received 8 October 1998)

A variation of the local density approximation (LDA)$+U$ method, appropriate for application to cerium f-state localization, and its implementation within a full-potential linear muffin-tin orbital method is described. The method, functionally similar to the self-interaction-corrected–pseudopotential method, is applied to a calculation of the optical conductivity and ground-state magnetic moments of the compounds CeSb and CeTe. We also briefly discuss application of the method to the equilibrium volume of fcc plutonium, giving about 94% of the experimental volume, a significant improvement over LDA results. We find that the off-diagonal conductivity of CeSb (which gives the magneto-optical behavior) agrees well with experiment, suggesting that the method correctly captures essential aspects of the electron correlation. The optical conductivity and ground-state moment of CeTe, however, show poorer agreement with experiment than for CeSb.

The widely used LDA (local-density approximation) and LSDA (local spin density approximation) methods for calculating electronic structure fail for highly correlated electron systems, and a number of modifications of these techniques have been proposed to allow their application to such materials. Such modifications include the LDA$+U$ method,[1–4] self-interaction-corrected[5–8] (SIC) calculations, and combination of LDA calculated parameters with model Hamiltonians.[9] Here we investigate a simple variation on the LDA$+U$ approach, appropriate for application to Ce and Ce compounds, and to some extent to actinide systems. We specifically examine the resulting optical conductivity and ground-state moments for CeSb and CeTe, and briefly indicate results for the atomic volume of fcc Pu.

The LDA$+U$ technique,[1] designed for systems in which a set of orbitals (typically d or f states) is highly localized, modifies the LDA energy functional by subtracting the LDA ''f-f'' interactions, replacing them with on-site, atomiclike interactions, using a Hartree-Fock form for the electron-electron interactions. This modified energy functional has explicit orbital dependence, and consequently the effective one-electron potential has an orbital dependence, where the addition to the effective potential consists of spatially constant matrix elements, $V_{m,m'}$, between f (or d) basis functions. The eigenstates of the modified one-electron Hamiltonian are then obtained. The one-electron eigenstates are not localized functions, but remain Bloch states. The primary effect is that the energy eigenvalues of the occupied f states are forced lower in energy (by roughly $U/2$), while unoccupied f states are raised in energy, thus, for example, providing the gap in Mott-Hubbard insulators.

For cerium systems, where the Ce localizes at most one f electron per site, this process represents a self-interaction correction, since the LDA self-interaction is subtracted, and the Hartree-Fock self-interaction is zero. In the SIC method (in atoms, for example[5]), the explicit subtraction of orbital self-interaction also lowers the eigenvalues of occupied (local) states, again by an amount on the order of $U/2$ (along with a smaller lowering of the total energy). The SIC method has been applied to crystalline materials, including Ce,[7] but its proper implementation for extended systems is somewhat involved, due to the necessity of obtaining localized one-electron eigenstates, in addition to extended states. This suggests a simpler form for the modified LDA$+U$ effective potential:

$$V_{i,j}=V_{i,j}^{\mathrm{LDA}}-U\langle i|f\rangle\langle f|j\rangle+U/2\delta_{ij}, \tag{1}$$

where i, j represent the orbital and spin quantum numbers, and m_l, m_s, and $|f\rangle$ is a particular member of the f multiplet. In this way one member of the f multiplet is forced lower in energy (by $U/2$) and the remainder of the f states are raised by $U/2$. [The method is then functionally very similar to the SIC-pseudopotential method,[8] where the pseudopotential is constructed to lower the eigenvalues of atomic (d or f) states to their SIC-all-electron values, but the pseudopotential is used as usual in bulk calculations, resulting in extended d or f bands, which are allowed to hybridize with all other states, but are lowered in energy. The present method also bears some resemblance to earlier calculations with state-dependent potentials.[10]] The projection operator $|f\rangle\langle f|$ determines which member $|f\rangle$ of the f multiplet is the occupied state, and we have arranged for any choice for this state: $|f\rangle=\Sigma_{m_l,m_s}A_{m_l,m_s}|m_l m_s\rangle$, where the arbitrary amplitudes A_{m_l,m_s} are not calculated but set by hand. The original LDA$+U$ method[1] resulted in occupied states that were

m_l, m_s eigenstates. With the intention that the localized states should be determined primarily by atomiclike energetics, and with just one localized electron per site, it is (for Ce with a large spin-orbit interaction) more physically sound to choose total angular momentum eigenstates (j, m_j eigenstates) for the occupied state. Our general expression for the multiplet member to be occupied allows exploration of the various choices.

One additional step was taken in our paper to eliminate a significant source of self-interaction in the calculated total energies. With one arbitrary member of the f multiplet occupied, the resulting f charge density is no longer spherically symmetric, and the associated effective potential would also be asymmetric. The interaction of the f charge with these aspherical contributions to the potential represents a self-interaction that significantly distorts the relative energetics of occupying differing members of the multiplet. This was eliminated by including only the spherical average of the f charge in the total charge density, while still calculating the full potential arising from the crystal. In this way the aspherical contributions to the self-interaction are eliminated, while the crystal-field effects are retained. (This approach is similar to the method employed[11] in Ref. 3.)

This variant of the LDA+U method was applied to the compounds CeSb and CeTe, through modification of our full-potential linear muffin-tin orbital technique.[12] [The spin moments were along the (001) axis for CeSb, and the (111) axis for CeTe, both with an NaCl structure. The U values were obtained from constrained LDA calculations, and were 6.7 eV for CeSb and 6.0 eV for CeTe. The smaller value for CeTe is suggestive of a greater hybridization and f delocalization relative to CeSb. We examined the effect of changing U by roughly 0.5 eV, and found that the calculated results were not sensitive to small variations in U.] Figure 1 shows both the LSDA density of states (with spin polarization and spin-orbit interaction included) and our "LDA+U" density of states for CeSb. The LSDA calculation[13] puts the $4f$ band at the Fermi level, with a net f occupation of very nearly one and a total magnetic moment of less than $0.1\mu_B$. The effect of the "U" addition is clear: the one occupied f state is forced down in energy, below the valence band of states, and the width of its band is quite narrow, indicating a lack of hybridization. The band of unoccupied $4f$ states is raised above the Fermi energy, remains within the band of valence states, and maintains its bandwidth.

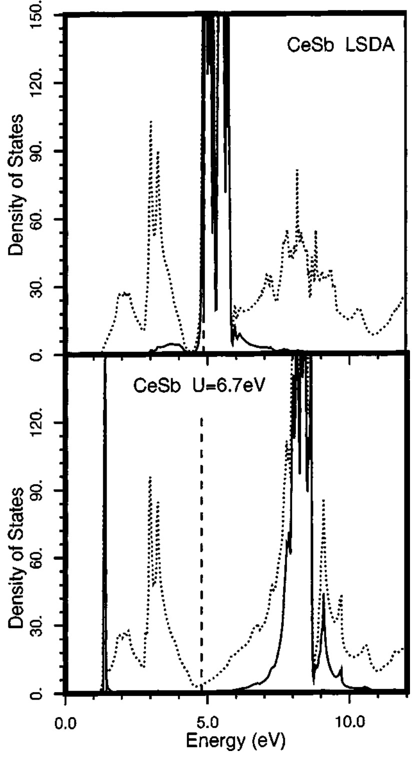

FIG. 1. The density of states of CeSb, calculated in the LSD and LDA+U approximations. The dotted line is the total density of states, the solid line is the f-projected density of states, and the vertical-dashed line is at the Fermi energy.

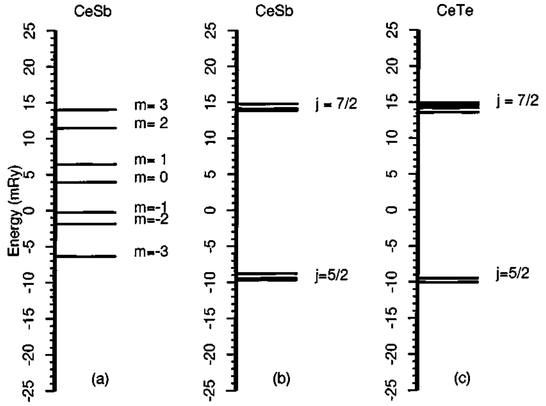

FIG. 2. The relative total energies, from the LDA+U calculation, for (a) CeSb with a m_l, m_s projection operator, (b) CeSb with a j, m_j projection operator, and (c) CeTe with a j, m_j projection operator.

The LDA+U density of states shown in Fig. 1 was obtained by occupying a $j=\frac{5}{2}$, $m_j=\frac{5}{2}$, $4f$ state. Figure 2 shows the relative total energies obtained through occupation of m_l, m_s and j, m_j eigenstates. The m_l, m_s energies closely follow our results[14] obtained using the original LDA+U method.[1] (Other applications of the LDA+U method to the optical properties of CeSb may be found in Refs. 3 and 4.) The level splittings obtained with the m_l, m_s occupations are

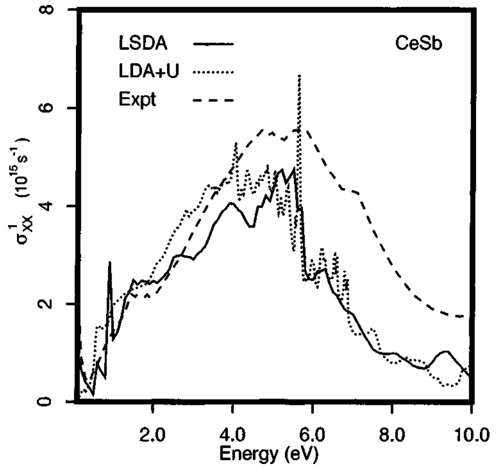

FIG. 3. The diagonal conductivity of CeSb from experiment (Ref. 16), an LSDA calculation (Ref. 12), and the present LDA+U calculation.

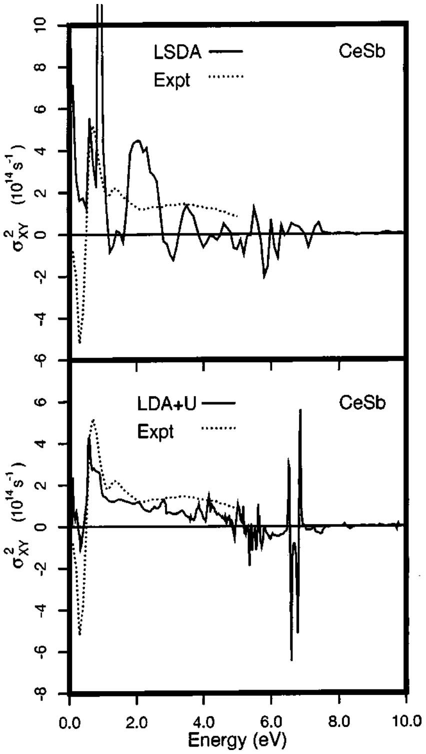

FIG. 4. The off-diagonal conductivity of CeSb from experiment (Ref. 16), an LSDA calculation (Ref. 12), and the present LDA $+U$ calculation.

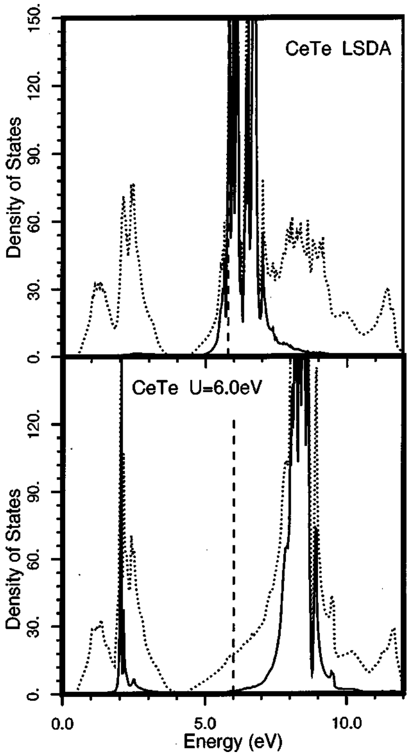

FIG. 5. The density of states of CeTe, calculated in the LSD and LDA$+U$ approximations. The dotted line is the total density of states, the solid line is the f-projected density of states, and the vertical-dashed line is at the Fermi energy.

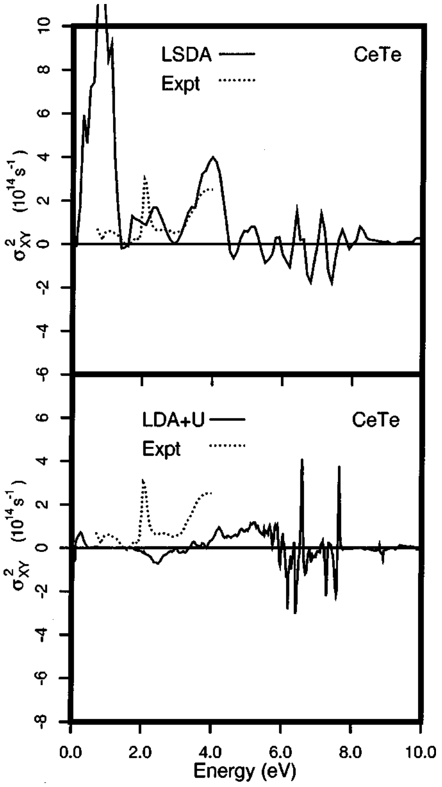

FIG. 6. The off-diagonal conductivity of CeTe from experiment (Ref. 18), an LSDA calculation (Ref. 12), and the present LDA $+U$ calculation.

far too large to reflect the experimentally observed[15] "crystal-field" splittings, and largely represent the expectation value of the spin-orbit term in the Hamiltonian for the various m_l, m_s states. The j, m_j total angular momentum eigenstates, however, are split into $j=\frac{7}{2}$ and $j=\frac{5}{2}$ sets, and each set shows a degree of splitting compatible with the observed magnitude of crystal-field splitting in CeSb. In addition, the $j=\frac{5}{2}$ energies are clearly lower than the lowest energy m_l, m_s state. The set of six $j=\frac{5}{2}$ states are split into a higher-energy $m_j=\frac{3}{2}$ level, and an essentially degenerate pair of $m_j=\frac{5}{2}$ and $m_j=\frac{1}{2}$ levels, roughly 1 mRy lower in energy. The total magnetic moments of these states are $1.22\mu_B$ ($m_j=\frac{3}{2}$), $0.55\mu_B$ ($m_j=\frac{1}{2}$), and $2.22\mu_B$ ($m_j=\frac{5}{2}$). We note that of the two lowest energy states, one has a net moment nearly equal to the experimental[16] ground-state value of $2.1\mu_B$.

Figures 3 and 4 show the LSDA and "LDA$+U$" results for the diagonal and off-diagonal optical conductivity of CeSb. (The LDA$+U$ results are again shown for the case of $j=\frac{5}{2}$ $m_j=\frac{5}{2}$. Variation of m_j within the $j=\frac{5}{2}$ multiplet did not appear to significantly change the calculated conductivity.) The diagonal conductivities are similar for the two calculations and in rather good agreement with experiment.[17] The LSDA off-diagonal conductivity arises from the interplay of spin-polarization and spin-orbit coupling, and the LSDA result shows substantial deviations from the experimental off-diagonal conductivity. Analysis shows that the excessive peaks around 1 eV arise from transitions involving f states, and the LDA$+U$ result improves the off-diagonal conductivity in the range 0.5–5 eV primarily by simply sweeping the f states away from the Fermi energy, so as to not influence the calculated conductivity in this energy range. The calculated ''LDA$+U$'' off-diagonal conductivity in this energy range is, however, in such remarkably good agreement with experiment that more subtle effects are also captured. As the transitions responsible for this part of the conductivity involve the non-*f* valence bands, and spin and orbital polarization is introduced to the LDA$+U$ calculation only through the forced occupation of one particular *f* state, this agreement with experiment strongly suggests the LDA $+U$ method is getting at least certain aspects of the localized-*f*/delocalized-valence hybridization qualitatively correct.

The LSDA and LDA$+U$ densities of states for CeTe are shown in Fig. 5, and it can be seen that the lowering of the occupied *f* state does not place it below the valence band, but rather within what is a largely Te *p*-derived band of states. The occupied *f* band is consequently somewhat more broadened than in the CeSb calculation. The energy level diagram for CeTe, shown in Fig. 2, is similar to that of CeSb, *but the order of levels within the* $j=\frac{5}{2}$ *multiplet is reversed*. Thus the lowest-lying state in CeTe is the $j=\frac{5}{2}$, $m_j=\frac{3}{2}$ orbital, with a calculated net moment of $1.38\mu_B$. This is suggestive of a reduced moment in CeTe, but fails to capture the net reduction of moment found in CeTe: the experimental moment[18] is $0.3\mu_B$. (The LSDA total moment[13] is $0.08\mu_B$, while that obtained from a model Hamiltonian calculation[9] incorporating LDA-calculated parameters is $0.3\mu_B$, in close agreement with experiment.) Similarly, while the CeTe calculated off-diagonal optical conductivity (Fig. 6) is greatly improved by the LDA$+U$ method (again largely by simply reducing the magnitude in the low-energy region), the remaining conductivity fails to show the structure found experimentally[17,19] in the CeTe off-diagonal conductivity.

Clearly, further work in this area could be very fruitful, and could include, along with other possible variations on the method, a means to obtain an optimal hybridization among the *f* states within the *j* multiplets, and so allow calculation of the minimum energy ground state. It seems, however, that the LDA$+U$ calculation would still fail to capture essential elements of the electronic structure of CeTe, since it failed to obtain a correct moment and failed to obtain good agreement with the off-diagonal conductivity.

Extension of this method to structural properties of correlated systems also appears to be promising: We have recently applied this variation of the LDA$+U$ method to the structural properties of Pu (as described in Ref. 20), successfully obtaining the expanded atomic volume of fcc plutonium. The LDA atomic volume for fcc Pu is about 30% smaller than the experimental value. This LDA$+U$ method, however, using a U value in the expected range of about 4 eV, gives a lattice constant of 8.6 a.u., compared to the experimental value of 8.77 a.u., or a volume that is 6% smaller than the experimental value. This success, much as in the case of the optical conductivity, is a result of the localized $5f$ states being swept out of the valence band, and so out of participation in electronic bonds. Further details will be reported elsewhere.

The research at West Virginia University was supported by NSF Grant No. DMR 91-20333.

---

[1] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991); V. I. Anisimov, M. A. Korotin, J. Zaanen, and O. K. Andersen, Phys. Rev. Lett. **68**, 345 (1992); V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993); I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, *ibid.* **50**, 16 861 (1994).

[2] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).

[3] A. I. Liechtenstein, V. P. Antropov, and B. N. Harmon, Phys. Rev. B **49**, 10 770 (1994).

[4] A. N. Yaresko, P. M. Oppeneer, A. Ya. Perlov, V. N. Antonov, T. Kraft, and H. Eschrig, Europhys. Lett. **36**, 551 (1996).

[5] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[6] R. A. Heaton, J. G. Harrison, and C. C. Lin, Phys. Rev. B **28**, 5992 (1983); M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **82**, 2688 (1985); A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990); M. Arai and T. Fujiwara, Phys. Rev. B **51**, 1477 (1995).

[7] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. Lett. **72**, 1244 (1994); A. Svane, Phys. Rev. B **53**, 4275 (1996); S. V. Beiden, W. M. Temmerman, Z. Szotek, and G. A. Gehring, Phys. Rev. Lett. **79**, 3970 (1997).

[8] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **54**, 5495 (1996).

[9] Q. G. Sheng and B. R. Cooper, Phys. Rev. B **50**, 965 (1994).

[10] S. Wakoh and J. Yamashita, J. Phys. Soc. Jpn. **35**, 1394 (1973).

[11] A. I. Liechtenstein, V. P. Antropov, and B. N. Harmon (private communication).

[12] D. L. Price, J. M. Wills, and B. R. Cooper, Phys. Rev. B **48**, 15 301 (1993); J. M. Wills (unpublished).

[13] S. P. Lim, D. L. Price, and B. R. Cooper, IEEE Trans. Magn. **27**, 3648 (1991).

[14] B. R. Cooper, S. P. Lim, I. Avgin, Q. G. Sheng, and D. L. Price, J. Phys. Chem. Solids **56**, 1509 (1995); S. P. Lim, B. R. Cooper, D. L. Price, and I. Avgin (unpublished).

[15] R. J. Birgeneau, E. Bucher, J. P. Maita, L. Passel, and K. C. Turberfield, Phys. Rev. B **8**, 5345 (1973).

[16] J. Rossat-Mignod *et al.*, J. Magn. Magn. Mater. **52**, 111 (1985).

[17] J. Schoenes and W. Reim, J. Less-Common Met. **112**, 19 (1985); W. Reim and J. Schoenes, in *Handbook of Ferromagnetic Materials*, edited by K. H. J. Baschow and E. P. Wohlfarth (Elsevier Science, Amsterdam, 1990) Vol. 5; J. Schoenes, in *Materials Science and Technology*, edited by J. H. J. Buschow (VCH, Weinheim, 1992), Vol. 3A.

[18] F. Hulliger, B. Natterer, and H. R. Ott, J. Magn. Magn. Mater. **8**, 87 (1978); H. R. Ott, J. K. Kjems, and F. Hulliger, Phys. Rev. Lett. **42**, 1378 (1979).

[19] J. Schoenes, J. Magn. Soc. Jpn. **11**, 99 (1991).

[20] N. Kioussis, P. Turchi, D. L. Price, B. R. Cooper, and A. Gonis (unpublished), P. E. A. Turchi, A. Gonis, N. Kioussis, D. L. Price, and B. R. Cooper, in *Electron Correlations and Materials Properties*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Kluwer Academic/Plenum, New York, 1999), p. 531.