ELSEVIER

Journal of Alloys and Compounds 444–445 (2007) 285–287

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Effect of spin–orbit coupling on an ab initio Gutzwiller approach for Pu

J.P. Julien [a,*], R.C. Albers [a], J. Bouchet [b]

[a] *Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[b] *CEA-DAM, Département de Physique Théorique et Appliquée, Bruyères-le-Châtel, France*

Received 2 August 2006; received in revised form 19 June 2007; accepted 20 June 2007
Available online 29 June 2007

Abstract

We present an improved version of our recently proposed ab initio Gutzwiller method to study solids with strong local Coulomb interactions as a correction to first principles DFT-LDA (density functional theory in the local density approximation). The variational (Rayleigh-Ritz) parameters are the probabilities of atomic configurations. The quasiparticle spectrum is obtained from the eigenvalues of an effective Hamiltonian with renormalized hopping and on-site terms. Our method includes both an ab initio, parameter free, realistic description of the energy bands, as well as strong correlation aspects of the coherent part of the spectrum. It can be considered as an improvement to the LDA + U method, which has the same starting Hamiltonian but where the interactions are calculated only at the mean-field level. Application to δ-plutonium is presented, with particular attention to possible scenarios to discriminate between localized and less localized states due to spin–orbit coupling. This provides new insight into the still controversial electronic structure of this element.

Keywords: Plutonium; Correlated electronic structure; Ab initio Gutzwiller method

1. Introduction

The electronic structure of δ-phase plutonium is still controversial, since many different types of calculations reproduce the experimentally observed large equilibrium volume of this high-temperature phase, in contrast to the paramagnetic results of standard Density Functional Theory in the Local Density Approximation (DFT-LDA) [1]. Attempts to overcome this difficulty can be classified into two categories: methods which assume a magnetic ground state, either ferro- or antiferromagnetic, and methods which try to better describe the correlated aspects of 5f electrons. To the first category belongs the approach where spin polarization in the generalized gradient approximation improves the equilibrium volume in both the ferro- and antiferro-magnetic states, with the lowest-energy ground state being predicted to be antiferromagnetic [2,3]. This mechanism is in disagreement with experiments, which do not observe any magnetism [4]. The second category includes the methods of LDA + U [5,6], DMFT [7,8] and our own ab initio Gutzwiller approach [9], where a local Hubbard-like term is added to a band Hamiltonian and the average Coulomb interaction of the LDA, the double counting correction, is subtracted. The differences between the different calculations of the second category resides in the way this interaction term is treated.

2. Method

Generalizing the density matrix approach of Nozières [10], which is equivalent to the traditional Gutzwiller method [11], we recently proposed [9] a method to find an approximate Gutzwiller Ground State (GGS), $|\Psi_G>$, of a multiband tight-binding Hamiltonian H that includes a local Coulomb interaction term for a subset of correlated orbitals (the f-orbitals in the present case). With usual notations, this Hamiltonian reads:

$$H = \sum_{i\neq j\alpha\beta} t_{i\alpha,j\beta} c^{\dagger}_{i\alpha} c_{j\beta} + \sum_{i\alpha\sigma} \epsilon^{0}_{i\alpha} n_{i\alpha} + \frac{1}{2}\sum_{i,\alpha\neq\beta} U_{\alpha\beta} n_{i\alpha} n_{i\beta} \quad (1)$$

where α is an individual particle state that can be either an $\ell m\sigma$ or jm_j state, depending on the most convenient basis used to describe electronic states, either LS or jj coupling. The hopping matrix element $t_{i\alpha,j\beta}$ and the on-site $\epsilon^{0}_{i\alpha}$ (which allows for a possible spin–orbit splitting) are obtained from an ab initio LMTO calculation [12,13]. As in LDA + U or LDA + DMFT, $\epsilon^{0}_{i\alpha}$ has been corrected from its LDA value to avoid double counting. The interactions $U_{\alpha\beta}$ can be

* Corresponding author. Present address: Institut Neel-CNRS, BP 166, 38042 Grenoble Cedex 9, France. Tel.: +33 4 76 88 78 99; fax: +33 4 76 88 79 88.
E-mail address: jpjulien@grenoble.cnrs.fr (J.P. Julien).

0925-8388/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2007.06.075

obtained from constrained LDA calculations and can be expressed in terms of the Slater integrals (for f-states, this requires F^0 to F^6) in either basis. The Gutzwiller method is a variational method where the probabilities of atomic configurations are treated as variational parameters to minimize the ground state energy $E_G = \mathrm{Tr}(\rho_G H)$. Explicitly, this leads to find a one-electron effective Hamiltonian H_{eff},

$$H_{\mathrm{eff}} = \sum_{i\neq j\alpha\beta} \tilde{t}_{i\alpha,j\beta} c^{\dagger}_{i\alpha} c_{j\beta} + \sum_{i\alpha} \epsilon_{i\alpha,} n_{i\alpha} + C \tag{2}$$

with renormalized hopping parameters $\tilde{t}_{i\alpha,j\beta} = \sqrt{q_{i\alpha}} t_{i\alpha,j\beta} \sqrt{q_{j\beta}}$ as well as renormalized on-site energy levels $\epsilon_{i\alpha} = \epsilon^0_{i\alpha} + 2e_{i\alpha}(\partial \ln(\sqrt{q_{i\alpha}})/\partial n_{i\alpha})$. The factor $q_{i\alpha}$, which reduces the kinetic energy and causes a band narrowing, is the appropriate quantity to examine for partial localization: it is equal to one in uncorrelated wavefunctions and is smaller than 1 otherwise. It is related to the variational probabilities:

$$\sqrt{q_{i\alpha}} = \frac{1}{\sqrt{n_{i\alpha}(1-n_{i\alpha})}} \sum_{L'_i} \sqrt{p(i\alpha : \mathrm{unocc}, L'_i) p(i\alpha : \mathrm{occ}, L'_i)} \tag{3}$$

Here, $p(i\alpha : \mathrm{occ}, L'_i)$ or $p(i\alpha : \mathrm{unocc}, L'_i)$ represent the probabilities of the atomic configuration of site i, where the orbital α is occupied or unoccupied and where L'_i is a configuration of the remaining orbitals of this site. This result is similar to the expression obtained by Bünemann et al. [14], but it is obtained more directly by a density matrix renormalization. Similarly to what happens in LDA + U method [15], a detailed study of the derivative involved in the formula of $\epsilon_{i\alpha}$, shows that the renormalizations push down levels that are more than half filled, and lift up those that are less than half filled. This important feature will have great consequences on the behavior of the Pu-f states that include the spin–orbit interaction, as we shall see later.

Since we include all valence electrons, we separate the spd electrons, which have their q-factors set to one since LDA is assumed to give reasonable results for these electrons, from the f-states, where we allow for flexible q-factors and renormalized on-site effects. This opens the possibility of treating Hamiltonians like Eq. (1) from a first principles approach. The low energy physics, close to the Fermi level E_F, i.e., the coherent part of the spectrum, which is given by the eigenvalues of Eq. (2), is known to be well described by the Gutzwiller method [16], and allows comparison with the photoemission spectra in this region.

3. Summary of previous calculations without spin–orbit coupling

Our previous papers that neglected spin–orbit coupling [9] were a step along the way to a more realistic description of Pu. These calculations were performed in an $\ell m\sigma$ basis and the valence states of the LMTO part were the 7s, 6p, 6d, 5f of Pu with 16 fully hybridized orbitals per site, the remaining orbitals being treated as core states. The crystal field splittings on f-orbitals, which are directly accounted for by the LMTO method, lift the f degeneracy into the six-fold (including spin) T_1, the six-fold T_2 and two-fold A_2 symmetries. In the first simplified paramagnetic version, we took an average occupation per f-orbital in the expression for q-factors, leading to a single q for all f-orbitals, regardless of the crystal field splitting. Consequently, the number of inequivalent atomic configurations necessary to perform the Gutzwiller part reduces to 14, because all atomic configurations having the same electronic occupancy are equivalent in this model. Within this model we were able to get the double-well feature of the total energy–volume curve, in agreement with DMFT results [7], with the absolute minimum close to the density of the α phase, and a local minimum at the experimental value of δ. The quasiparticles density of states (DOS) in the vicinity of E_F was in rather good agreement with photoemission experiments [17]. We have also performed a more involved calculation, including crystal field splitting with three different q's, one per crystal f-symmetry with $(6+1)\times(6+1)\times(2+1) = 147$ variational parameters; the DOS at the equilibrium δ-volume was not sensitive to this detail. This reflects the small f-crystal field splitting in plutonium. However, the total energy curve lost its double-well feature, having therefore a single minimum at the position of the absolute one. So an improved version is necessary, especially to include spin–orbit.

4. Effect of spin–orbit coupling on the Gutzwiller method

Here, we show how the spin–orbit effects can be included in our Gutzwiller approach, first by a simpler approximation and then by more refined calculations. The inclusion of the spin–orbit term $\xi l \cdot s$ in the band structure mainly splits the f-states into a 5/2 subset with degeneracy 6, and a 7/2 subset with degeneracy 8. The 5/2 subset has an on-site energy lowered by a factor of -2ξ, while the 7/2 states are pushed towards higher energies by a factor of $+3/2\xi$. Our first LDA estimate of ξ for δ-Pu, at its experimental volume, is of the order of 0.4 eV which is slightly higher than the value of 0.28 eV for α-Pu [18]. This separation of on-site energies cause the 5/2 states to be filled first: the average occupation of f-levels, which is close to 5.5 electrons, has 4.5 electrons in the 5/2 states and only 1 electron in the 7/2 states. These differences affect both the bandwidth renormalization q_α and, more importantly, the effective on-site levels ϵ_α, because of the tendency to lower states more than half filled, i.e., the 5/2 states and the opposite behavior for the 7/2 states that are less than half filled. In this way, the splitting between 5/2 and 7/2 states is increased. This scenario is illustrated in Fig. 1 for a rectangular model with an f-bandwidth W of 4 eV and no spin–orbit term in the upper panel. The middle panel shows the effect of spin–orbit splitting on the electronic structure. The lower panel

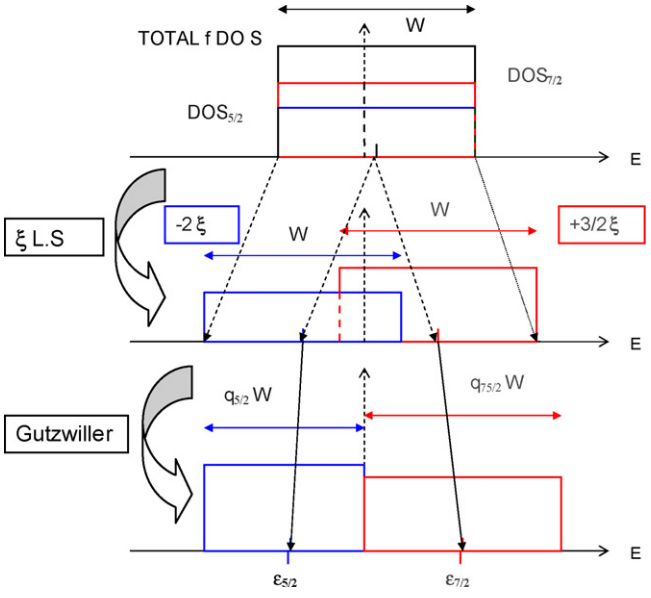

Fig. 1. Schematic effect of spin–orbit coupling of f-states (see text).

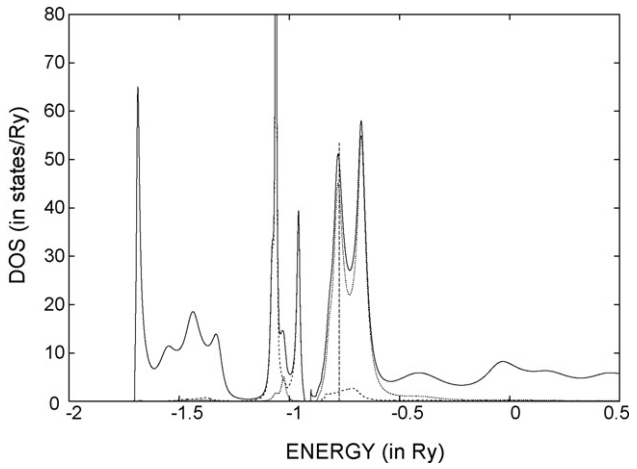

Fig. 2. Total, 5/2 and 7/2 projected Gutzwiller quasiparticles for a large interaction of 0.9 Ry (about 12 eV). The Fermi level is indicated by a vertical line.

presents the result of a Gutzwiller approach on the former one: the reduction of the bandwidth with different q factors and the lowering of 5/2 states which could gain more electrons due to increasing the separation between the 5/2 and 7/2 states. One could imagine that the extreme limit of this simplified model, where the 5/2 states are full and the 7/2 states are empty, could lead to a metal–insulator transition, with a non-magnetic state $J = 0$ and could be an argument for explaining the absence of experimental magnetism. After minimization, we obtain that for any number of f-electrons, between 5 and 6, the renormalizations of levels produce at least a pinning of E_F at the bottom of 7/2 DOS. Therefore, one has a nearly full 5/2 DOS, which can have a reduced bandwidth and an enhanced, by a factor of $1/q$, DOS and an empty 7/2 DOS. The lower panel of Fig. 1 illustrates this situation for the case of 6f electrons. For a different set of parameters (spin–orbit coupling and/or f-bandwidth), it was even possible to get a gap between the 5/2 and 7/2 DOS. So if the number of f-electrons is slightly smaller than 6, as suggested by our LDA result, it is possible to have at the same time a nearly full 5/2 band leading to a reduced total angular momentum, $J \sim 0$, as well as an enhanced DOS at E_F (for less than 6f electrons) that increases the electronic specific heat term with respect to LDA calculations, which are too small when compared to experiment.

To clarify this point, we have performed more realistic detailed ab initio Gutzwiller calculation with the correct bands for all states instead using the simplified rectangular f bands. In fact, we do not observe such drastic behavior as obtained for the rectangular DOS, even for interaction energy U as large as 0.9 Ry (about 12 eV); note that 0.3 Ry (4 eV) is usually considered to be a more realistic value. From the perspective of these calculations, one can consider Pu to be close to this kind of peculiar metal–insulator transition while remaining metallic. The oversimplification of the rectangular model is neglecting the fine details of the DOS and the mixing, through hybridization, of the f-orbitals with spd states. This modifies the position of E_F, and also leads to tails in the DOS (see Fig. 2) that prevent the possible appearance of the gap we obtained between 5/2 and 7/2 states in the rectangular model as well as the pinning of E_F at the bottom of 7/2 band.

5. Conclusion

We have investigated the electronic structure of δ-Pu with the Gutzwiller method, and have now included spin–orbit interactions in *jj* coupling. An oversimplified model with only a rectangular correlated f band was shown to possibly lead to an approximately $J = 0$ state. We have also shown that a more complete model where hybridization between f and other orbitals is included prevents this scenario from occurring.

References

[1] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) 864;
W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) 1133.
[2] A.L. Kupetov, S.G. Kupetova, J. Phys.: Condens. Matter 15 (2003) 2607;
A.L. Kupetov, S.G. Kupetova, J. Magn. Magn. Mater. 272–276 (2004) e329.
[3] P. Söderlind, B. Sadigh, Phys. Rev. Lett. 92 (2004) 185702.
[4] J.C. Lashley, A.C. Lawson, R.J. McQueeney, G.H. Lander, Phys. Rev. B 72 (2005) 054416.
[5] J. Bouchet, S. Siberchicot, A. Pasturel, F. Jollet, J. Phys.: Condens. Matter 12 (2000) 1723.
[6] A.O. Shorikov, A.V. Lukoyanov, M.A. Korotin, V.I. Anisimov, Phys. Rev. B 72 (2005) 024458.
[7] S.Y. Savrasov, G. Kotliar, Phys. Rev. Lett. 84 (2000) 3670;
S.Y. Savrasov, G. Kotliar, E. Abrahams, Nature 410 (2001) 793.
[8] A. Georges, G. Kotliar, W. Krauth, J. Rozenberg, Rev. Mod. Phys. 68 (1996) 13.
[9] J.-P. Julien, J. Bouchet, Prog. Theor. Chem. Phys. B 15 (2006) 509;
J.-P. Julien, J. Bouchet, Physica B 359–361 (2005) 783.
[10] P. Nozières, Magnétisme et localisation dans les liquides de Fermi, Cours du Collège de France, Paris, 1986.
[11] M.C. Gutzwiller, Phys. Rev. Lett. 10 (1963) 159.
[12] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
[13] O.K. Andersen, O. Jepsen, D. Gloetzel, Highlights of Condensed Matter Theory – Varenna notes – Proceedings of The International School of Physics Enrico Fermi, North Holland, New York, 1985.
[14] J. Bünemann, F. Gebhard, W. Weber, J. Phys.: Condens. Matter 9 (1997) 7343.
[15] V.I. Anisimov, J. Zaanen, O.K. Andersen, Phys. Rev. B 44 (1991) 943.
[16] D. Vollhardt, Rev. Mod. Phys. 56 (1984) 99.
[17] A.J. Arko, J.J. Joyce, L. Morales, J. Wills, J.C. Lashley, F. Wastin, J. Rebizant, Phys. Rev. B 62 (2000) 1773.
[18] A. Hjelm, J. Trygg, O. Eriksson, B. Johansson, J. Wills, Phys. Rev. B 50 (1994) 4332.