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Per Soderlind

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# Quantifying the importance of orbital over spin correlations in δ-Pu within density-functional theory

Per Söderlind
Lawrence Livermore National Laboratory, Livermore, California 94550, U.S.A.

## ABSTRACT

The electronic structure of plutonium is studied within the density-functional theory (DFT) model. Key features of the electronic structure are correctly modeled and bonding, total energy, and electron density of states are all consistent with measure data, although the prediction of magnetism is not consistent with many observations. Here we analyze the contributions to the electronic structure arising from spin polarization, orbital polarization, and spin-orbit interaction. These effects give rise to spin and orbital moments that are of nearly equal magnitude, but anti-parallel, suggesting a magnetic-moment cancellation with a zero total moment. Quantifying the spin versus orbital effects on the bonding, total energy, and electron spectra it becomes clear that the spin polarization is much less important than the orbital correlations. Consequently, a restricted DFT approach with a non-spin polarized electronic structure can produce reasonable equation-of-state and electron spectra for δ-Pu when the orbital effects are accounted for. Hence, we present two non-magnetic models. One in which the spin moment is canceled by the orbital moment and another in which the spin moment (and therefore the orbital moment) is restricted to zero.

## INTRODUCTION

Plutonium metal shows many intriguing properties, most which are poorly understood on the electronic level. Perhaps the most natural starting point in understanding this metal is its fascinating and highly complex phase diagram, see Fig. 1.
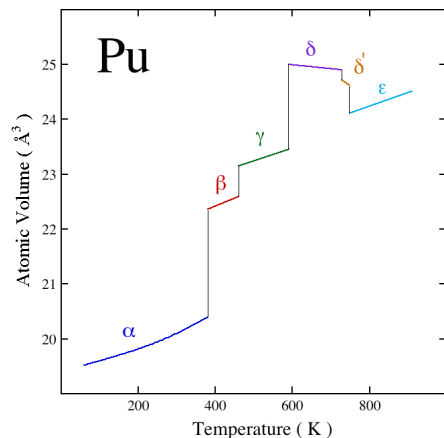


**Figure 1 Pu phase diagram.**

Here we have vastly different crystal structures, α is monoclinic and δ face-centered-cubic (fcc), with remarkably different atomic volumes, all taking place in a relatively narrow temperature range. It is reasonable to assume that the phase diagram is dictated by an electronic structure that is highly sensitive to the atomic geometry and density. The available techniques to calculate these properties from first-principles theory rely on the density-functional theory

(DFT). This approach is free of adjustable parameters and its results are true predictions of the model. When applied to plutonium metal, several obstacles need to be addressed before a reliable answer can be obtained. The most obvious are the very complex crystal structures, the presence of f-electrons in the bonding, and strong relativistic effects. Modern DFT codes are equipped to handle these difficulties, but the fundamental issue of electron correlation is modeled by the electron exchange and correlation energy functional. The approximation of this functional has improved considerably during recent years and presently includes not only the electron density but also various gradients of it. The correctness of this energy functional and its corresponding potential is validated by experimental data.
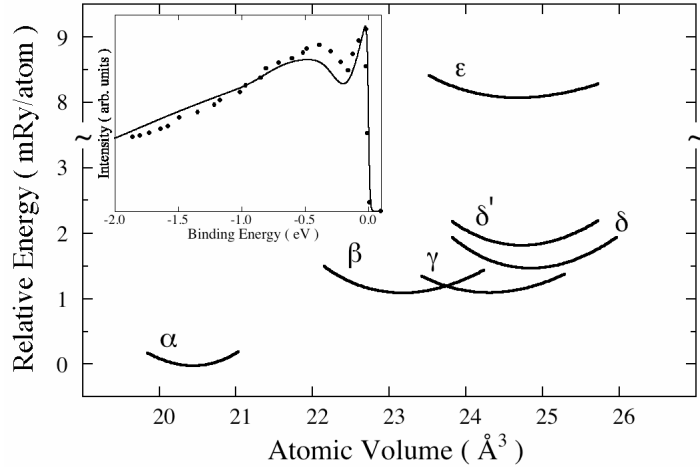


**Figure 2 Pu DFT energies [1] and electronic spectra.**

Generally, for the actinide elements, the DFT with the generalized gradient approximation for the exchange and correlation functional is accurately describing the stability and ground-state phases. In some cases new pressure-induced phases have been predicted and later confirmed experimentally [2]. For plutonium, spin and orbital polarized DFT calculations [1] reproduce the order of all the known phases and the volume differences between them, see Fig. 2. Also, in the inset of Fig. 2, the calculated electron density-of-states is shown to compare well with PES data for δ-Pu. The DFT, however, predicts formation of magnetic moments that have not been confirmed by any experimental probes. Alternative models for the electronic structure in δ-Pu include variations of the LDA+U and dynamical mean-field theory. In the latter a non-magnetic state is possible with a reasonable electronic spectra [3].

In this paper, we examine the DFT electronic structure for plutonium and how it is related to the lack of observed magnetic moments. In the next section we briefly describe some technical aspects of our calculations. We then proceed to present our results and conclude with a discussion of these.

## COMPUTATIONAL DETAILS

The electronic structure and total energy are obtained from two versions of the linear muffin-tin orbitals method (LMTO). A full potential (FP) version is used for calculating the equation-of-state for δ-Pu, similar to what was previously done for all Pu phases [1]. The more approximate application of the LMTO is within the atomic sphere approximation (ASA) that is here combined with the fixed-spin-moment method (FSM) that allows the spin moment to be

constrained. This is particularly useful when investigating the influences the spin moment has on the orbital moment, total energy, and the electronic structure in general.

The FPLMTO implementation [4] has been used extensively and successfully for actinide metals [5] and allow for spin-orbit coupling, spin, and orbital polarization in the customary ways [6]. The "full potential" refers to the use of non-spherical contributions to the electron charge density and potential. This is accomplished by expanding these in cubic harmonics inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for the semi-core 6s, 6p, and valence 7s, 7p, 6d, and 5f states, these pairs are different. Spherical harmonic expansions are carried out through $l_{max} = 6$ for the bases, potential, and charge density. For the electron exchange and correlation energy functional, the generalized gradient approximation is adopted.

The LMTO-ASA applies a spherical approximation to the electron charge density and potential and is therefore less suitable for open crystal geometries. Here, however, we are only considering the close-packed fcc ($\delta$) phase of Pu. The present implementation of this technique includes the FSM that is a pedagogical tool when investigating the effects of spin polarization. The FSM has been described [7] in the literature, but briefly it poses a boundary condition on the total spin moment in the calculation. This is accomplished by defining a separate Fermi level for each spin band. By adjusting these levels a chosen total spin moment is established for which the self-consistent total energy and other properties are evaluated.

The spin-orbit coupling (SO) and orbital polarization (OP) schemes are identical for both the FP and the ASA methods. The orbital polarization is accomplished as described before [6]. The energy of orbitals with the spin, orbital, and magnetic quantum numbers ($\sigma$, $l$, $m_l$) are shifted an amount proportional to $L_\sigma m_l$. Here $L_\sigma$ is the total orbital moment from electrons with spin $\sigma$. This self-consistent technique attempts to generalize Hund's second rule for an atom to the condensed matter and enhances the separation of the $m_l$ orbitals caused by the spin-orbit interaction. It is important to note that SO and OP influence the electronic structure regardless of the spin polarization even though the total orbital moment, $L = \Sigma_\sigma L_\sigma$, will cancel for zero spin moment.

**RESULTS**

In Fig. 3 we show LMTO-ASA total energies and magnetic moments of $\delta$-Pu as functions of the spin moment. The total energy is minimized for a spin and orbital moment of about 3.4 and –2.8 $\mu_B$, respectively. The magnitude of the total moment is thus finite but relatively small (0.6 $\mu_B$). Notice, however, that for any spin moment below about 3 $\mu_B$ there is essentially a complete cancellation with a resulting zero total moment. For small corrections of the spin moment, the total energy is hardly affected at all, suggesting that a minor adjustment has little overall effect on the electronic structure.
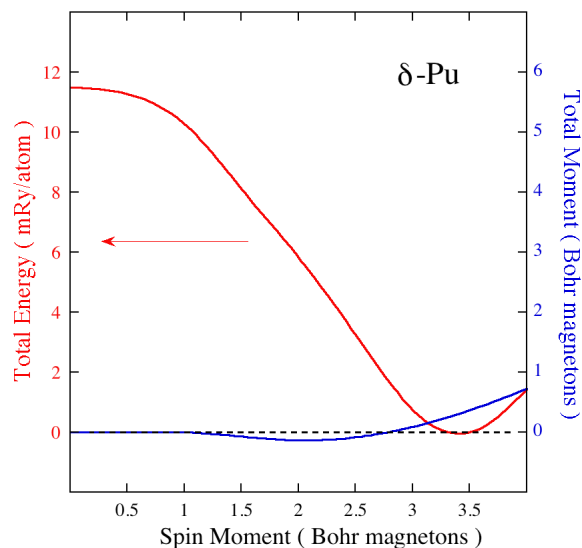
**Figure 3 LMTO-ASA total energy and magnetic moment, as functions of the spin moment.**

In Fig. 4 we show the $m_l$-projected electron density-of-states (DOS) for the cancellation model ($\mu_S = 2.8$, $\mu_L = -2.8$ $\mu_B$), with red (black) being spin up (down). The spin up $m_l = -3, -2, -1$, are the dominant contributors to the negative orbital moment.
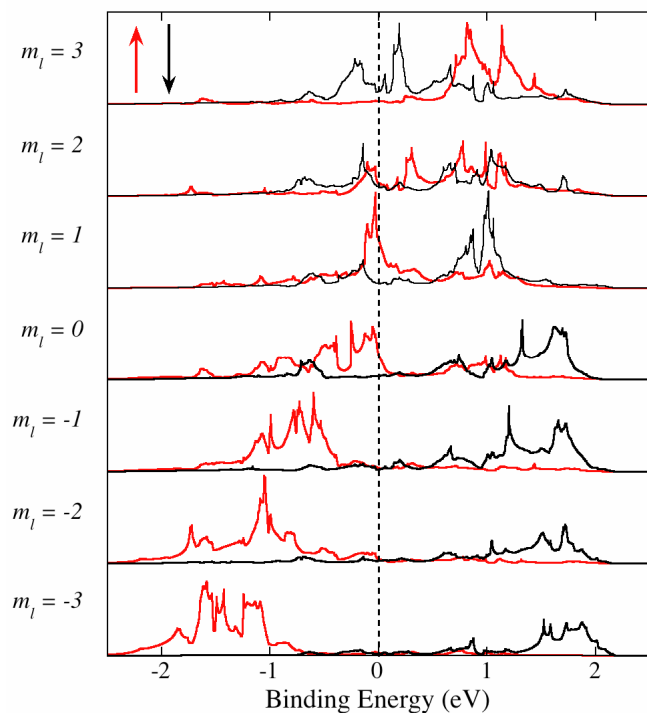


**Figure 4 LMTO-ASA DOS from the cancellation model.**

Clearly, orbital correlations are very important in plutonium, as evidenced by the substantial calculated orbital moments. An interesting question is how important are the orbital correlations relative to the spin polarization. In Fig. 5 we show FPLMTO total energies for four treatments of δ-Pu. First, we exclude both explicit spin and orbital effects, denoted by NM: No SO. This very restricted calculation provides a much too small atomic volume, and must be

deemed completely unrealistic for δ-Pu. When including the spin-orbit interaction (SO), still with no spin (NM: SO), the atomic volume expands about 10%, and the total energy drops significantly. Allowing the full orbital-correlation treatment, by also including the orbital polarization (OP), the atomic volume expands once again and lowers the total energy a substantial amount. This non-magnetic (NM: SO+OP) treatment allows absolutely no magnetic moments at all, but still predicts a quite reasonable atomic volume for the δ phase (~24 Å$^3$). Notice also that the ferromagnetic calculation with the full orbital correlations (FM: SO+OP) lowers the energy a minor amount compared to the SO+OP effect on the total
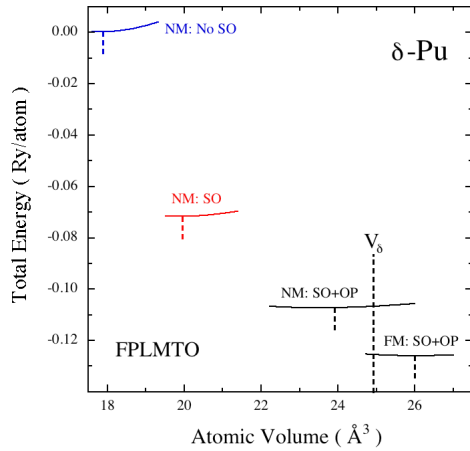


energy.            **Figure 5 FPLMTO total energies for various treatments of δ-Pu.**

       To further quantify the importance of orbital over spin effects in Pu we plot in Fig. 6 the total energy as a function of spin moment at the δ volume with no orbital part (No SO), with spin-orbit interaction (SO), and also with orbital polarization added (SO+OP). This plot nicely shows that without the orbital part, δ-Pu strongly spin polarize (5 $\mu_B$), with a gain of about 0.4 Ry in spin-polarization energy. Notice, however, that when SO is included the total energy gain is about 0.8 Ry with the ferromagnetic spin-polarization energy adding only little. This is even more pronounced for the full orbital treatment (SO+OP), where the orbital-energy correction is close to 0.11 Ry and the additional spin-polarization energy is only about 0.01 Ry. Hence, these calculations suggest that the orbital contributions are far more important than the spin correlations, in complete agreement with the interpretations of electron energy loss spectra
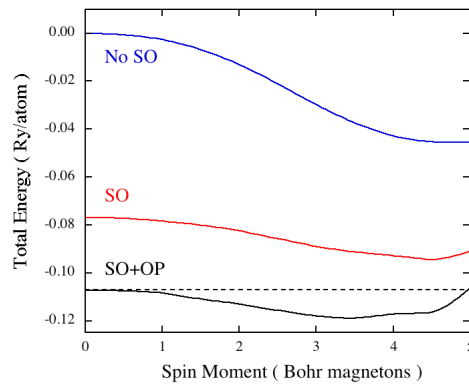


recently published [8] for Pu.           **Figure 6 LMTO-ASA total energies for various treatments of δ-Pu.**

## CONCLUSIONS

We have analyzed the electronic structure of plutonium within the DFT model. Two important facts have been recognized. First, there is a strong tendency towards magnetic-moment cancellation. If this is the case, it should make it difficult to expose the magnetic moment in various measurements. It would require techniques able to decompose the orbital and spin moments from the total moment, assuming that the spin and orbital components show long-range order, which may not be the case (disorder).

The second important conclusion from the present study is that the orbital correlations, in terms of spin-orbit coupling and orbital polarization, overwhelms the spin polarization. This fact agrees nicely with experimental findings [8] and also explain why an unambiguously non-magnetic model, with spin and orbital moments both equal to zero, can reproduce reasonably well the lattice constant of $\delta$-Pu. Upon closer examination, this latter model is also able to predict electronic spectra [9] with peak-locations remarkably close to that of previous DFT calculations (not shown) that are known to well reproduce the measured spectra (inset in Fig. 2).

## ACKNOWLEDGMENTS

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