Spin-orbit coupling in the actinide elements: a critical evaluation of theoretical equilibrium volumes

J.M.Wills¹, P.H.Andersson², L.Nordström², P.Söderlind³, and O.Eriksson¹,²

1. Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87544
2. Department of Physics, Uppsala University Box 530, Uppsala, Sweden
3. Physics Directorate, Livermore National Laboratory, Livermore, California 94550

In a recent paper by Jones et al.¹, it is argued, based on FP-LAPW band-structure calculations, that previous calculations of ground-state properties for actinides, using the FP-LMTO method implemented by J.M. Wills², are in error. We demonstrate in this paper that the conclusions of Jones et al.¹ are unfounded. Calculations using the FP-LMTO method are compared with calculations performed with the FP-LAPW method and, in contradiction to statements by Jones et al., they agree very well. The limitation of the present implementation of the spin-orbit coupling is discussed, where especially the 6p states pose a difficulty. The observed discrepancy (0-10%) between the FP-LMTO calculations and the recent FP-LAPW calculation of Jones et al.¹ is shown to be due to the choice of muffin-tin radius in the calculations. We argue that the choice of a constant muffin-tin radius, common for all calculated volumes, is less satisfactory compared to the choice of a muffin-tin radius that scales with the volume, especially when a large volume interval and open packed structures are considered. The conclusion of Jones et al.¹ that α-Pu has partially delocalized 5f electrons is argued to be erroneous.

I. INTRODUCTION

During the past three decades many first principles calculations of cohesive properties and electronic structure of the light actinides have been published. The calculations have been done with various degrees of sophistication, ranging from being scalar relativistic and based on the local density approximation (LDA) within the atomic sphere approximation to fully relativistic, full potential calculations based on the generalized gradient approximation (GGA). Due to different approximations involved, somewhat different agreement in equilibrium volumes and bulk moduli has been obtained, but typically the calculations underestimate the experimental values of equilibrium volume. This overestimate of the chemical bond leading to somewhat small equilibrium volumes occur for all metals in the periodic table and is a well known shortcoming of the LDA commonly referred to as the “LDA contraction”. To some extent the GGA corrects this systematic error of the LDA and has therefore been a common replacement for the LDA in recent calculations. Calculations utilizing the GGA for the light actinide metals results in equilibrium volumes within a few percent of the experimental data. The accuracy of these (LDA and GGA) calculations may best be realized by bearing in mind that the experimental volumes change drastically over the series (the volume of the first actinide, Ac, is roughly twice as large as the last of the light actinides, α-Pu), resulting in drastically different electron densities. More importantly, an understanding of the nature of the chemical bonds and electronic structure in the actinides has emerged from those calculations, explaining ground-state properties such as the equilibrium volume, structural stability, elastic constants, and cohesive energy. The key concepts are (i) 5f electrons form band states for the light actinides Th→α-Pu, and hence they contribute to the chemical bonding according to the Friedel model and (ii) the narrow bandwidth of the 5f-electron states provides a Peierls/Jahn-Teller like symmetry breaking mechanism that stabilizes open and low symmetry structures in the light actinides. Based on calculations and this physical picture it was predicted that U, Np, and Pu should undergo phase transitions to more close-packed structures such as bcc, hcp, or fcc, a prediction that has been born out by experiments. This picture outlined above is also consistent with the experimental observation of a pressure induced bct phases in Th and Ce-Th alloy systems. For these systems theory was in fact able to reproduce the experimental data in great detail. In addition, calculations of the structural behavior of uranium up to 1 Mbar was shown to be in excellent agreement with diamond anvil cell measurements. This set of results, demonstrates that our theoretical approach is able to produce results that are comprehensive, detailed, consistent, and, most importantly, explain experimental low temperature properties of the light actinides.
The present authors have participated in this theoretical advancement using a first-principles relativistic, full-potential technique implemented using the linear muffin-tin orbitals method. A large percentage of these results have been on elemental actinides. In these studies, the FP-LMTO method has been successfully applied to structural, cohesive, magnetic, and elastic properties of actinide elements and compounds. These calculations include both bulk and surface properties.

In a recent paper, Jones et al. argued that the bulk of the FP-LMTO calculations (30 publications or more) mentioned above were "at best ambiguous" and that there is "an error" in these calculations. They base this conclusion upon one single fact: their calculated equilibrium volumes for the light actinides are closer, on average, the difference is a few percent, to experimental data than the previously published FP-LMTO results. The calculations by Jones et al. were performed with two methods, the established FP-LAPW method and a, for the heavier elements less used, Gaussian-orbital method. Some of the calculations were too complex for this latter method and a complete set of calculations were only presented for the FP-LAPW method in their paper. For that reason, we will below focus most of our attention on the FP-LAPW results and make a critical analysis of the possible sources for the claimed differences between the FP-LMTO and FP-LAPW methods.

II. COMPARING THE FP-LAPW AND FP-LMTO METHODS

The results obtained from FP-LMTO and FP-LAPW calculations have, over the years, been compared with each other and the conclusion has been that these two methods, when carefully used, produce nearly identical results independent of the systems that have been studied. For instance, calculated data for W, published using FP-LAPW and FP-LMTO, as well as for published results for La using FP-LAPW and FP-LMTO, show that these methods give the same results. There is absolutely no reason why these two methods should give different results, they do use different expansions of basis functions but when those are sufficiently converged the results should be equivalent. Therefore, it is most surprising that Jones et al. claim that they have found an exception to this very well established fact. Without worrying why this is the case, they instead take the position that all FP-LMTO calculations that have been performed by the present authors are simply wrong. In the present paper we address the question that Jones et al. should have done in their paper: why do their FP-LAPW results of the equilibrium volumes for the light actinides differ from our published FP-LMTO results?

In examining the results presented by Jones et al., it is clear that the element for which the FP-LAPW equilibrium volume compares worst with our FP-LMTO equilibrium volume is Th. The calculations were done employing the same version of the GGA and the spin-orbit coupling was implemented in a similar fashion (only inside the muffin-tin spheres). We note that there is a difference in treating the spin-orbit coupling, but that the second variation implementation of the spin-orbit interactions should, when carried to completion, give results as accurate as those obtained by the more complete FP-LMTO implementation. The published FP-LMTO result was about 11% lower than the room temperature equilibrium volume, whereas the FP-LAPW calculation by Jones et al. gave an equilibrium volume about 2% smaller than experiment. This difference is somewhat surprising and motivated us to investigate the reason in detail. In order to do so, we performed in parallel FP-LMTO and FP-LAPW calculations for Th. The FP-LAPW code is described by Singh and is actually the same code that Jones et al. were using. Throughout this comparison we performed calculations in as similar fashion as possible, concerning exchange/correlation functional, k-space integration, truncations in potential and density expansions, choice of muffin-tin radii etc.

In Fig. 1 we show scalar relativistic and fully relativistic FP-LMTO total-energy calculations as a function of volume for two types of choices of muffin-tin radius; one using a constant muffin-tin volume for all calculated volumes and one using a constant ratio between the muffin-tin volume and unit cell volume, for all calculated points. On way to characterize this is to introduce the ratio between the muffin-tin radius and the Wigner-Seitz radius, which is called \( \alpha \) in the remaining part of the manuscript. Hence in one of the calculations we kept \( \alpha \) constant, in the manner done in our published FP-LMTO calculations, and in the other we varied \( \alpha \) with the volume such that the muffin-tin radius, \( r_{mt} \), was kept constant. This latter approach, we speculate, is the approach taken by Jones et al. in their calculations, since it is more commonly used in the LAPW method. Note from the figure that the scalar relativistic calculations show negligible dependence of the choice of \( \alpha \) and the calculated curves lie nearly on top of each other, whereas for the fully relativistic calculations there is a rather large difference between the total-energy curves, resulting in differences in equilibrium volumes of some 1-2 \( \text{Å}^3 \). We illustrate this further in Table I we show results from calculations using a fixed muffin-tin radius. We note first that if the spin-orbit coupling is omitted the calculated total energy, as well as equilibrium volume, is the same irrespective of the choice of \( r_{mt} \). However, for the calculations including spin-orbit interaction we obtain a shift of \( \sim 4 \% \) for calculations including spin-orbit interaction but with different muffin-tin radii. Hence, for certain choices of muffin-tin radius (or \( \alpha \)) we agree with the FP-LAPW results by Jones et al. as we mentioned in our discussion above. Table II also displays the uncertainty in
total energy, that is up to 15 mRy/atom, which will effect the cohesive energy by the same amount, depending upon choice of \( r_{mt} \). The calculated results from the FP-LAPW method showed a similar behavior, i.e., when the spin-orbit coupling is considered inside the muffin-tin sphere, the calculated equilibrium volume and total energy depends on the choice of muffin-tin radius (see Fig.2), but that the calculated results are not sensitive when spin-orbit coupling is neglected. The numbers obtained from the FP-LAPW method are given in Table 1 and we note that the two methods (FP-LMTO and FP-LAPW) give very similar results.

Our conclusion from the exercise above is that the conventional wisdom still holds, FP-LMTO and FP-LAPW produce nearly identical results when used in a careful manner i.e., having converged basis functions, dense k-space summation, using the same choice of muffin-tin radius as a function of volume etc. Hence, the conclusion of Jones et al., that there is an error in our calculational procedure, is incorrect. Nevertheless, the sensitivity of calculated volumes (to a few percent) with respect to computational parameters is unsatisfactory and it is valid to question, if this signals an error in the implementation of relativity in the current version of the FP-LMTO method, but as was discussed above, the FP-LAPW method developed by Singh and co-workers displays similar sensitivities and the problem seems to be more general. Careful analysis of this problem implies that the theoretical treatment of the spin-orbit coupling for the 6p semi-core states is less accurate in the implementation used in the FP-LMTO and FP-LAPW methods. The reason for this is that the spin-orbit coupling is larger than the band-width of the 6p band, resulting in two separated 6p\(_{1/2}\) and 6p\(_{3/2}\) bands. Since the radial basis function used for both bands is obtained from a differential equation with the same energy parameter, of necessity chosen somewhere between the 6p\(_{1/2}\) and 6p\(_{3/2}\) bands, a somewhat poorer treatment of these states is obtained. To test this hypothesis we have performed FP-LMTO calculations incorporating the spin-orbit coupling for all electron states except the 6p states, and the sensitivity of ground-state properties upon muffin-tin radius disappears, confirming our hypothesis that the relativistic treatment of the 6p’s does produce a dependence of the equilibrium volumes with an uncertainty of a few percent for U, Np, and Pu and with a somewhat larger uncertainty for Th. One could of course avoid this problem by ignoring the spin-orbit interaction all together and obtain larger equilibrium volumes. However, apart from not being based on theoretical grounds, such a procedure sometimes degrades drastically the structural stability of the actinides. As an example we mention that the bcc-fcc energy difference of Pu (V \(\sim\) 20 Å\(^3\)) is 17 mRy in a scalar relativistic treatment, whereas a calculation which includes the spin-orbit interaction gives a value of 11 mRy. In this particular case the neglect of spin-orbit interaction introduces an error of \(\sim 50\%\). Although there is some sensitivity on equilibrium volumes on the choice of muffin-tin radius, all other calculated properties such as structural stability, electronic structure, and transition pressures for phase transitions are much less dependent on this choice of muffin-tin radius. It would of course be desirable to have a better treatment of the spin-orbit interaction for the 6p semi-core states, and to resolve this problem one has to go one step further and develop a full potential method using the relativistic \((j, \kappa)\) basis in which the spin-orbit coupling is implicit and exact. To date such method has not been developed.

### III. THE ANOMALOUS UPTURN IN ATOMIC VOLUME FOR \(\alpha\)-PU

Although the main motivation for the paper by Jones et al. seems to be to discredit previous FP-LMTO calculations they do discuss some physics regarding the observed anomalous upturn in equilibrium volumes going from \(\alpha\)-Np to \(\alpha\)-Pu. Their calculations do not show this upturn, instead the Np and Pu equilibrium volumes were found to be identical at room temperature (when thermal expansion was taken into account). Our previous studies of Np and Pu show an upturn, although smaller that the observed 4\% increase going from Np to Pu. In Fig. we show the equilibrium volumes calculated using the FP-LAPW and previous FP-LMTO calculations. In this figure we correct for thermal expansion both for Np and Pu in the theoretical data in order to more accurately compare with the room temperature experimental data. This correction is especially important for Pu because this metal has an anomalously large thermal expansion. We note that the FP-LAPW calculations almost reproduce the experimentally observed upturn when going from Np to Pu, and they certainly have a trend that is improved over that given by the Friedel model. The FP-LMTO calculations reproduce the experimental trend better although the upturn is somewhat smaller than the experimental observation. It is clear from both these calculations that a parabolic decrease, as expected from the Friedel model of bonding 5f electrons, is absent between Np and Pu. This behavior is also supported by very recent full charge density (FCD) calculations of Vitos et al. that show an upturn in equilibrium volumes between Np and Pu. The conclusion is that it is very important to consider the correct crystal structure of Pu and that when this is done the correct trend in equilibrium volume is obtained. As a whole, theoretical calculations (FCD and FP-LMTO) strongly suggests that the experimental upturn in the volumes can be accounted for when careful calculations, in the correct ground-state crystal structures and corrected for thermal expansion, are performed. Although an improved energy functional may improve on the final few percent of the volumes of \(\alpha\)-Pu, there seems to be little need in arguing for semi localized states in \(\alpha\)-Pu.
Jones et al., argue that α-Pu has semi-localized electrons and take support in the fact that Penicaud, who solved the Dirac equation \((j, \kappa)\) adopting the atomic sphere approximation (ASA), did not obtain the anomalous upturn for Pu when considering the fcc crystal structure. As has been observed many times before the correct crystal structure must be considered to reproduce the upturn in volume between Np and Pu. In addition Penicaud did not observe an increased volume when considering relativity, and the explanation for this result is straightforward. Again it is related to the treatment of the 6p semi-core states in the calculation. Penicaud treated the 6p states in a separate energy panel and for that reason those states were unable to hybridize with the valence states and the hybridization mechanism suggested by us \(\text{that explains the lowering of equilibrium volume, is naturally absent. (We note here that the mechanism for reduction in chemical bonding of the 5f states due to spin-orbit splitting has never been questioned by us, we simply state that the 6p contribution has an opposite effect.) To investigate this issue we performed calculations similar to those of Penicaud (solving the Dirac equation and adopting the ASA), but with the flexibility to allow the 6p states to hybridize with the valence states. The results from these calculations proves our argument, i.e., if the 6p’s are not allowed to hybridize with the valence states, spin-orbit coupling does not reduce the volume whereas if we allow for this hybridization the reduction in bond distance occur. In addition we performed calculations where the 6p states were allowed to hybridize, and we switched of the relativistic spin-orbit coupling of the 6p states only. This procedure increased the equilibrium volume, in agreement with the discussion above.}

IV. CONCLUSION

After careful examination of the approximations involved in the FP-LAPW and the FP-LMTO calculations, especially regarding the 6p states and the spin-orbit interaction, we conclude that there are no errors in our previously published FP-LMTO results for the equilibrium volume of Th or any other element, and that the FP-LMTO and FP-LAPW method give very similar results when used consistently. We have shown that both the FP-LMTO and FP-LAPW methods show some sensitivity in calculated equilibrium volumes and total energy with respect to muffin-tin radius, which also must be the case in the calculations of Jones et al. although no such tests were reported. Hence, the closer agreement with experiment in the data of Jones et al. compared to previously published FP-LMTO calculations, is very likely a result of choosing a muffin-tin radius that fortuitously gives good agreement between calculated and experimental volumes. (the total energy of the two methods was unfortunately never compared in Ref.1). This brings up an interesting point, if there is one choice of muffin-tin radius that is better than any other. From a pragmatic point of view one may argue that the choice which results in best agreement with experiment is better, but it would be much more desirable to have a theoretical guidance in this choice. The rational behind the choice of a constant ratio between muffin-tin to unit cell volume is that one then maximizes the region in space where spin-orbit coupling is incorporated, not only for the lowest volume but for all volumes. If one adopts this approach, one normally considers the crystal structure with smallest interatomic distance and makes the muffin-tin radius near touching for this geometry. This was done in all our calculations of equilibrium volumes as well as for the many successful studies of structural phase stability and pressure induced phase transitions in the actinides. If one were to chose a constant muffin-tin radius and keep this radius the same for all volumes one could end up with a muffin-tin radius dictated by for instance the α-Pu structure (which has a very small nearest neighbor distance) at a volume of 0.2 V\(_0\) (if a large part of the equation of state needs to be investigated), resulting in an almost vanishingly small muffin-tin radius that when used at volumes close to the equilibrium volume ignores relativity for the majority of the unit cell. The latter approach must be less attractive than the former, especially for equation of state studies or investigations of pressure induced phase transitions. We also note that since any calculational method which treats spin-orbit coupling in an \(\ell s\)-basis and that includes the 6p states of the actinides as bands states, should have some dependence (a few percent) of the equilibrium volume on the choice of muffin-tin radius, it seems at best puzzling that Jones et al. claim an accuracy of two different methods (one that does not construct at muffin-tin) within 1%. It would have been very useful to compare the total energy of the two methods but this was unfortunately never done.

We also note here that the usefulness in LDA or GGA calculations is of course not the reproduction of experimental data to within the second or third decimal point, but rather the physics that is learned from the calculation, and from that point of view the choice of muffin-tin radius becomes less critical since two different types of choices give similar trends in the equilibrium volume (Fig.3). However, one must be careful with these types of calculations since due to the choice of muffin-tin radius Jones et al. draw the erroneous conclusion that the 5f electrons in α-Pu are semi-localized. There is no theoretical evidence that there are quasi localized 5f-electron states in α-Pu that causes the experimental upturn between Np and Pu. This upturn can be reproduced from accurate, and carefully performed, density-functional calculations, such as the FP-LMTO and FCD methods. Moreover, if the conclusion by Jones et al. was correct, the electronic structure obtained from completely itinerant calculations would be wrong for α-Pu and it would be most unlikely that such calculations could reproduce the correct (and very complex) monoclinic ground-
state crystal structure of Pu (including pressure induced phase transitions). However, this has already been done in calculations by Söderlind et al., again suggesting that Jones et al. have come to the wrong conclusion regarding the electronic structure of α-Pu.

V. ACKNOWLEDGMENT

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FIG. 1. Calculated FP-LMTO total energy of Th for fixed muffin-tin volume and for fixed fraction of the muffin-tin volume, in the scalar and fully relativistic approximation.

TABLE I. Equilibrium volumes and energies calculated with LDA (Hedin-Lundqvist) as function of constant muffin-tin radius ($r_{mt}$). Both with and without spin-orbit interaction. The muffin-tin radius is given in units of $a_0$ and the volumes are given in units of $a_0^3$ and normalized with respect to $V_0 = 221.759 \ a_0^3$. Total energies are given in units of mRy and referenced with respect to $E_0 = -53045146.629 \ $mRy.

| $r_{mt}$ | V/V<sub>0</sub> | E-E<sub>0</sub> | V/V<sub>0</sub> | E-E<sub>0</sub> |
|---------|--------------|----------------|--------------|----------------|
|         | spin-orbit   |                | no spin-orbit|                |
|         | FP-LMTO      |                | FP-LAPW      |                |
| 2.994   | 0.894        | -348.8         | 0.908        | -199.6         |
| 3.085   | 0.905        | -343.2         | 0.909        | -199.9         |
| 3.179   | 0.924        | -336.8         | 0.910        | -200.1         |
| 3.227   | 0.935        | -333.0         | 0.912        | -200.2         |
| 2.46    | 0.895        |                | 0.907        |                |
| 3.18    | 0.910        |                | 0.906        |                |
FIG. 2. Calculated FP-LAPW total energy of Th for different but fixed muffin-tin volumes, in the fully relativistic approximation.

FIG. 3. Experimental and calculated (FP-LMTO and FP-LAPW) equilibrium volumes of the light actinides. The FP-LMTO calculation is by the authors and the FP-LAPW is calculation is from Ref. 18.