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

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The difficulty of converging the contribution of the spin-orbit interaction to the total energy within an *ls* basis in actinide electronic structure calculations is discussed in detail. In particular, it is demonstrated that the source of the poor convergence is the treatment of the actinide $6p$ states. The limitation of the standard approach to relativity in full potential methods is manifested in muffin-tin based methods by a dependence of the total energy on the choice of muffin-tin radius. Despite this limitation it is found that structural phase stabilities are not affected, nor are pressure induced phase transitions. In order to treat the relativistic spin-orbit coupling in as large a part of space as possible one should, in muffin-tin based calculations, use a radius that is touching, or near touching, for all calculated volumes.

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I. INTRODUCTION

During the past three decades, many first principle calculations of cohesive and structural properties and the electronic structure of the light actinides have been published.[1–13] These calculations have been done with varying degrees of sophistication, ranging from scalar relativistic local density approximation (LDA) calculations within the atomic sphere approximation to relativistic full potential calculations based on the generalized gradient approximation (GGA). Due to different approximations involved, somewhat different results for equilibrium volumes and bulk moduli have been obtained; typically, theoretical volumes are less than experimental volumes. In addition, localization phenomena,[3] thermal expansion,[13] cohesive energies,[2,3] and structural properties of the actinides at both ambient and elevated pressure[9–11,13] have been calculated; agreement with experiment for these properties is generally good.

Although some aspects of actinide electronic structure theory have been quite well developed, predicting, for example, pressure induced phase transitions,[9–11,13] we have found that there are limitations, even with state of the art theoretical full potential methods, to the usual treatment of relativity in the actinides; i.e., with the diagonalization of the Dirac Hamiltonian within a finite scalar-relativistic basis. In this paper we illustrate the problem, discuss its origin, and evaluate the extent to which it influences calculated ground state properties, such as equilibrium volumes, the equation of state, and cohesive energies. We will focus in particular on the calculation of equilibrium volumes. To insure that our results are independent of computational method, we have used two different methods, the FPLMTO[14] and a FLAPW[15] method. These methods are demonstrated, in this paper, to give essentially identical results.

Due to the increased attention that is recently being paid to the electronic structure of the actinides, and since relativistic effects are known to be important for these systems, it is important to clarify this issue. In particular, it is important to establish the extent to which the poor convergence of the total energy, arising from the diagonalization of the spin-orbit interaction in a finite *ls* basis, influences calculated ground state properties, and to estimate the magnitude of these effects.

II. CALCULATIONS

Calculated results in this paper were obtained using two full-potential electronic structure methods, the FPLMTO method,[14] and the FLAPW method.[15] We have treated thorium, a monoatomic actinide metal with a simple (fcc) structure, but the conclusions drawn from our paper are valid for all the actinides and even the lanthanides. The calculations presented here used the GGA formulation of Perdew and Wang, sixty points in the irreducible part of the fcc Brillouin zone,[16] and an angular momentum cutoff $l_{\max}=8$. The FPLMTO calculations used $6s$, $6p$, $7s$, $7p$, $6d$, and $5f$ functions, in a single, fully hybridizing basis set. Both the $6s$ and $6p$ and the $7s$ and $7p$ states were treated with a ''triple-kappa'' basis, while d and f bases were treated with a ''double-kappa'' basis. The FLAPW calculations used a basis set with a plane wave cutoff of $k_{\max}S_{\mathrm{mt}}=11$. All other parameters were set as close as possible to the FPLMTO calculations.

We have discovered that the treatment of the spin-orbit interaction in the FLAPW method requires special treatment when applied to actindes. Both the FPLMTO and FLAPW methods diagonalize a relativistic Hamiltonian using a scalar relativistic (*ls*) basis set. In the FPLMTO method, this is done in a ''first variational'' step. This means that the full Hamiltonian, including the spin-orbit interaction, is diagonalized in a single step, using the full basis set. In the FLAPW method, a ''second variational'' method is used.[15] In this method, one first diagonalizes a scalar relativistic Hamiltonian, to give scalar relativistic eigenvalues and eigenvectors, then the lowest of these scalar eigenvectors are used as a restricted basis set for diagonalizing the full Hamiltonian (including the spin-orbit interaction). The second variation is used, of course, to reduce the size of the secular matrix of the full Hamiltonian.[1] The size of this secular matrix can be characterized by an energy cutoff. It is usually

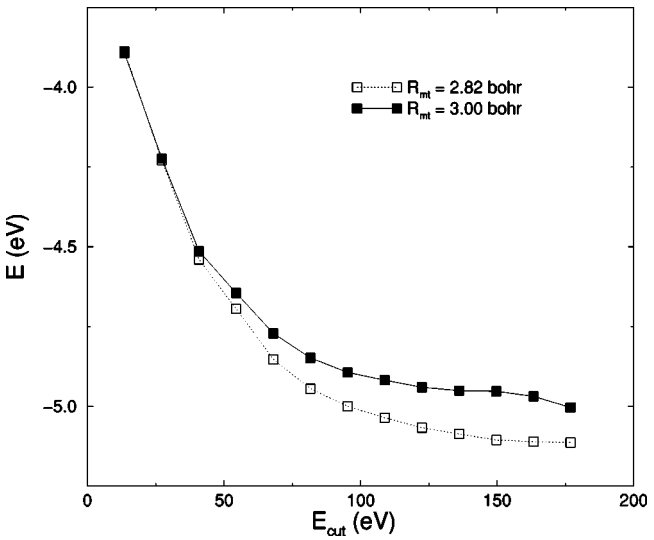

FIG. 1. The total energy, E, of fcc Th as a function of the second-variation cutoff energy, E_{cut}, for two different muffin-tin (R_{mt}) radii.

found that only the occupied eigenstates and a few of the states just above the Fermi energy are needed to describe relativity quantitatively. In the actinides, this turns out to be not true. To illustrate this, the calculated total energy of fcc Th, using the FLAPW method, as a function of cutoff in basis functions in the second variational method is displayed in Fig. 1. The results for two different muffin-tin radii are presented in this figure. The most important result of Fig. 1 is that the traditional truncation in the second variational method, usually less than ~50 eV, is far from appropriate for the actinides. In order to obtain converged total energies, one needs to include essentially all of the scalar relativistic states, i.e., the first-variational method is necessary. The reason for this will be clear from the following discussion.

III. RESULTS

In Fig. 2 we show scalar relativistic and relativistic (including the spin-orbit coupling inside the muffin-tin sphere) FPLMTO 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 volume/energy points 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 α in the rest of the manuscript. Hence in one of the calculations we kept α constant, in the manner usually done in published FPLMTO calculations, and in the other we varied α with the volume such that the muffin-tin radius, r_{mt}, was kept constant. Note from the figure that the scalar relativistic calculations show negligible dependence on the choice of α, and the calculated curves lie essentially on top of each other. In contrast, there is a larger difference between the total-energy curves for the relativistic calculations, resulting in differences in equilibrium volumes of some 1–2 Å^3.

Once convergence in the second variational approach has been established as discussed in the previous section, the total energies calculated using the FLAPW method are essentially identical to those calculated using the FPLMTO method. We establish this by displaying energy-volume curves calculated using both methods for several muffin-tin radii in Fig. 3. It is clear from this figure that the two methods give similar results, as has been noted in past studies.[17–20] . In particular, the sensitivity in total energy with respect to muffin-tin radius is equally pronounced in the FLAPW method and the FPLMTO method.

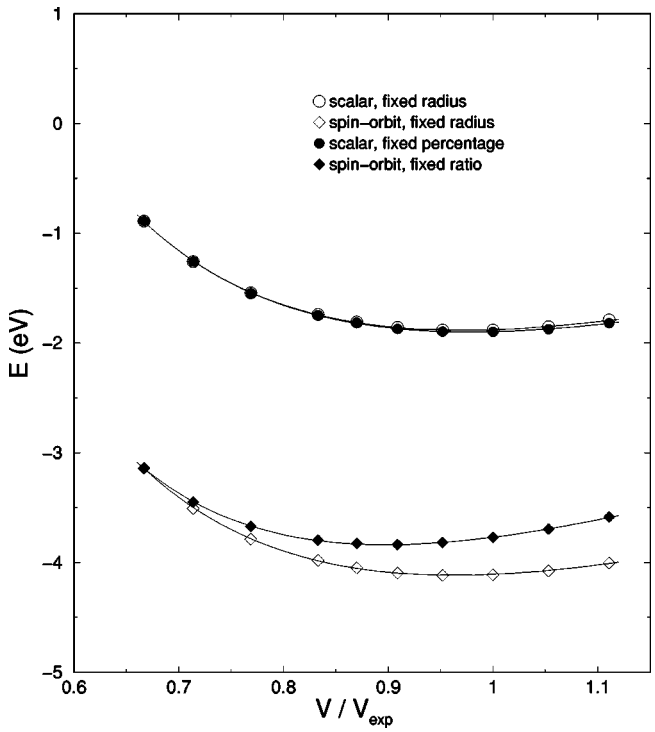

FIG. 2. Calculated FPLMTO total energy of Th for fixed muffin-tin volume and for the muffin-tin volume being a fixed fraction of the unit cell volume, in the scalar and relativistic approximation.

We thus arrive at the conclusion that calculated total energies are sensitive to the value chosen for the muffin-tin radius in muffin-tin based full-potential calculations. It might be supposed that this sensitivity arises directly because the Hamiltonian depends on the muffin-tin radius, since the spin-orbit interaction is included in the muffin-tin region but not in the interstitial region. The discussion which follows makes it clear that this is not the only reason.

Careful analysis of the problem reveals that the source of the sensitivity is the resolution of the actinide $6p$ states. The nominal valence bases of the actinides are $7s$, $7p$, $6d$, and $5f$ derived states. In lighter elemental materials, transition metals, for example, material properties near ambient pressure are well described with localized, rather than itinerant, high-lying core states (semicore states). We have found, however, that for actinides[9] and even for rare-earths that it is necessary to the description of material properties to include at least the high-lying core p-states ($6p$ states for actinides) as well as the valence p states ($7p$ states for actinides) in a fully hybridizing basis set.[9] We now demonstrate that ac-

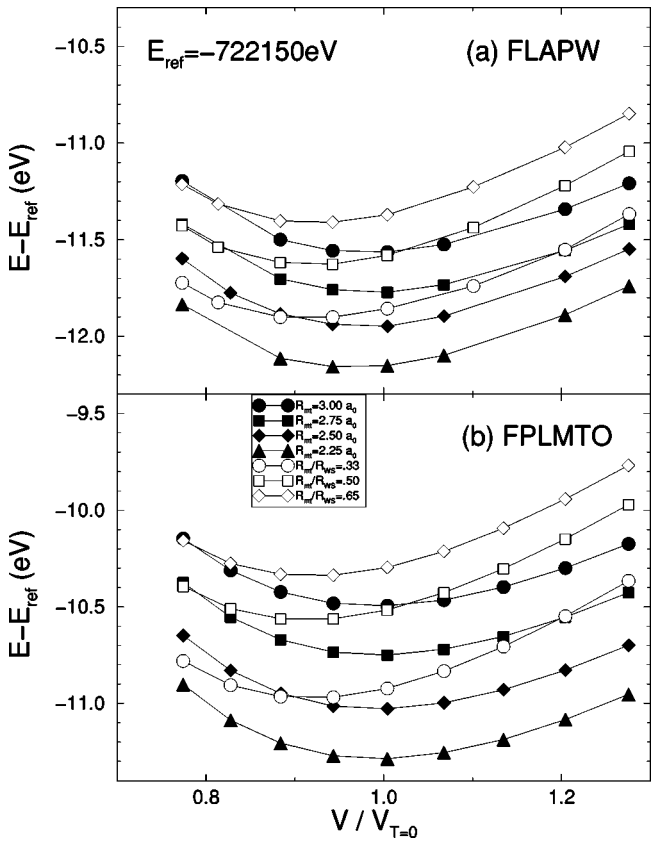

FIG. 3. Energy vs volume calculated by the (a) FLAPW and (b) FPLMTO methods for several different treatments of the muffin-tin radius. The difference in energy scale is illustrative of the sensitivity to the treatment of the $6p$ states.

tinide $6p$'s are the source of the problem by performing a simple test. The matrix elements of the spin-orbit interaction involving the $6p$ basis functions are put to zero, then we repeat the calculations as described for Figs. 1, 2, and 3. The result of this test is that total energies show negligible sensitivity to the muffin-tin radius, which identifies the $6p$'s as the source of the problem.

It is easy to understand why relativity is less well described for the $6p$ states, in comparison with higher lying states. The reason for this is that the spin-orbit coupling is larger than the width of the $6p$ band, resulting in two separated $6p_{1/2}$ and $6p_{3/2}$ bands. If the dominant energy of the $6p$ states is the spin-orbit energy, basis functions calculated using a Hamiltonian containing every contribution except the spin-orbit term may be a poor starting point for the description of these states. The problem is thus poor convergence in the contribution of the $6p$ states to the total energy, and the sensitivity to the muffin-tin radius is a manifestation of the poor quality of the basis for this set of states: a small perturbation on the basis set causes a relatively large effect on the total energy. We have performed a series of calculations, using the FPLMTO method, in which the basis set is increased by the addition of higher energy p states ($8p$,$9p$, etc.). The energy change on enriching the basis in this manner is much greater than the energy change on changing the muffin-tin radius. Enriching the basis with states derived from other angular momenta produce little change.

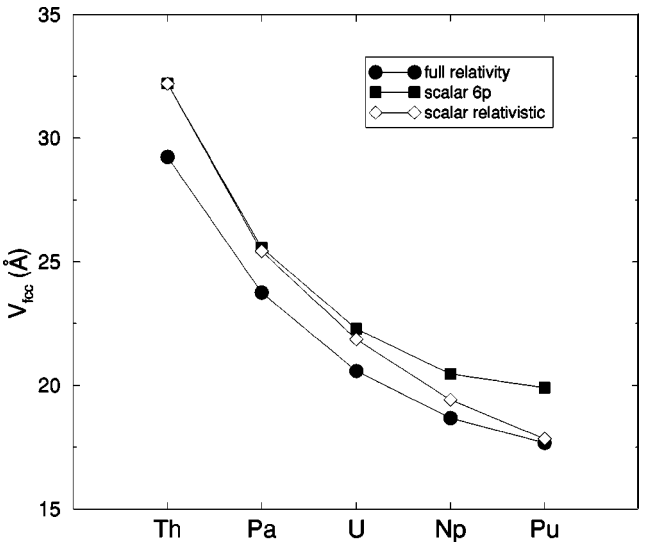

FIG. 4. Calculated equilibrium volumes of the light actinides in a (hypothetical) fcc structure. Three calculations are compared: a relativistic calculation (filled circles), a scalar relativistic calculation (open diamonds), and a calculation in which full relativity is applied to all bases except the $6p$ bases (filled squares).

It has been known for some time that an $l=1$ basis calculated from an atomic-like wave equation, necessarily zero near the origin, cannot describe the $p_{1/2}$ state in this region, since the $p_{1/2}$ is finite at the origin. In principle, it is impossible to represent a $p_{1/2}$ state with a linear combination of scalar relativistic basis functions. When we compare electron densities from $6p$ states calculated using different muffin-tin radii, we find a negligible difference *except near the origin*, verifying this conventional wisdom. The region near the origin is small yet it has a significant effect on the magnitude of the total energy. In addition, there occurs a linearization problem, since the radial basis function used for both the $6p_{1/2}$ and $6p_{3/2}$ bands is obtained from a differential equation with the same energy parameter, ϵ_ν, of necessity chosen somewhere between the $6p_{1/2}$ and $6p_{3/2}$ bands. We conclude from the discussion above that the problem of treating relativity in an *ls* basis is not specific to muffin-tin based methods but is generic to scalar bases, i.e., bases not incorporating directly the spin-orbit interaction. Depending on how one decides to divide space in muffin-tin spheres and an interstitial region, somewhat different binding energy curves, equilibrium volume, bulk modulus, and cohesive energy are obtained. This may seem alarming but the effect is of a few percent in equilibrium volume, as Fig. 3 demonstrates, for fcc Th and for the heavier actinides the effect is similar. This can be seen in Fig. 4 where we show the calculated equilibrium volumes of the actinides using different choices of muffin-tin radius.

One could, of course, avoid the problem described above simply by ignoring the spin-orbit interaction all together. As has been shown before this results in larger equilibrium volumes for the light actinides,[9] and better agreement with experiment. 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 ($V \sim 20\,\text{Å}^3$) 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 ~50%. Although there is some sensitivity in 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 (data not shown).

IV. DISCUSSION AND CONCLUSION

We have shown that both the FPLMTO and FLAPW methods show some sensitivity in calculated total energy and hence all ground state properties, with respect to muffin-tin radius, when performed relativistically. The effect is demonstrated to be of order of a few percent for the light actindies. One may now ask whether one choice of muffin-tin radius is better than any other. From a pragmatic point of view one may argue that the choice that results in best agreement with experiment is better, but it would be much more desirable to have a theoretical guidance in this choice. The rationale 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 previous calculations of equilibrium volumes as well as for the many successful studies of structural phase stability and pressure induced phase transitions in the actinides.[9–11,13] 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, for instance, $0.2\,V_0$ (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. On balance we believe that the latter approach is less attractive than the former, especially for equation of state studies or investigations of pressure induced phase transitions. However, even if a constant ratio is chosen one may for very compressed volumes and hence small muffin-tin radii encounter a situation where the contribution to relativity from the interstitial region becomes important. In reality this is not expected to be a serious problem, of for instance equation of state studies, since for very compressed volumes essentially all other contributions to the total energy (e.g., band contribution, overlap repulsion, and Coulomb interaction) become very large in magnitude and the total energy changes very rapidly with volume.

In addition, we have demonstrated that for the light actinides the second variation approach of incorporating the spin-orbit coupling needs to be handled with great care and convergence in number of basis functions used is not reached until almost all scalar relativistic states have been included, reducing the second variation approach to the first variation method. The reason for this is of course that the basis functions used are not very well adapted to describe the relativistic $6p$ states, and as a consequence convergence is extremely slow. In a recent paper by Jones *et al.*[21] FPLAPW calculations including the spin-orbit coupling were reported for the light actinides. In this paper the second variational approach was used. However, no tests of convergence in cutoff energy in the second variational step were reported, and since a standard use of the second variational method seems to have been adopted (truncating at $E\text{cut} \sim 40-50\,\text{eV}$) a glance at Fig. 1 reveals that these calculations most likely were unconverged.

Although we have focused here on the light actinides, in particular Th, the demonstrated drawback is of a more general nature and will be found in any system that has relativistic deep lying valence states (for instance, Y or Ce). It would of course be desirable to have a better treatment of the spin-orbit interaction for the $6p$ semicore states, and to resolve this problem one could go one step further and develop a full potential method using the Dirac relativistic (j,κ) basis in which the spin-orbit coupling is implicit and exact; such calculations would also help resolve the debate over whether to keep the muffin-tin radius constant or to maintain a constant ratio of muffin-tin radius to cell volume.

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