

Electronic structure of fcc Th: Spin-orbit calculation with $6p_{1/2}$ local orbital extension

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Ab initio electronic structure calculations of actinide compounds have a weak point when the spin-orbit coupling is treated using a scalar-relativistic basis and the second variational method due to the poor description of the $6p$ states. We extend the basis set of the second variational step by including relativistic $p_{1/2}$ local orbitals for the description of the $6p$ states. Our results show that the additional $p_{1/2}$ local orbitals significantly improve the description of actinides.

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A recent paper by Nordström *et al.*¹ presents a critical analysis of the total energy calculations in actinide systems performed on the scalar-relativistic basis but with the spin-orbit coupling (SOC) included. In particular fcc-Th is studied using full-potential linearized-augmented-plane-wave (FLAPW) and full-potential linear-muffin-tin-orbital (FPLMTO) methods. It was shown that the calculated total energies and the related equilibrium lattice constants are not very reliable because of their dependence on the computational parameters. Furthermore they obtained results that differ from a previous FLAPW study.² This deficiency was traced to an inadequate description of the $6p$ states by the scalar relativistic basis, which is manifested by a rather poor convergence of the total energy with the cutoff energy³ in the second-variational-step and by the dependence of the total energy on the muffin-tin radius.

In this paper we present FLAPW total energy calculations for fcc-Th using a standard FLAPW basis set including local orbitals (LO's) for the low lying $6p$ semicore states.^{3,4} These extra LO's for semicore states are necessary to unambiguously calculate equilibrium volumes.⁵ In the second-variational-step this basis is extended by additional LO's with a $p_{1/2}$ radial wave function as suggested by Singh.³ Before we describe this approach we find it useful to recall the meaning of the scalar-relativistic basis and the second variational step. In most orbital based bandstructure methods the procedure of finding the ground state of a given Hamiltonian is divided in two steps. First, a basis set is chosen which is complete enough to provide a reasonable description for the occupied states and is computationally manageable at the same time, i.e., the basis set is adapted to the Hamiltonian. Second, the Hamiltonian matrix is constructed in the subspace spanned by the adapted basis. If one includes SOC in the Hamiltonian but uses a scalar-relativistic basis, this means that the basis is not well adapted, since, e.g., a $p_{1/2}$ radial basis function is missing.

The second variational step method,⁶ which makes use of the scalar-relativistic basis, constitutes a time-saving computational scheme based on a well controlled reduction of the

original basis. In the first step of this approach, the scalar-relativistic part of the Hamiltonian is diagonalized in the scalar-relativistic basis. In the second step the full Hamiltonian matrix including SOC is constructed using the eigen-

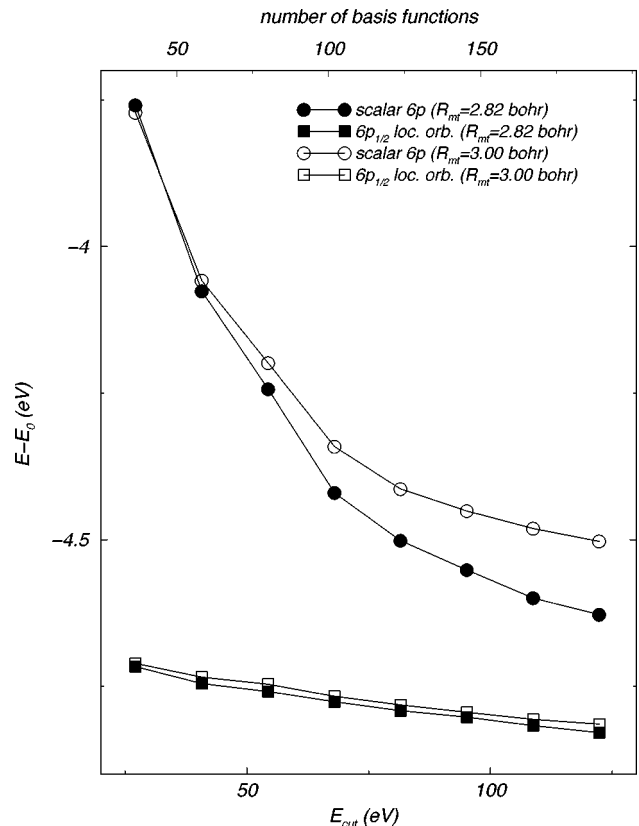


FIG. 1. The total energy E as a function of the second-variational cutoff energy E_{cut} (the approximate size of the second-variational-step basis, including spin, is marked on the top axis) for two different muffin-tin radii. The standard FLAPW results are marked with circles, the results obtained with the additional $p_{1/2}$ local orbitals are marked with squares (the latter energies were increased by 3 eV in order to show the curves on the same plot).

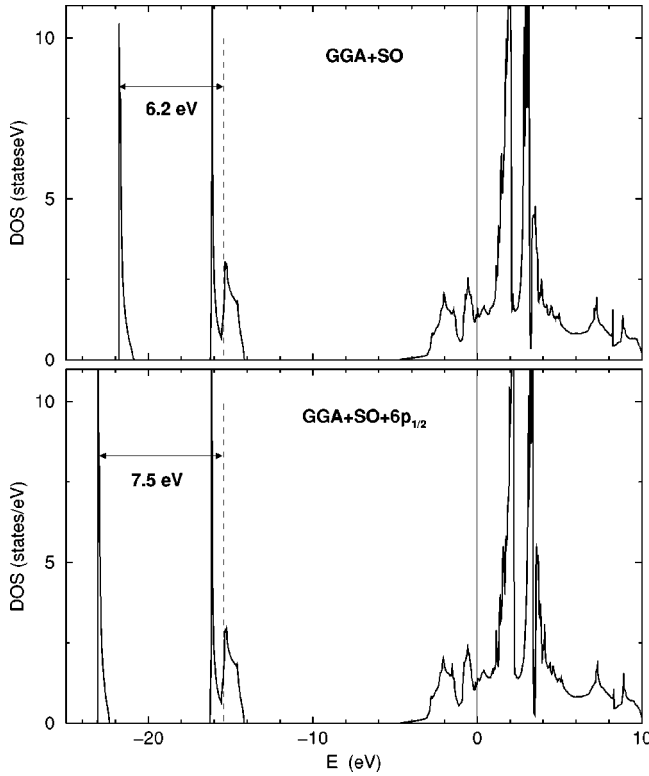


FIG. 2. Density of states calculated with the scalar relativistic basis (top panel) and with the $p_{1/2}$ local orbitals extended basis (bottom panel). The splitting between the centers of $6p_{1/2}$ and $6p_{3/2}$ bands is shown.

functions of the first step Hamiltonian. Only a limited number of the low lying eigenfunctions, controlled by an energy cutoff E_{cut} , is usually used. However, for a large enough energy cutoff the second step basis reduces to a unitary transformation of the original basis.

The present computational scheme is based on adding an additional basis function (so called local orbitals in the FLAPW method) to the second step basis. The radial part of the additional local orbital is obtained as a solution of the Dirac equation for $l=1$ and $j=1/2$. Extension of the basis requires the solution of a generalized eigenvalue problem instead of just a diagonalization in the second variational step. The method was implemented in the WIEN97 code.⁴

By employing the standard FLAPW with the second-variational-step treatment of SOC (Ref. 7) we reproduced the poor convergence of the total energy with respect to the cutoff and the dependence on the muffin-tin radius as obtained by Nordström *et al.*¹ However, we found that the extension with $p_{1/2}$ local orbitals significantly improves the total energy convergence and removes to a large extent the dependence on the muffin-tin radius as is shown in Fig. 1. The results were obtained with the GGA exchange-correlation functional but almost identical results were found for the LDA exchange-correlation functional differing only by a rigid energy shift. The calculations were performed with $k_{\text{max}}R_{\text{mt}}=9.5$ corresponding to 137 plane waves at the Γ point. Calculations performed with more plane waves showed that the observed behavior does not depend on this number.

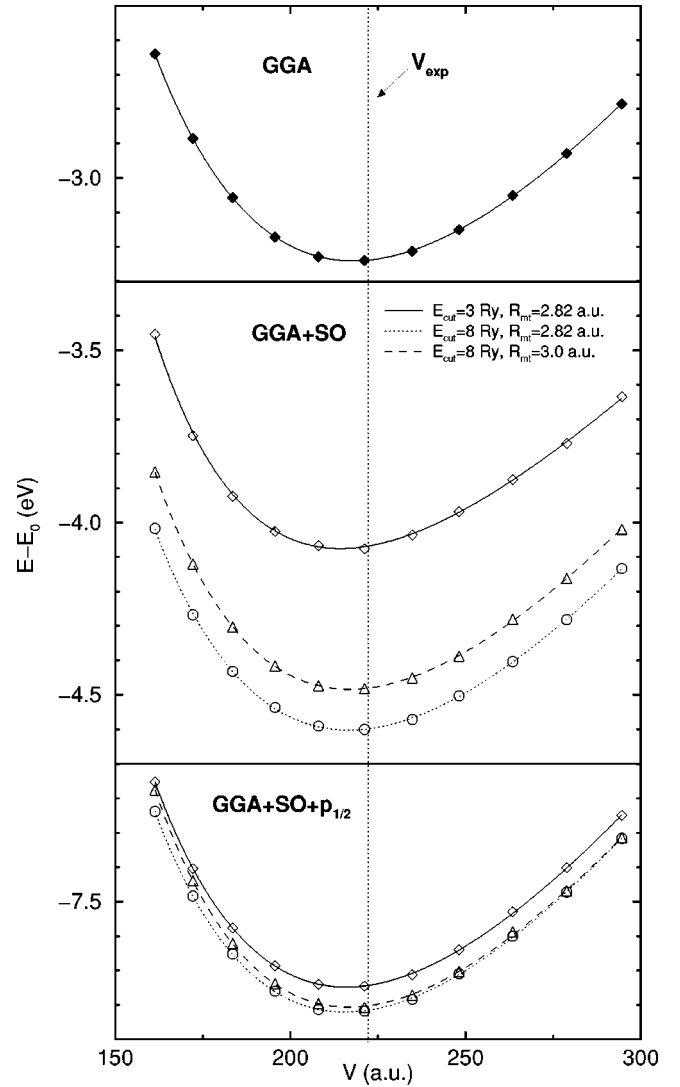


FIG. 3. The total energy E vs volume calculated for various basis set parameters without spin-orbit coupling (top panel), with the scalar-relativistic basis (middle panel) and with $p_{1/2}$ local orbitals (bottom panel).

In order to visualize the role of the $p_{1/2}$ local orbitals we calculated the density of states (DOS) shown in Fig. 2. The most obvious effect is the increase of $6p_{1/2}$ - $6p_{3/2}$ splitting from about 6.2 to 7.5 eV upon addition of the $p_{1/2}$ local orbitals. Note that the bandwidth of the $p_{3/2}$ manifold is about 2 eV. If the $6p$'s are treated as “core” states, i.e., using the fully relativistic atomic description, this splitting equals 7.2 eV indicating that the $p_{1/2}$ local orbitals provide a rather good description of the relativistic effects.

Finally we studied how the addition of the $p_{1/2}$ local orbitals affects the equilibrium volume. Figure 3 shows the total energy vs volume calculated for various choices of basis set parameters. The corresponding equilibrium volumes are summarized in Table I. The results are in good agreement with a previous FLAPW study,² suggesting that the addition of $p_{1/2}$ local orbitals has no significant impact on the equilibrium volume. This is not surprising, since SOC has only a small effect on the bonding in the present case and its inclu-

TABLE I. Equilibrium volumes (in a.u.) calculated for various choices of basis set parameters.

E_{cut} (Ry), R_{MT} (a.u.)	GGA	GGA+SO	GGA+SO+ $p_{1/2}$
3, 2.82	218.0	214.5	216.0
8, 2.82		216.7	215.7
8, 3.00		216.9	216.7
Experimental	221.7 Ref. 8		

sion results in a moderate reduction of the equilibrium volume only. This is in contrast to the large variation in equilibrium volume found by Nordström *et al.*¹ We suspect that this comes mainly from their variation of sphere radii with volume, a procedure that we do not recommend from our experience, since the augmentation of the plane-wave basis

should be kept fixed in order to have comparable numerical accuracy.

We can conclude, in agreement with Nordström *et al.*, that the treatment of actinide systems on the scalar-relativistic basis suffers from an inaccurate description of the $6p$ states. The inclusion of the $p_{1/2}$ local orbitals, however, significantly improves the stability of the calculated total energies with respect to the computational parameters. Already a small energy cutoff, which is desirable for real applications, leads to satisfactory convergence. The present results show that the second-variational-step method can, after some modifications, be successfully used for the treatment of states whose radial part is modified by SOC and that the solution of the more demanding Dirac equation can be avoided.

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