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The Dirac equation in electronic structure calculations: Accurate evaluation of DFT predictions for actinides

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ABSTRACT

Brooks, Johansson, and Skriver [1], using the LMTO-ASA method and considerable insight, were able to explain many of the ground state properties of the actinides. In the many years since this work was done, electronic structure calculations of increasing sophistication have been applied to actinide elements and compounds, attempting to quantify the applicability of DFT to actinides and actinide compounds and to try to incorporate other methodologies (i.e.DMFT) into DFT calculations. Through these calculations, the limits of both available density functionals and ad hoc methodologies are starting to become clear. However, it has also become clear that approximations used to incorporate relativity are not adequate to provide rigorous tests of the underlying equations of DFT, not to mention ad hoc additions. In this talk, we describe the result of full-potential LMTO calculations for the elemental actinides, comparing results obtained with a full Dirac basis with those obtained from scalar-relativistic bases, with and without variational spin-orbit. This comparison shows that the scalar relativistic treatment of actinides does not have sufficient accuracy to provide a rigorous test of theory and that variational spin-orbit introduces uncontrolled errors in the results of electronic structure calculations on actinide elements.

[1] Brooks MSS, Johansson B, and Skriver HL, *Handbook on the Physics and Chemistry of the Actinides*, ed. Freeman AJ and Lander GH, Elsevier, 1984, p. 153.

The Dirac equation in electronic structure calculations: Accurate evaluation of DFT predictions for actinides

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RSPt is a FP-LMTO based electronic structure method useful for many things, but particularly for calculating the properties of complex materials with heavy element constituents. We have developed an implementation of RSPt that uses solutions to the Dirac equation as bases. Our motivation is to minimize uncertainty in the evaluation of the underlying equations in DFT calculations, particularly as applied to the properties of heavy materials, in order to develop and evaluate new density functionals that incorporate relativity and confinement physics. In this talk we:

- Compare the results of using Dirac bases with those obtained in RSPt using scalar relativistic bases, with and without the spin-orbit interaction,
- demonstrate the perils of evaluating the spin-orbit interaction perturbatively in actinides, and
- conclude that the use of a Dirac basis provides essential accuracy with little increase in computational complexity or time.

An implementation of RSPt with Dirac bases

RSPt is an all-electron, full-potential, LMTO based electronic structure method.

- All-electron basis set based on a muffin-tin potential (atomic like in muffin-tin spheres and constant in the interstitial between the spheres). This basis is used to variationally solve for the electronic structure and total energy of a periodic solid with the full potential.
- The underlying equation for the basis and the variational calculation is the Dirac equation; bases are four-component spinors.
- Basis functions are site-centered Dirac spherical waves in the interstitial attached continuously to solutions of the Dirac equation (and its energy derivative) for the spherical component of the potential in a muffin-tin sphere.

Adapting RSPt to Dirac:

- The scalar relativistic version of RSPt uses four-spinors (Koelling-Harmon functions) anyway. The only change in size is the use of four-spinors (spin-orbit split) in the interstitial as well as four-component Fourier transforms.
- Consequently, the Dirac version not much slower than the spin-polarized scaler relativistic version.
- Many phenomenological adaptations -- *e.g.* DMFT as implemented in RSPt -- are easily adapted to a Dirac basis.

To compare with what's currently done ...

Incorporating Relativity:
Scalar Relativistic (SR), SR+perturbative spin-orbit (SO), and Dirac

In all-electron methods (FPLMTO and FLAPW, for example, there is an equation (or equations) used to produce a basis, and an equation solved variationally. In RSPt, bases are based on the Koelling-Harmon equation, and the Dirac equation is solved variationally. In the Dirac version, the Dirac equation is used for both.

Underlying equation:

In all electron codes, relativity is generally dealt with in one of three ways:

- bases (ψ) generated using the Dirac equation:

$$(\mathcal{H}_D + V - mc^2)\psi = e\psi, \quad \mathcal{H}_D = c\alpha \cdot p + \beta mc^2$$

The Dirac equation can be written in terms of the Koelling-Harmon equation:

$$(\mathcal{H}_D + V - mc^2 - e)\psi = (\mathcal{H}_{SR} - e)\psi - V_{SO}\sigma \cdot \mathcal{L}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\psi$$

D. D. Koelling and B. N. Harmon, Journal of Physics C: Solid State Physics 10, 3107 (1977)

- The scalar relativistic approximation (SR) amounts to setting $V_{SO} = 0$.
- SR + perturbative spin orbit (SO): using SR bases, solve the full Koelling Harmon equation with V_{SO} treated variationally.

(*) atomic-like in spheres surrounding atoms, constant in between

Why use SR or SO? ...

Motivation for using the K-H equation with/without spin-orbit coupling:

- avoid dealing with lower component of Dirac spinors (save space/computation)
- maybe avoid negative energy states (not a problem with all-electron methods)
- preserve the (lm_lm_s) identification of basis-/eigen-states.

Issues arising when incorporating relativity:

- Interaction between core and valence states

\- Core states are states with zero amplitude outside the muffin-tin sphere. They are integrated “exactly” over the spherical part of the potential in the sphere.

\- Core states and valence states should be calculated with the same underlying equation to:

  - avoid spurious core/valence interaction
  - allow core states to transition rigorously to valence states under pressure

\- Since core states should be Dirac states, SR and SO can only be used for the valence if core states are well separated from valence states. This is a questionable approximation in rare earth- and *5d* transition-metals and is numerically unstable in actinides.

- Treating p states with the SR equation in heavy elements

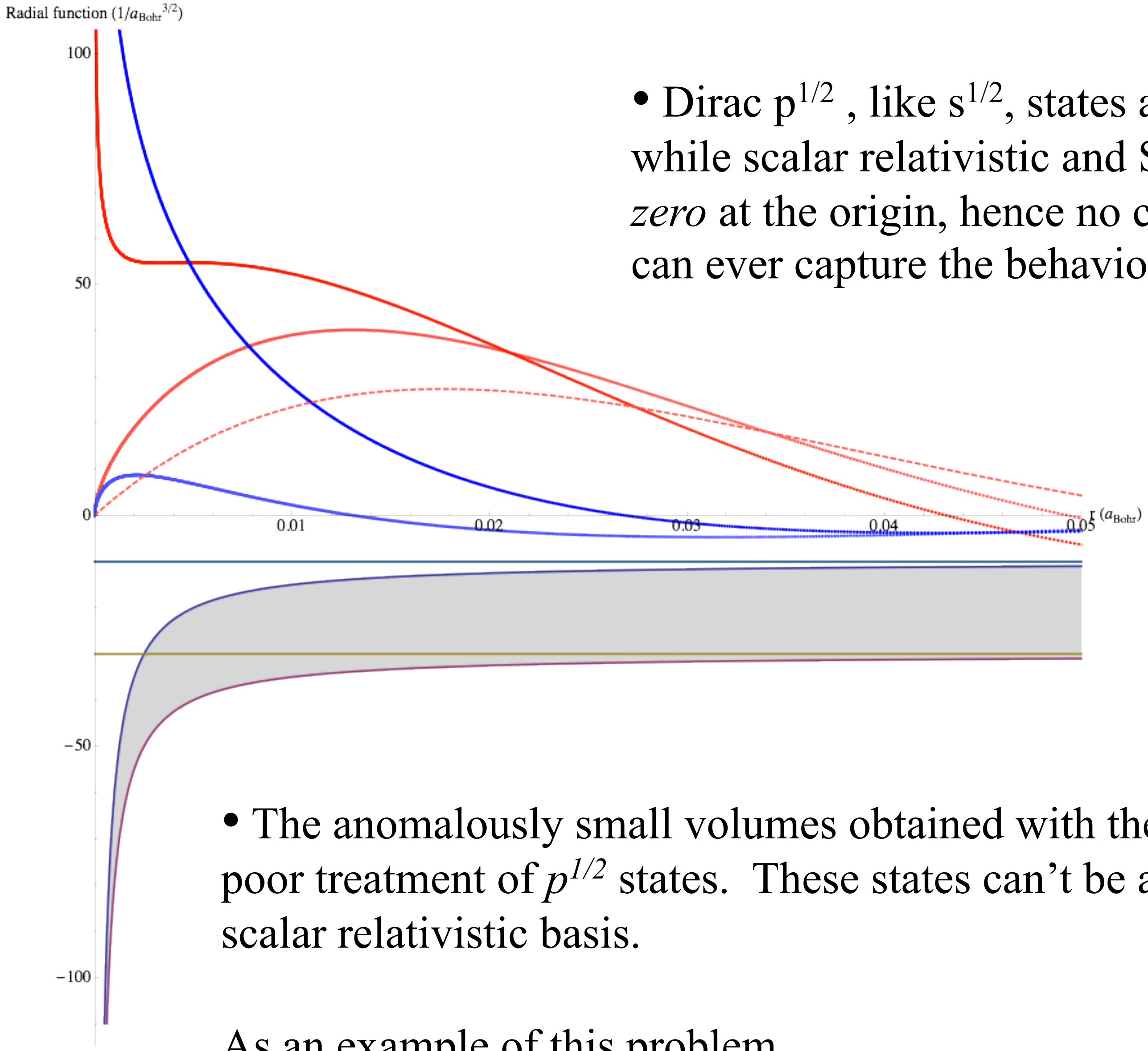
\- spin-orbit coupling ($\sim\nabla V$) has a large effect on core p states, lowering the energy substantially, and making a perturbative treatment inappropriate.

\- no variational treatment of the spin-orbit interaction can produce the correct behavior of a $p_{1/2}$ state at the origin. Because of this,

\- a perturbative spin-orbit approach sin actinides introduces large errors in, *e.g.*, the predicted volume.

To make the second point concrete ...

The radial function for the upper components (red) and the lower components (blue) of the $6p_{1/2}$ state,
calculated with the Harmon and Koelling scalar relativistic equation (lighter), the Dirac equation (darker),
and the Schrödinger equation (dashed).
Note the discrepancy at the origin.

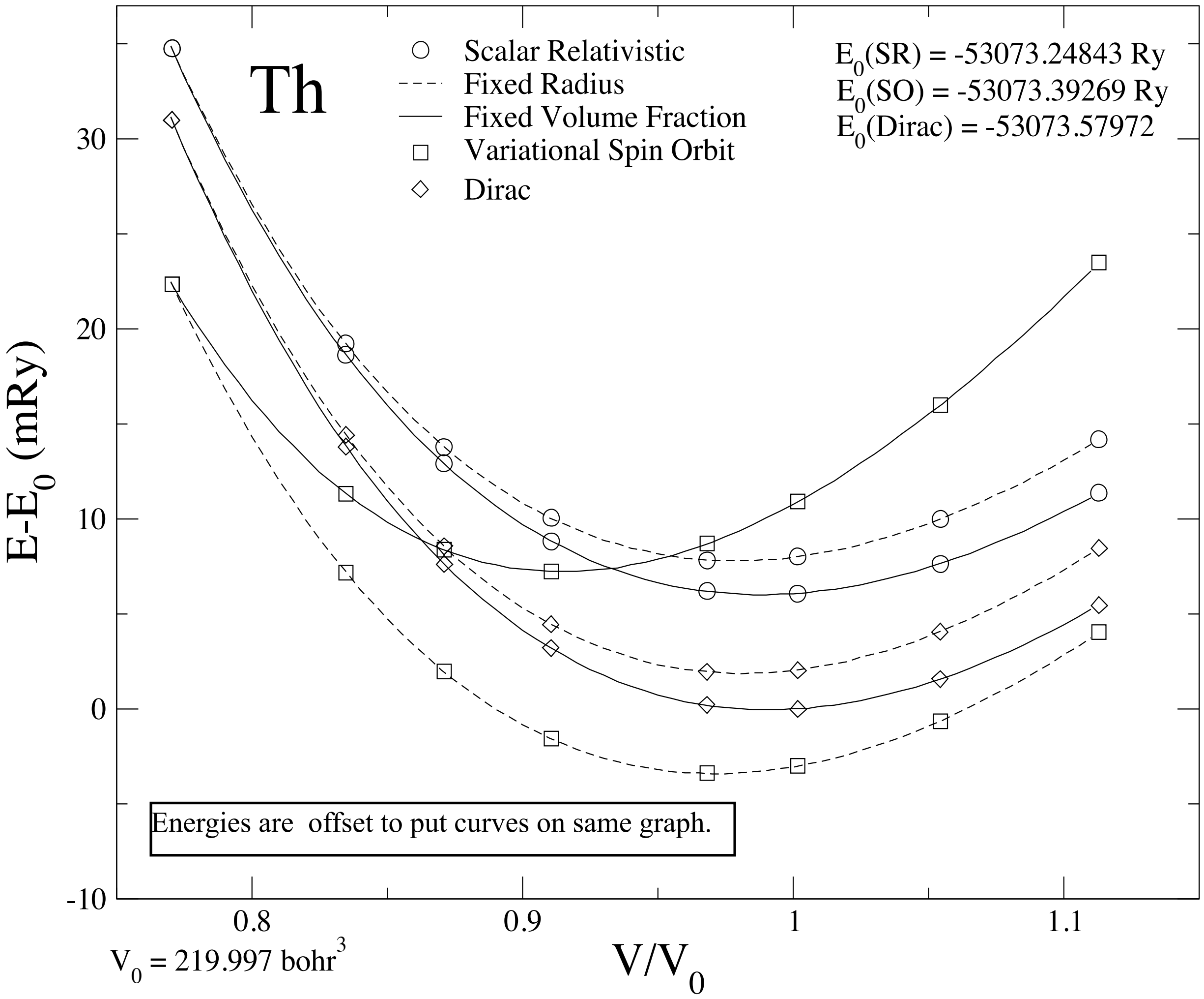


- Dirac $p^{1/2}$, like $s^{1/2}$, states are *non-zero* at the origin, while scalar relativistic and Schrödinger p states are *zero* at the origin, hence no combination of K-H bases can ever capture the behavior of Dirac $p^{1/2}$ states.

- The anomalously small volumes obtained with the SO method are due to a poor treatment of $p^{1/2}$ states. These states can’t be adequately captured in a scalar relativistic basis.

As an example of this problem ...

Compare volume-energy curves for Th ...



Predicted equilibrium volume

- (This figure has two curves per method from two ways of treating the muffin-tin volume).

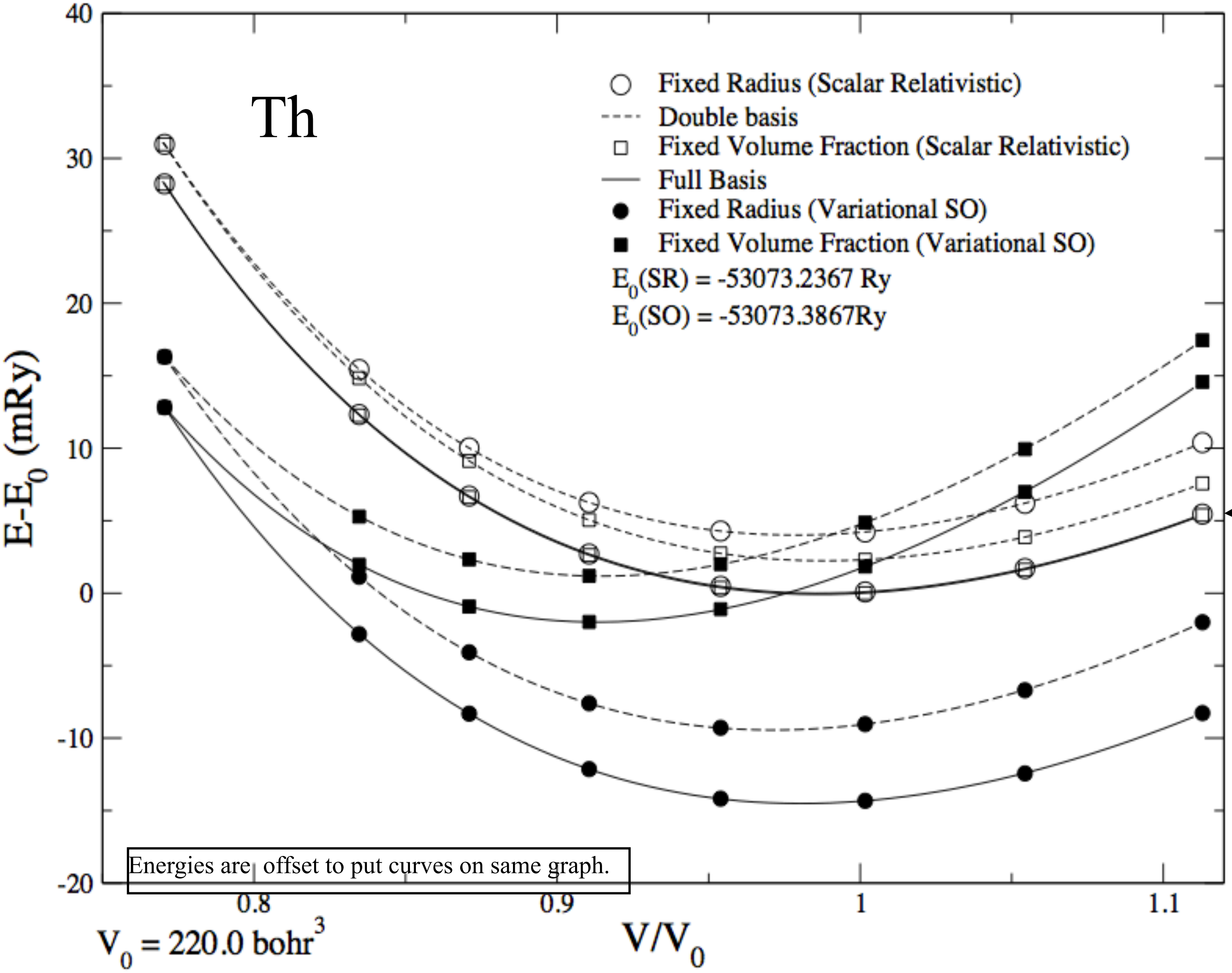
\- in actinides, the “semi-core” *6p* states must be included in the variational basis for numerical stability.

\- however, doing so in SO causes a relatively large *decrease*, compared to SR, in the equilibrium volume. On the other hand, Dirac bases *increase* the equilibrium volume compared to SR.

The spin-orbit interaction should increase the predicted equilibrium volume.

- Splitting an *l*-band into two (narrower) sub-bands decreases the bonding energy and, all else being equal, should increase the predicted equilibrium volume.

Lest you conclude that this results from poor basis convergence ...



Energies are offset to put curves on same graph.

$V_0 = 220.0$ bohr^3

A demonstration of basis convergence.

Dotted lines are same as in previous figure.

Double basis not converged

Triple basis converged.

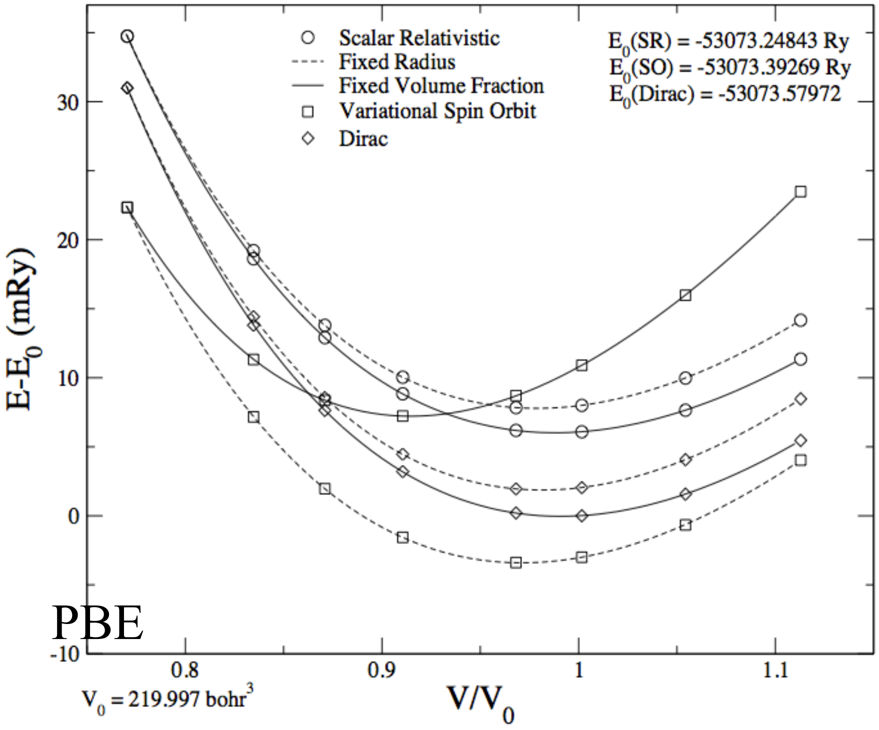
Basis sets have multiplicity both in muffin-tins and in the interstitial; “double” and “triple” have conventional meaning.

Sensitivity to calculational detail

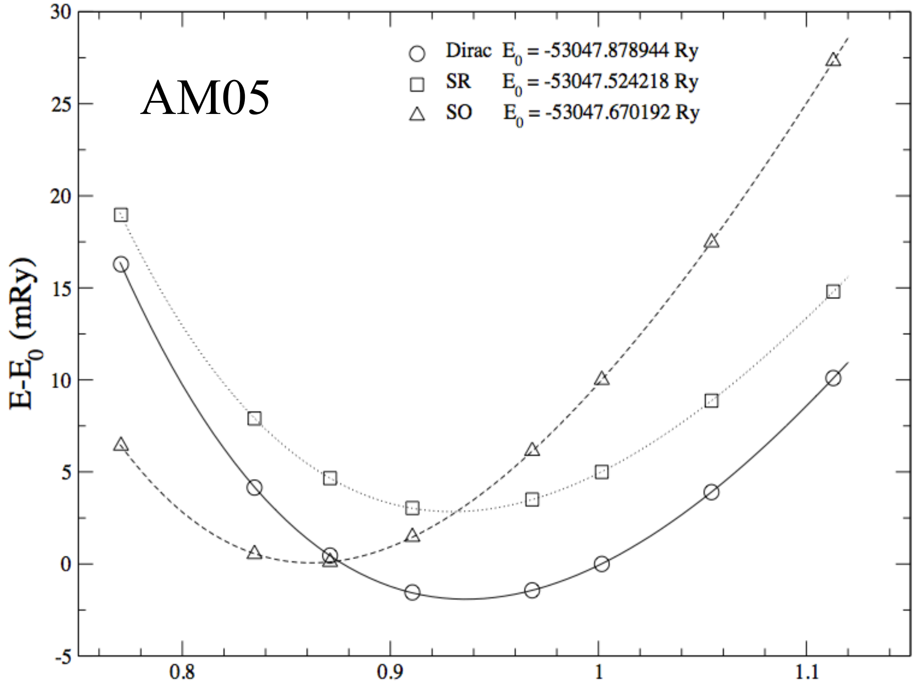
- The energy curves above compare results of SR and SO with two methods for determining muffin-tin volumes: fixed-fraction ($V_{mt}/V=constant$)* and fixed radius ($V_{mt}=constant$)*. With a converged basis, SR is insensitive to this difference; *converging the basis does not improve SO.* The small volume is not a convergence issue.

*FPLMTO generally uses $V_{mt}/V=constant$; FLAPW uses $V_{mt}=constant$

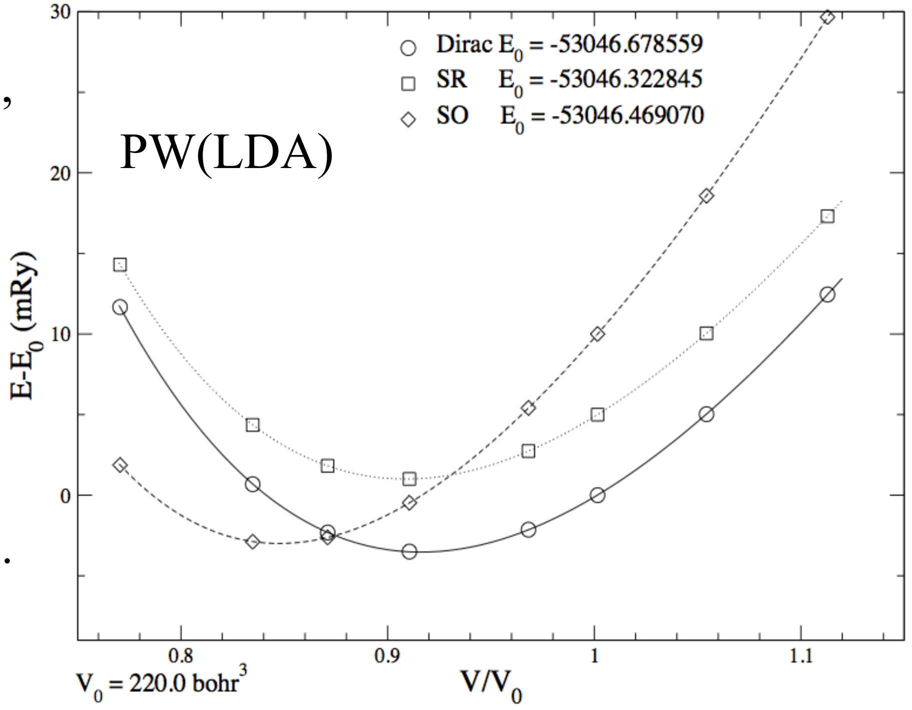
To show the functional dependence of these calculations, ...



Th



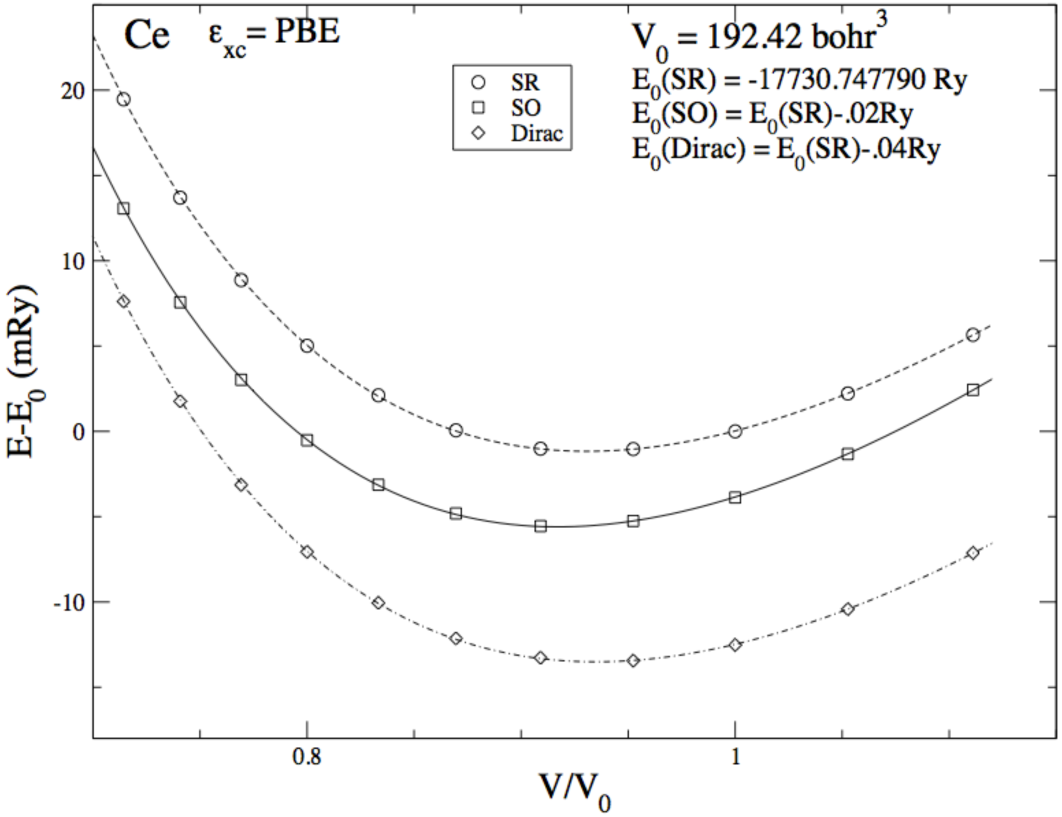
- Energy/volume curves for Th, calculated with PBE, AM05, and PW exchange/correlation functionals, using scalar relativistic bases with (SO) and without (SR) the spin-orbit interaction, and using Dirac bases. The three functionals give curves that are qualitatively similar, apart from overall volume shifts. SR and Dirac curves are qualitatively the same, apart from a volume shift while the SO curve is qualitatively different and has the smallest volume.
- AM05 generally gives better volumes(*); PBE anomalously gives better volumes for actinides.

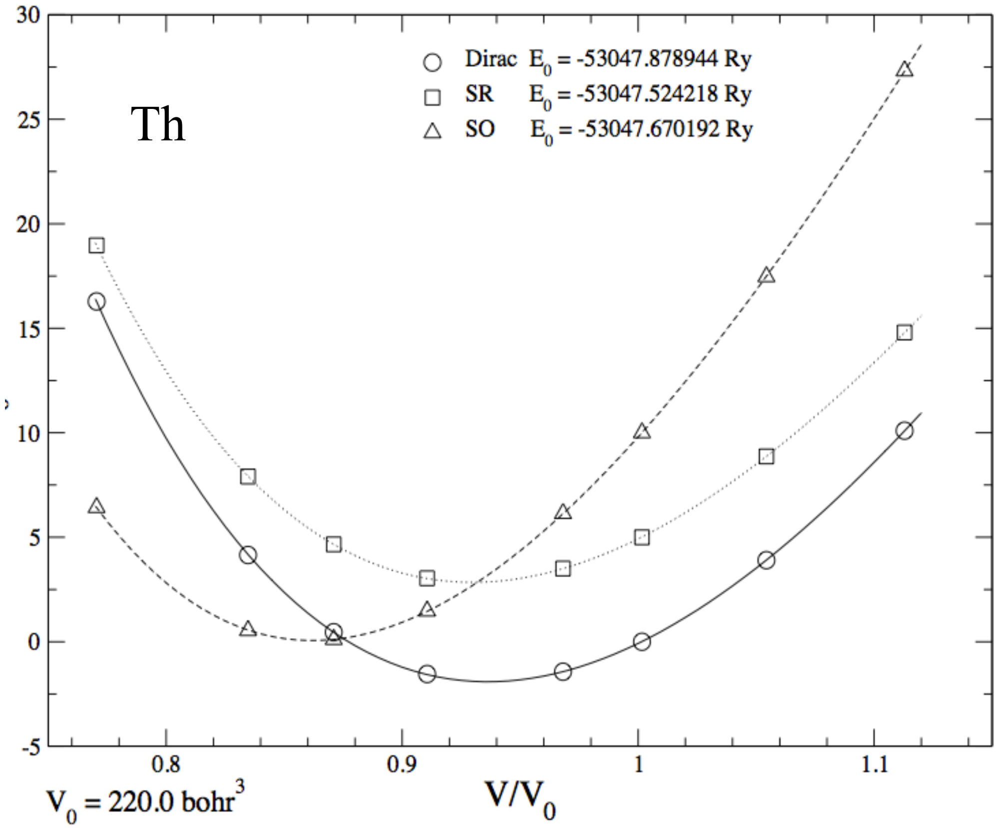


(*) Haas 2009: P. Haas, F. Tran, and P. Blaha, Phys. Rev. B 79, 085104 (2009)

To compare with a lighter, still relativistic, element ...

fcc Ce and *fcc* Th with PBE ε_{xc} and SR, SO, and Dirac methods

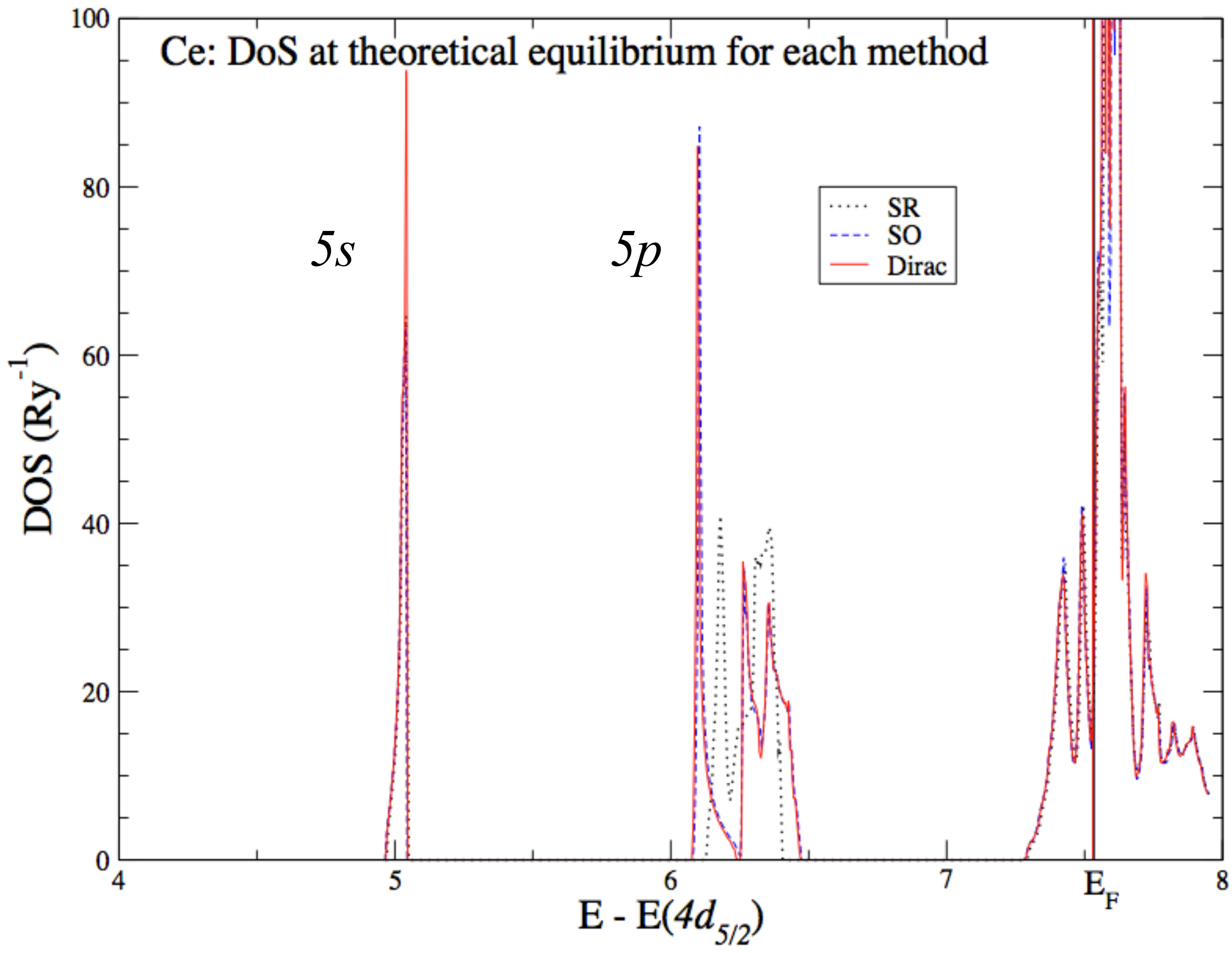




Compare Ce and Th

- The behavior (SO with a smaller volume than SR, Dirac with a larger volume than SR) is similar but much less striking than in Th.
- In Ce, semi-core states are optional, while they are essential for numerical stability in Th calculations.

Comparing density of states is another way to look at the difference ...



DoS for Ce

Calculated at theoretical equilibria with AM05 using

- SR (black dotted)
- SO (blue dashed)

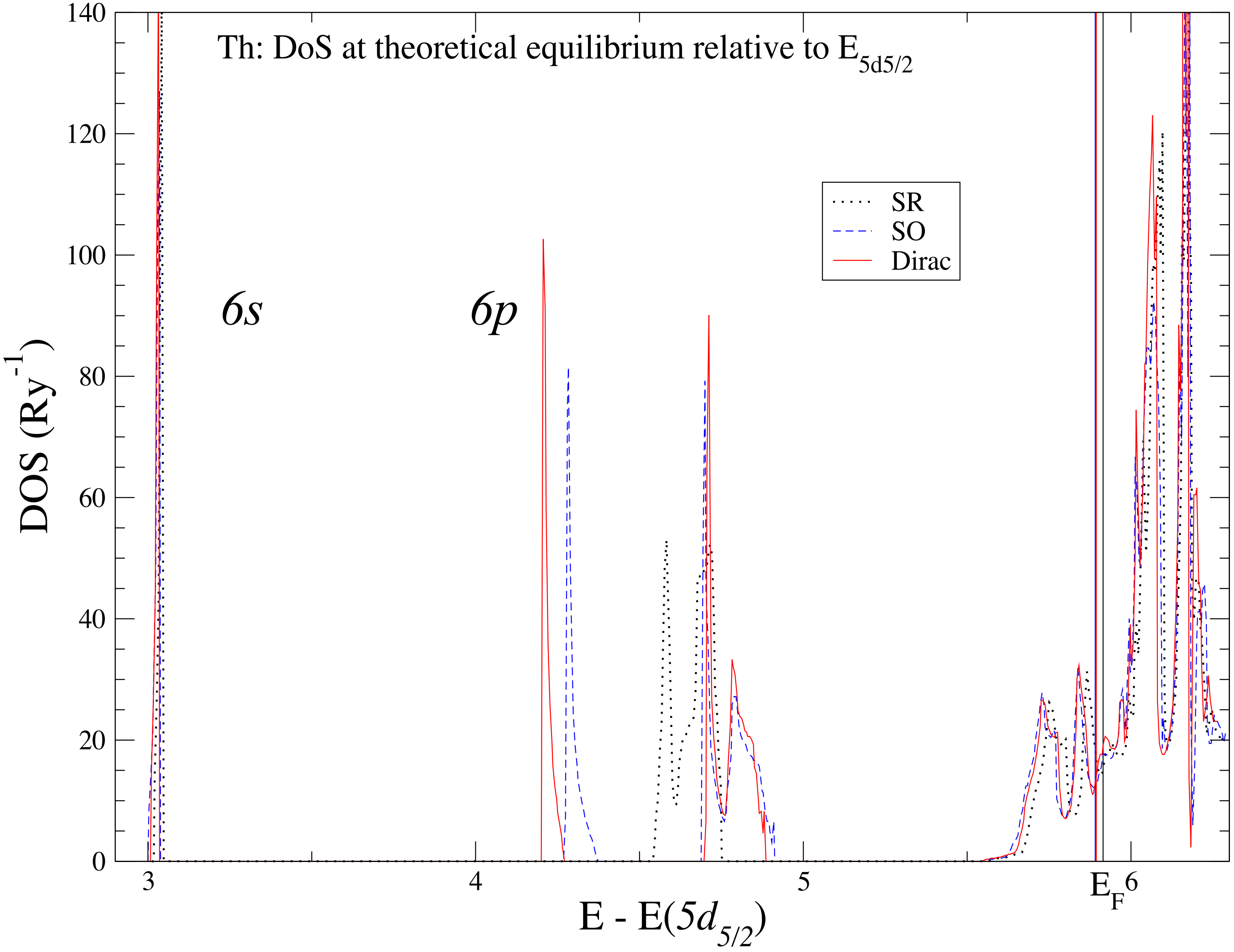
and

- Dirac (red solid)

Energies are relative to the Ce $4d_{5/2}$ core state, which should be a common point of reference in all three methodologies.

- Dirac and SO seem to give almost identical DOS, at least for occupied states.
- All DOS align except for the SR 5p states; treating these states as SR would be clearly inaccurate.

As with E-V curves, differences are more pronounce in Th ...



DoS for Th

Calculated, as in Ce, at theoretical equilibria with AM05 using

- SR (black dotted)
- SO (blue dashed)

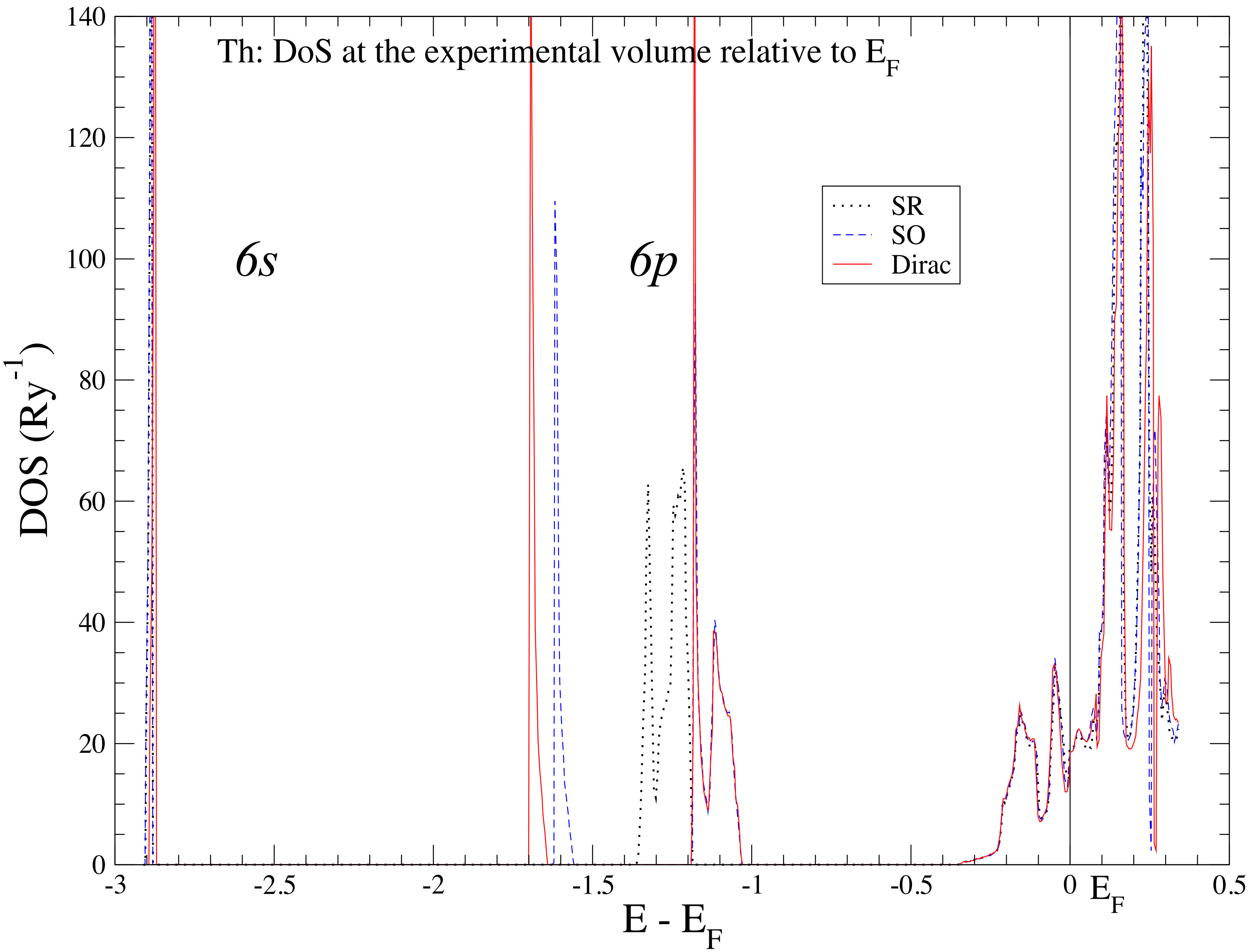
and

- Dirac (red solid)

Energies are now relative to the Th $5d_{5/2}$ core state, again a common reference.

- In contrast to Ce, DOS don't consistently align. The *6s* are almost identical, but valence Dirac and SO are shifted relative to SR and the Dirac and SO $6p_{1/2}$ differ.
- SO is at a lower volume, with a more condensed density (and higher ∇V), and so, all else being equal, should be more split that Dirac; it isn't. SR is just different.

Compared another way ...



DoS for Th

Calculated at the <u>experimental volume</u> with AM05 using
- SR (black dotted)
- SO (blue dashed)

and
- Dirac (red solid)

Energies are relative to the E_F in each case.

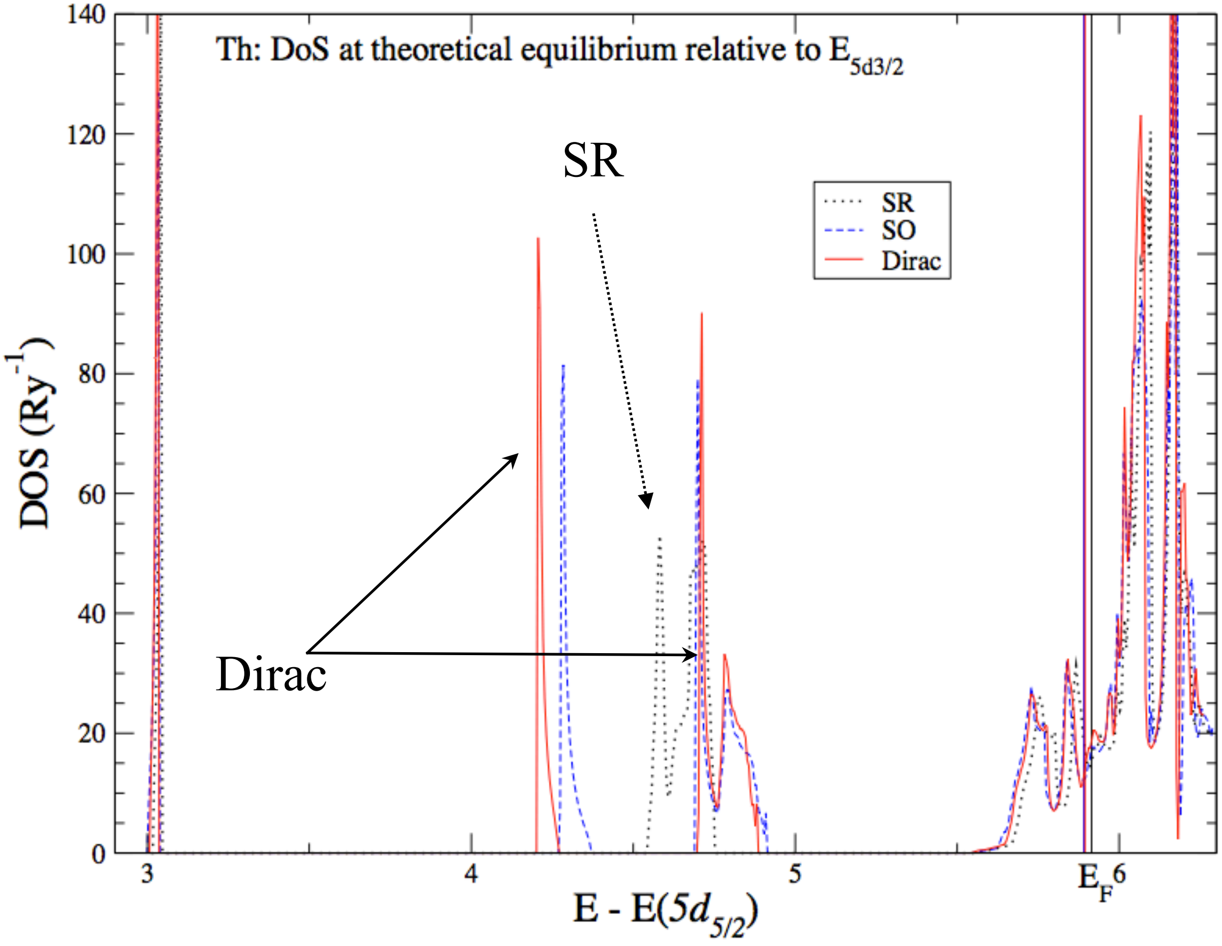
- <u>All states align</u> except for the *6p* states, and SO and Dirac *6p*$_{5/2}$ are very different.
- Valence states (occupied at least) all align.
- SR for *6p* states clearly isn't justified.

Attempts to patch up the 6p volume error ...

Patching up the 6p error

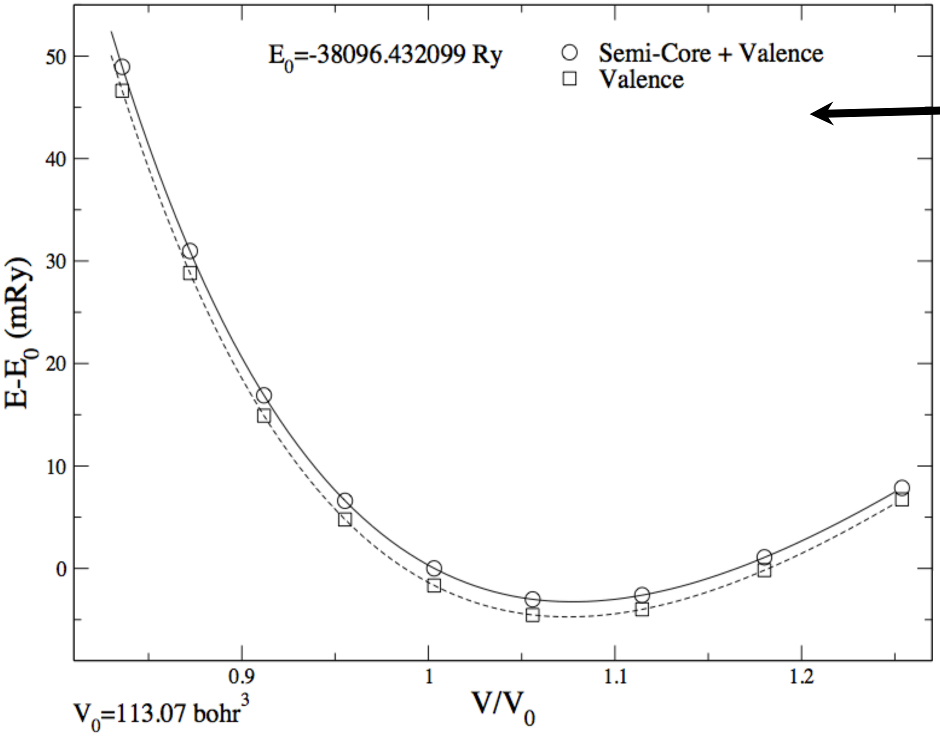
Incorporating a Dirac 6p state as a local orbital (Wien)

- FLAPW includes semi-core states as local orbitals. Using a Dirac 6p state as a local orbital seems to fix the volume problem. This would have implications under pressure.



Zeroing spin-orbit matrix elements for semi-core p-states

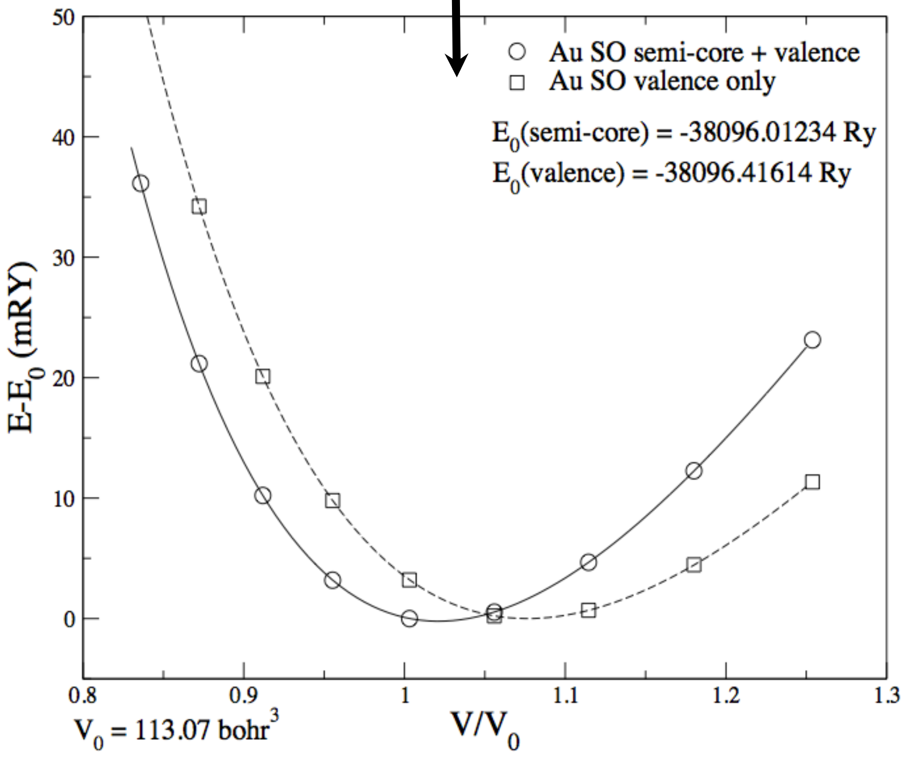
- Improves the volume problem.
- DOS looks very different than the correct DOS.



Energy vs Volume for Au calculated with Dirac bases, with valence only and semi-core+valence configurations.

- The semi-core (5p) orbitals are deep below the valence states, allowing calculation of properties with and without semi-core states.
- Results for Dirac show only a small decrease in energy due to residual hybridization.
- SO results show a large volume shift, despite the energy separation.

Energy vs Volume for Au calculated with SO bases, with valence only and semi-core+valence configurations.



Conclusions

- RSPt with Dirac bases provides an accurate (and relatively fast) platform with which to calculate the properties of heavy (and not so heavy) materials with DFT as well as with phenomenological inclusions such as DMFT. It's almost as efficient as SR and SO RSPt both in time and storage.
- A scalar relativistic basis with variational spin-orbit coupling cannot treat heavy elements accurately due to the inadequate treatment of the 6p states. This is a large energy and cannot be treated as a perturbation.
- Using a Dirac basis allows all states -- core and valence -- to be treated in the same way and consistently incorporate the same underlying equation. The Dirac equation provides the most accurate platform for development of DFT as well as DFT+whatever to accurately predict the properties of heavy elements.