LA-UR- 12-00933

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Title:	Predictive equation of state methods for heavy materials based on the Dirac equation and density functional theory.
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Intended for:	APS March Meeting Boston, Massachusetts 2/27-3/2

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Form 836 (7/06)

Abstract to be submitted to the APS March Meeting
27 Feb -- 2 Mar 2012
Boston, Massachusetts

Predictive equation of state methods for heavy materials based on the Dirac equation and density functional theory.

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Density functional theory (DFT) provides a formally predictive base for the prediction of equation of state. Currently available approximations to the exchange/correlation functional have provided accurate predictions of material properties for many materials in the periodic table. For heavy materials however, DFT-based calculations, using available functionals, fail to provide quantitative predictions of material properties, and often fail to be even qualitative. This deficiency is due both to the lack of the appropriate confinement physics in the exchange/ correlation functional and to approximations used evaluate the underlying equations. In order to assess and develop accurate functionals, it is essential to eliminate all other sources of error. In this talk we describe an efficient first-principles electronic structure method based on the Dirac equation and compare the results obtained with this method with other methods generally used. Implications for high-pressure equation of state of relativistic materials are demonstrated in application to Ce and the light actinides.

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Predictive equation of state method for heavy materials based on the Dirac equation and density functional theory.

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- Describe an all-electron method (RSPt) with full Dirac bases
  - convergence
- Compare energy and volume curves with other commonly used methods
- Compare calculated results for equilibrium properties in Ce and Th
- Demonstrate the inherent instability of variational spin-orbit for actinides

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

- bases (ψ) generated using the Dirac equation: "Dirac"

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

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

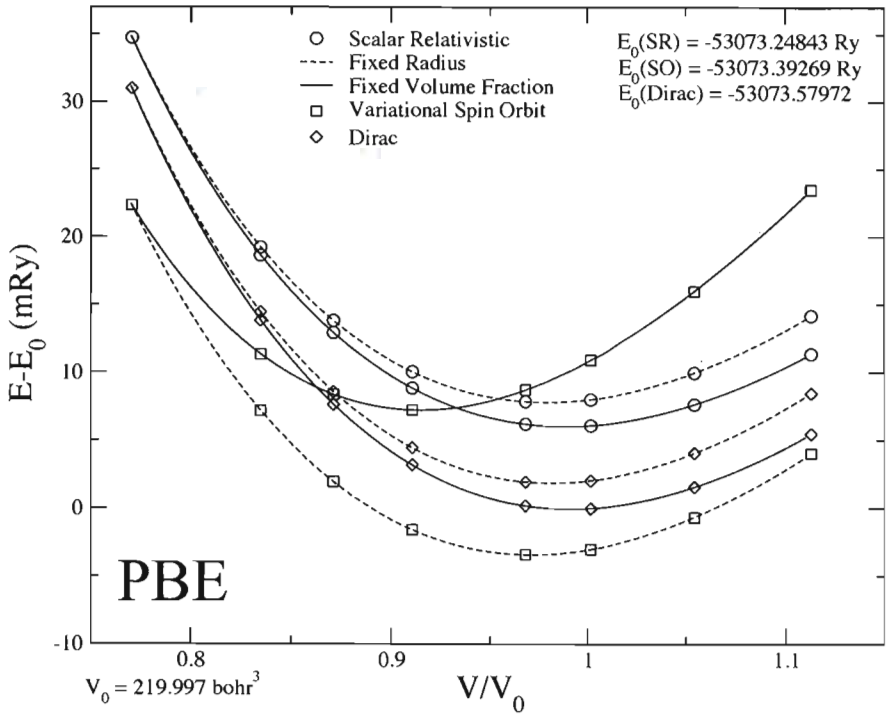
$$(\mathcal{H}_D + V - e)\psi = (\mathcal{H}_{SR} - e)\psi - V_{SO}(r)\sigma \cdot \mathcal{L} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \psi$$

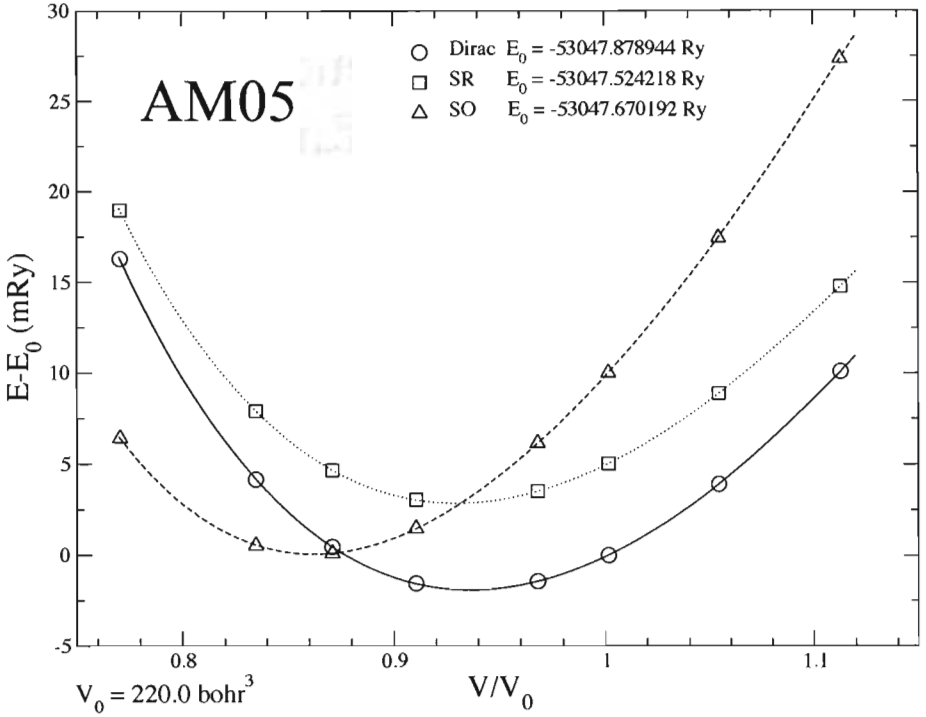
D. D. Koelling and B. N. Harmon, Journal of Physics C: Solid State Physics 10, 3107 (1977)

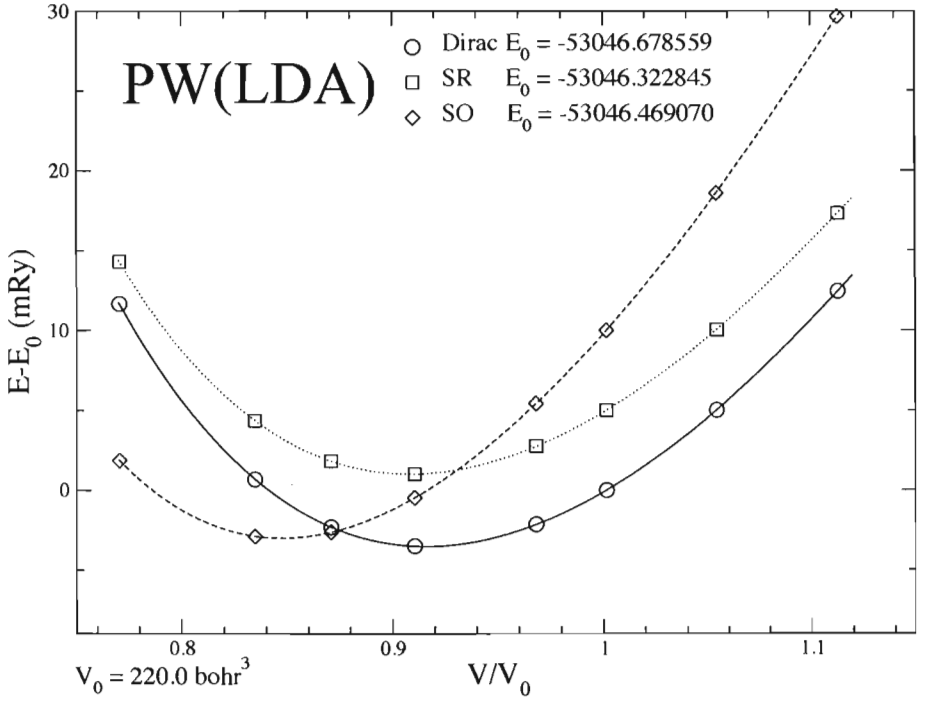
- The scalar relativistic approximation (SR) amounts to ignoring V_{SO}. "SR"

- SR + variational spin orbit (SO): using SR bases, solve the full Koelling Harmon equation with V_{SO} treated variationally. "SO"

In this presentation, we apply these equations to three materials (Th, Al, and Au) and examine the accuracy of each.







- Energy/volume curves for Th calculated with three different functionals: PBE, AM05, and PW. The curves are qualitatively the same, apart from a volume shift.
- Note that Dirac gives a small expansion over SR, while SO curves are anomalously small.

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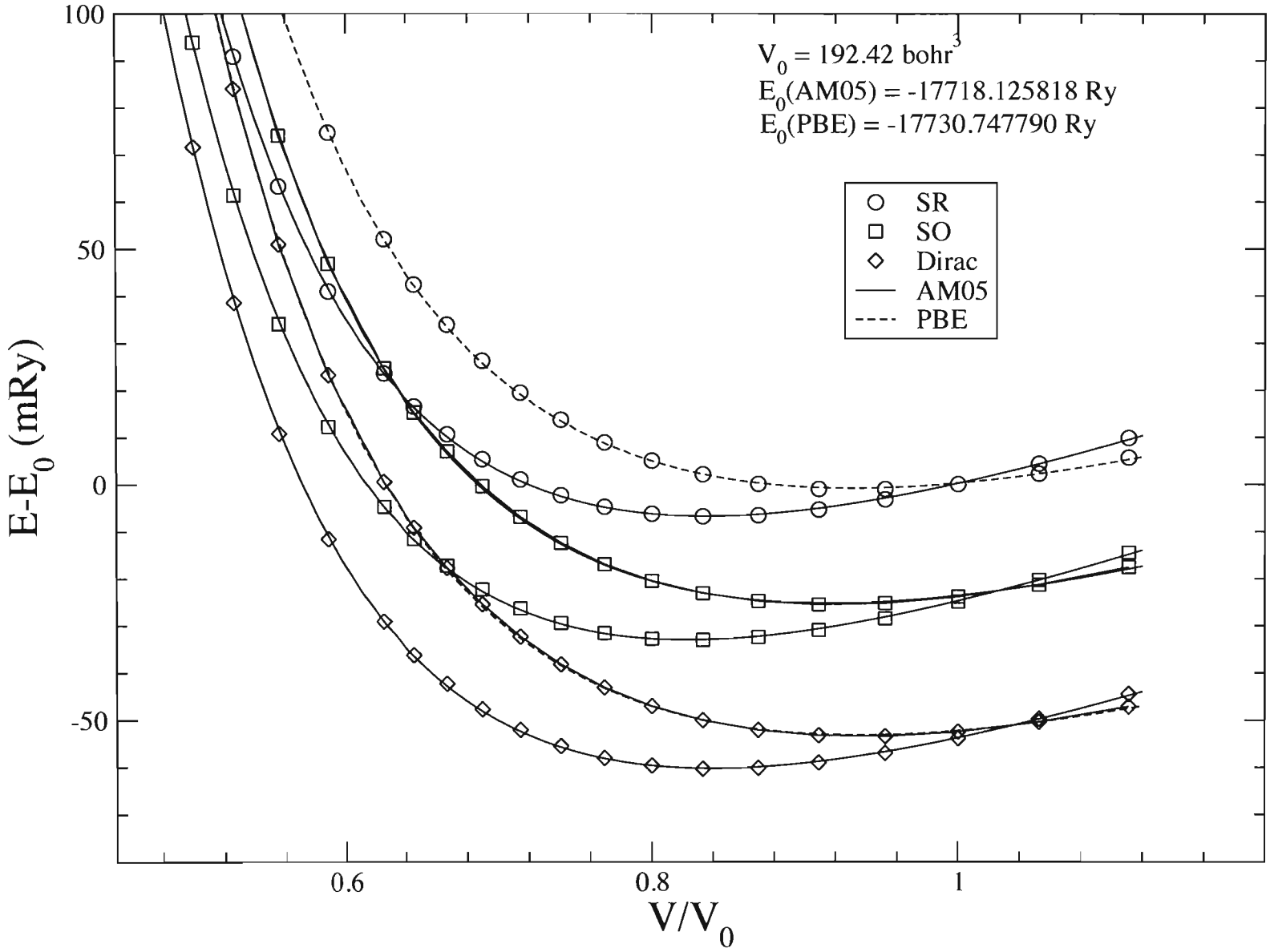

Energy/volume curves for Ce for AM05 and PBE. The trends are similar to the Th curves, with PBE giving larger volumes and SO anomalously small volumes for both functionals.

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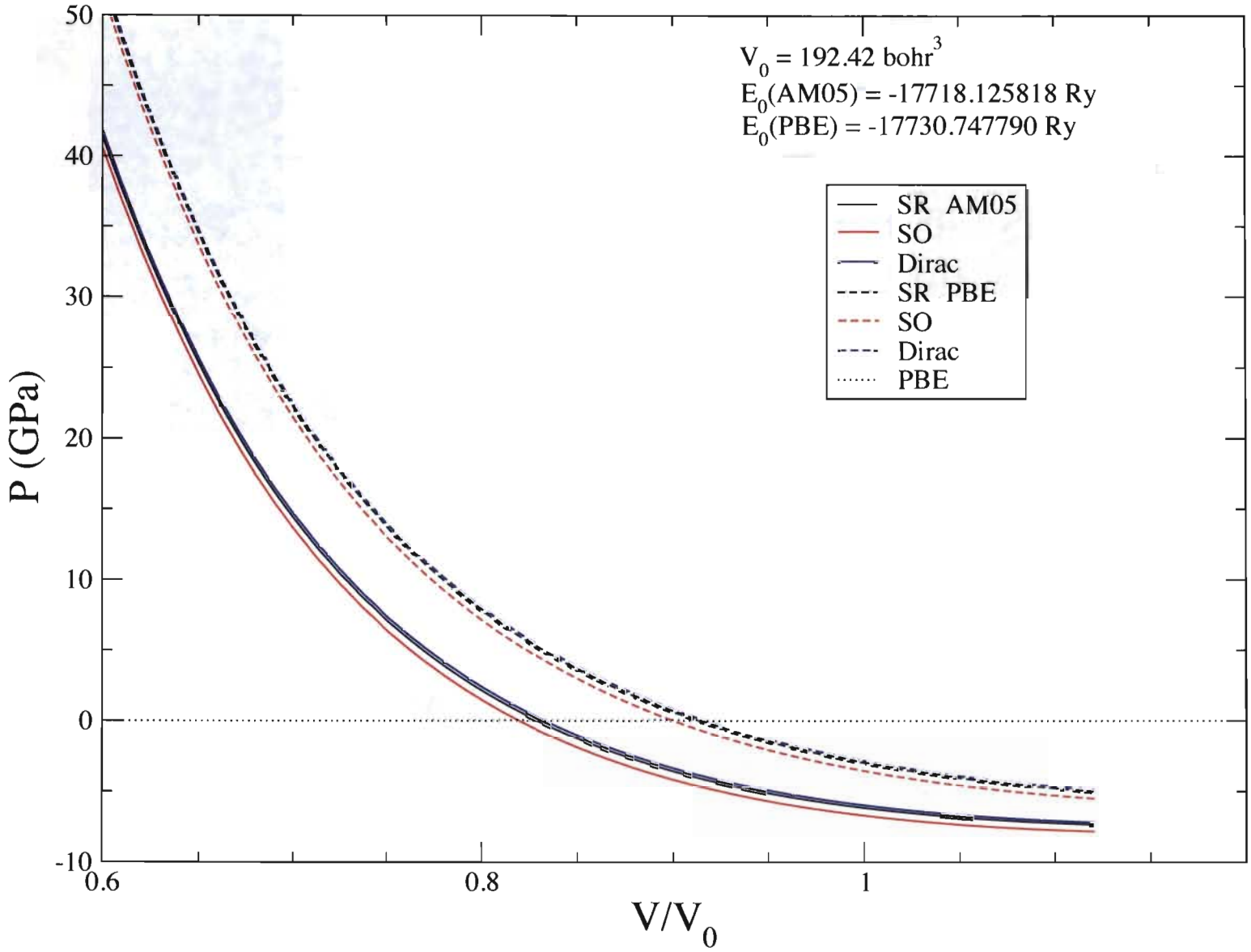

Pressure/volume curves for Ce at "low" pressure. Note the volume shift, and the anomalously small volume, obtained with SO.

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TABLE I: Thorium equilibrium volumes in cubic bohrs and bulk moduli in GPa calculated with scalar relativistic, scalar relativistic with variational spin-orbit, and full Dirac methodologies, using AM05[16], PBE[2], and PW[17] functionals as described in the text. The zero temperature experimental volume, with zero point motion subtracted, is 220.00 bohr^3[13]. Reference 13 gives 205.14 for AM05. 218.02 for PBE, and 200.89 for PW.

	V/a_0^3			B (GPa)		
	AM05	PBE	PW	AM05	PBE	PW
Scalar Relativistic	204.55	217.36	199.89	58.9	54.5	65.5
Scalar Relativistic+Spin Orbit	189.62	201.21	186.45	74.1	68.6	80.4
Full Dirac	205.98	217.98	201.54	62.4	58.3	68.0

V(bohr^3)	AM05	PBE	PW(LDA)
SR	159.3	175.3	155.4
SR^3	159.1		
SO	157.4	172.8	153.4
SO^3	158.1		
Dirac	160.0	180.0	

Equilibrium volumes obtained for three different functionals and SR, SO, and Dirac. Triple basis results are also included.

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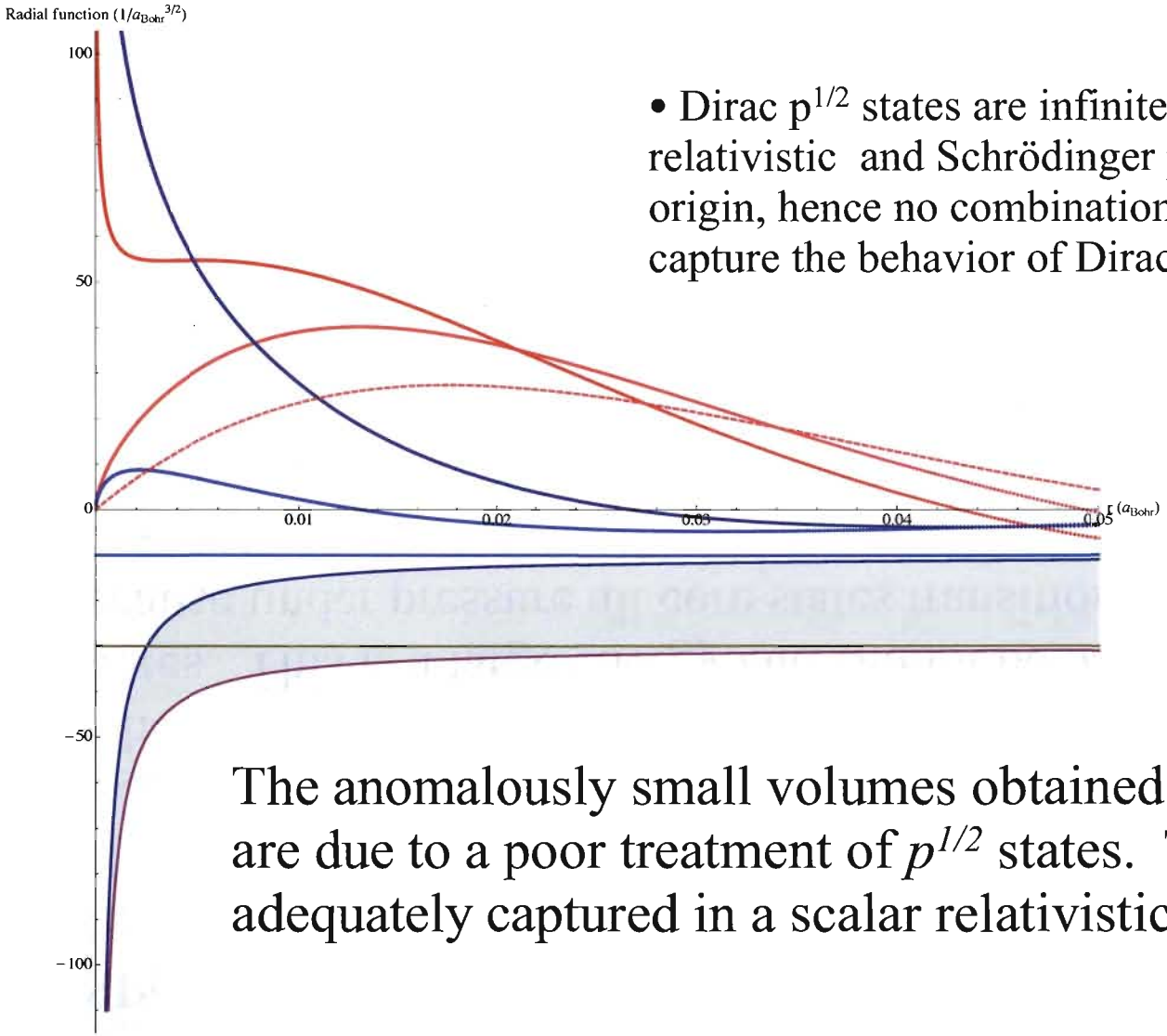
The radial function for the upper components (red) and the lower components (blue) of the $6p_{1/2}$ state, calculated with the Harmon and Koelling scalar relativistic equation (lighter), the Dirac equation (darker), and the Schrödinger equation (dashed).
Note the discrepancy at the origin.



- Dirac $p^{1/2}$ states are infinite at the origin and scalar relativistic and Schrödinger p states are finite 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

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Conclusions

- RSPt with Dirac bases provides an accurate platform within which to evaluate the effects of functional approximations as well as phenomenological inclusions such as DMFT.
- 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.
- Because under pressure all core states transition to itinerant, it is necessary to treat all states the same -- as Dirac states -- in order to not introduce anomalies into the equation of state.