LA-UR- 11-06808

Approved for public release;
distribution is unlimited.

Title: Predicting the properties of heavy elements: the Dirac equation in electronic structure calculations (U)

Author(s): John M Wills, Los Alamos Natl Laboratory
Ann E Mattsson, Sandia Natl Laboratories

Intended for: Presentation to the International Conference on Advanced Materials (ICAM-2011), PSG College of Technology, Coimbatore, India, 12-16 December 2011.

Los Alamos
NATIONAL LABORATORY
EST.1943

Abstract to be submitted to the International Conference on Advanced Materials" (ICAM-2011)
PSG College of Technology, Coimbatore, India
12-16 December, 2011
LAUR 11-03317

Predicting the properties of heavy elements: the Dirac equation in electronic structure calculations

John M Wills(*) and Ann E Mattsson(**)
(*) Los Alamos National Laboratory, Los Alamos, NM 87522 USA
(**) Sandia National Laboratory

The heavy elements -- rare-earths and actinides, and their compounds -- exhibit unique structural and electronic properties. The f-electrons in these materials change from localized to itinerant over a relatively narrow range of temperature, pressure, and chemical environment. The precise treatment afforded by an accurate first-principles calculation based on the full Dirac equation allows definitive predictions of material properties and provides a stringent test of new density functionals designed to accurately capture the behavior of heavy relativistic materials.

In this talk we describe the use of electronic structure calculations based on the full Dirac equation to predict the structural properties of selected lanthanide and actinide elements. It has been demonstrated [1] that even the most basic property of these materials -- the equilibrium volume -- is impossible to predict with certainty without using the Dirac equation to produce semi-core p-bands. In this work we demonstrate the effect of full relativity on phase stability, elasticity, and electron energy spectra and compare with previous calculations obtained using less accurate approaches.

[1] Nordstrom, L., et al., *Physical Review B* **63**, 035103 (2001)

Predicting the properties of heavy elements: the Dirac equation in electronic structure calculations

John M Wills[1] and Ann E Mattsson[2]
[1]Los Alamos National Laboratory
[2]Sandia National Laboratories

The heavy elements -- rare-earths and actinides, and their compounds -- exhibit unique structural and electronic properties. The f-electrons in these materials change from localized to itinerant over a relatively narrow range of temperature, pressure, and chemical environment. The precise treatment afforded by an accurate first-principles calculation based on the full Dirac equation allows definitive predictions of material properties and provides a stringent test of new density functionals designed to accurately capture the behavior of heavy relativistic materials.

- Relativity is fine detail in most materials but an essential detail in heavy elements such as rare-earths and actinides.
- Electron confinement -- localization -- is a fine detail in many materials, but an essential detail in materials such as oxides, rare-earths, and actinides.
- Confinement is treated inaccurately by currently available approximations to the exchange/correlation energy in DFT. Hence materials where confinement is important in practice depend on ad hoc mergers of DFT and phenomenology. Examples are LDA+U and LDA+U+DMFT. The interface between DFT and phenomenology is ill defined, leading to uncertainty in the accuracy and precise meaning of results of these calculations. An approximation to the exchange/correlation energy that deals with confinement in a fundamental way would solve many problems in dealing with confined materials.
- In order to develop such functional approximations, errors introduced by other approximations should be eliminated.
- In this talk, different schemes of dealing with relativity are evaluated, including a full Dirac basis implementation of the FPLMTO code RSPt.

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

- the Dirac equation:

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

- the scalar Dirac equation: (the Koelling-Harmon equation)

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

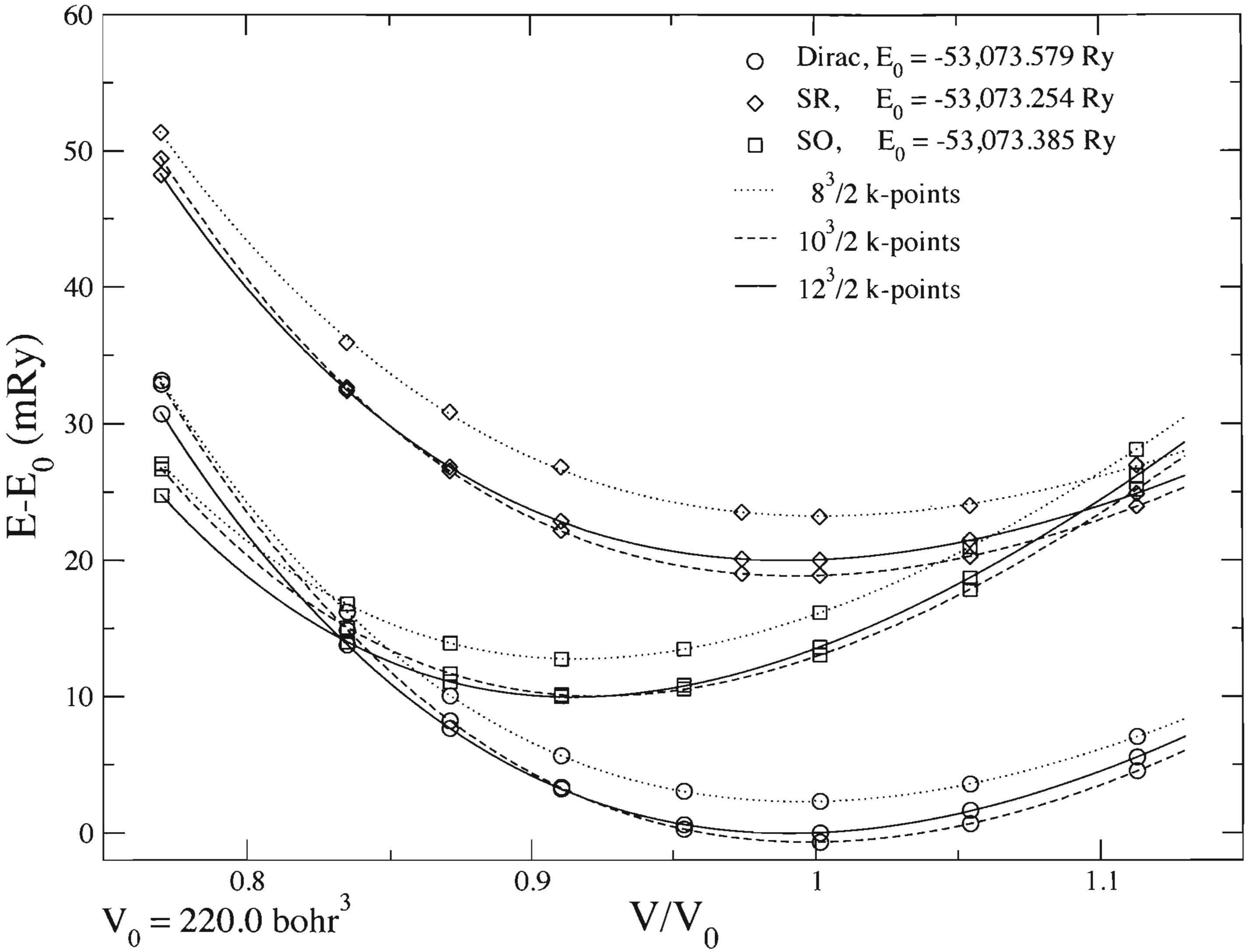
D. D. Koelling and B. N. Harmon, Journal of Physics C: Solid State Physics 10, 3107 (1977)

the scalar relativistic approximation (SR) amounts to ignoring V_{SO}.

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

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

Energy vs Volume for Th



$V_0 = 220.0$ bohr^3

Comparing
- Dirac, SR, and SO methods
- three k-point sets.

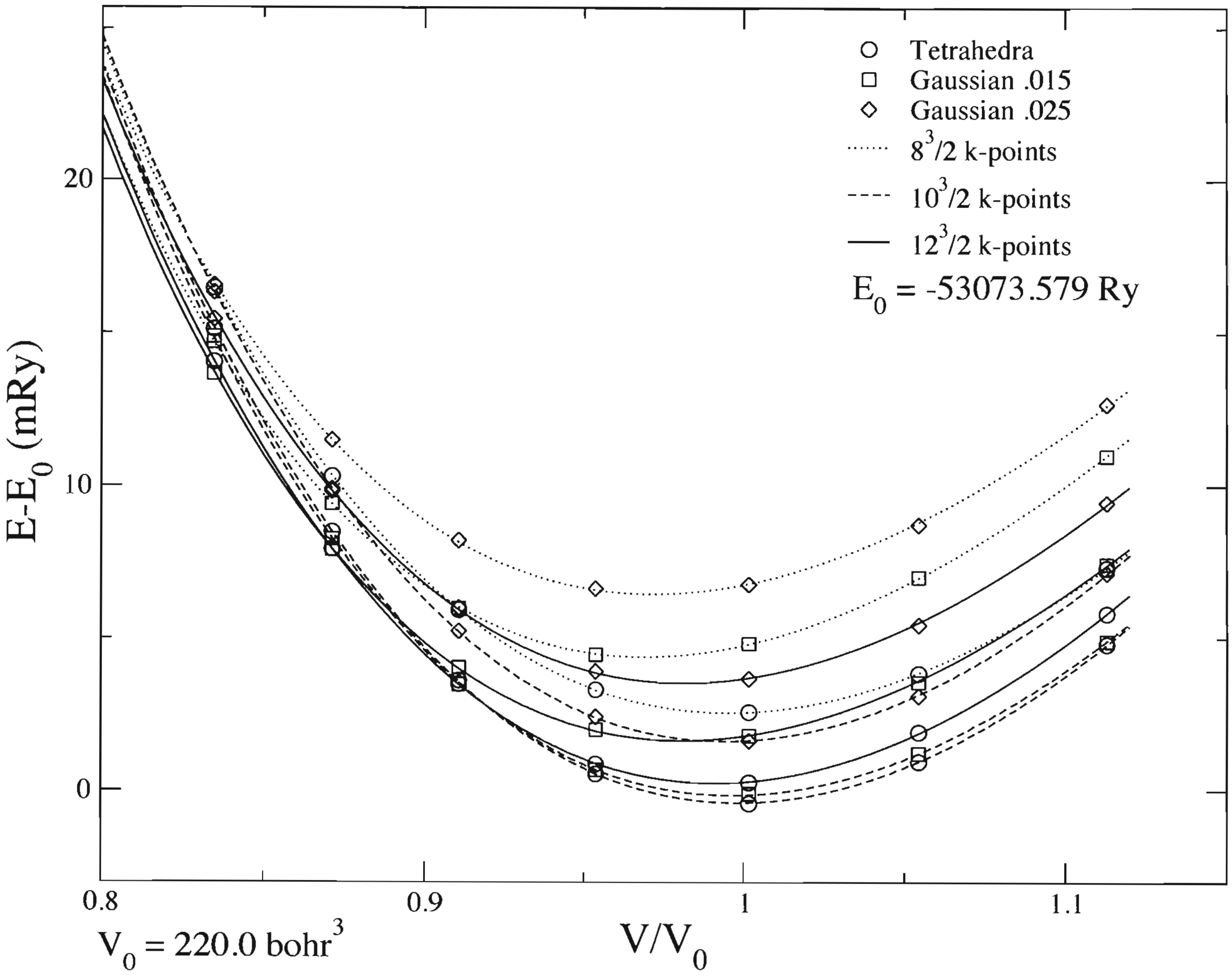
Interstitial volume is a fixed fraction (FF) of the total volume.

PBE exchange/correlation

$V_{exp} = 220.00$ bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- The convergence pattern is the same for Scalar Relativistic (SR), Scalar Relativistic with variational Spin-Orbit coupling (SO), and Dirac treatments.
- Since the Dirac treatment is the main focus in this article, further k-point convergence testing is done with this relativistic method.

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



Energy vs Volume for Th using the Dirac method.

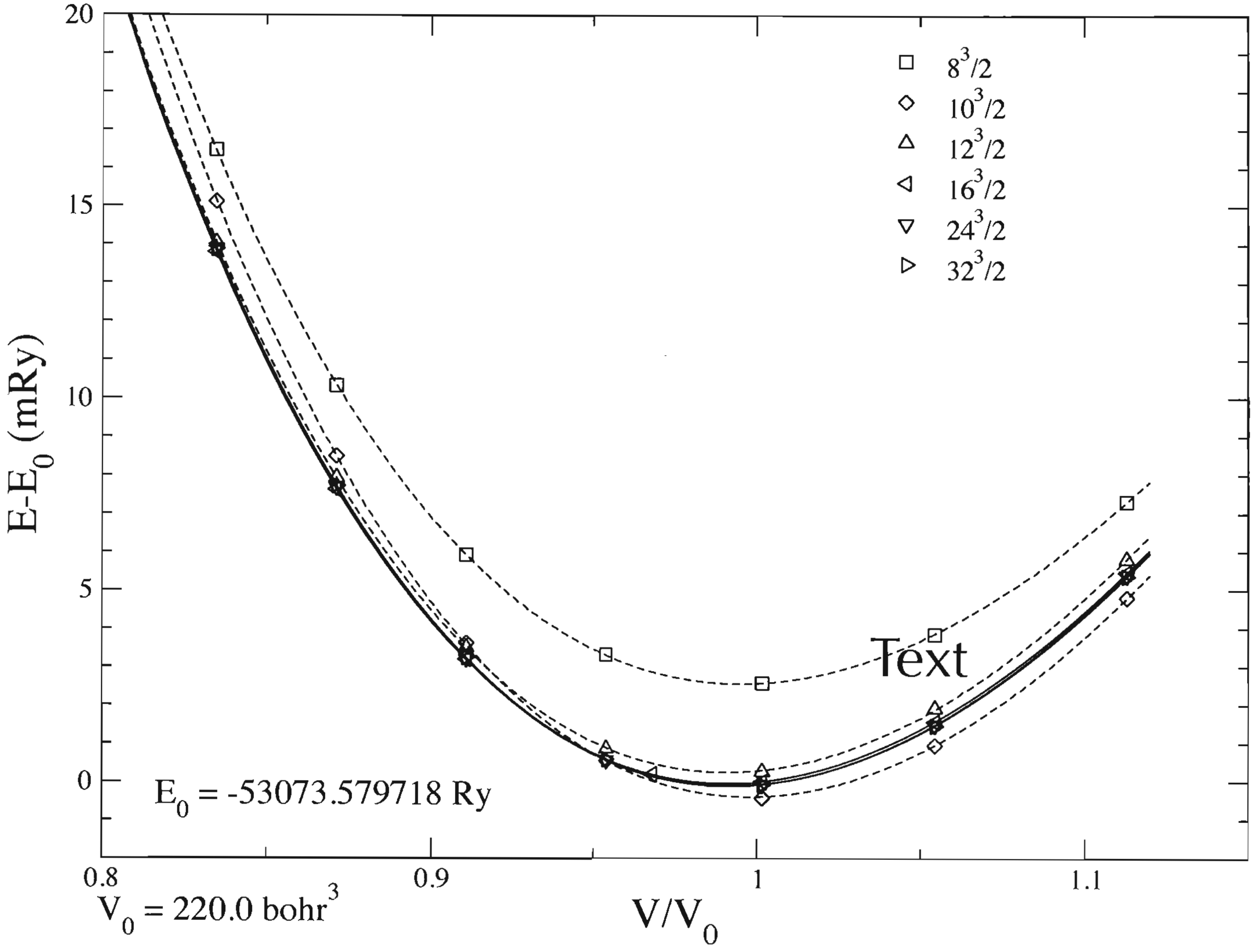
Comparing
- linear interpolation and
- special points (Gauss)

Interstitial volume is a fixed fraction (FF) of the total volume.

PBE exchange/correlation

V_{exp} = 220.00 bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- Within a specified size of the k-point sampling (same color), decreasing the width of the Gaussian sampling from 0.025Ry to 0.015Ry shows convergence towards the tetrahedron method.
- The tetrahedron method converges faster.
- $12^3/2$ sampling is not converged.



Energy vs Volume for Th using the Dirac method.

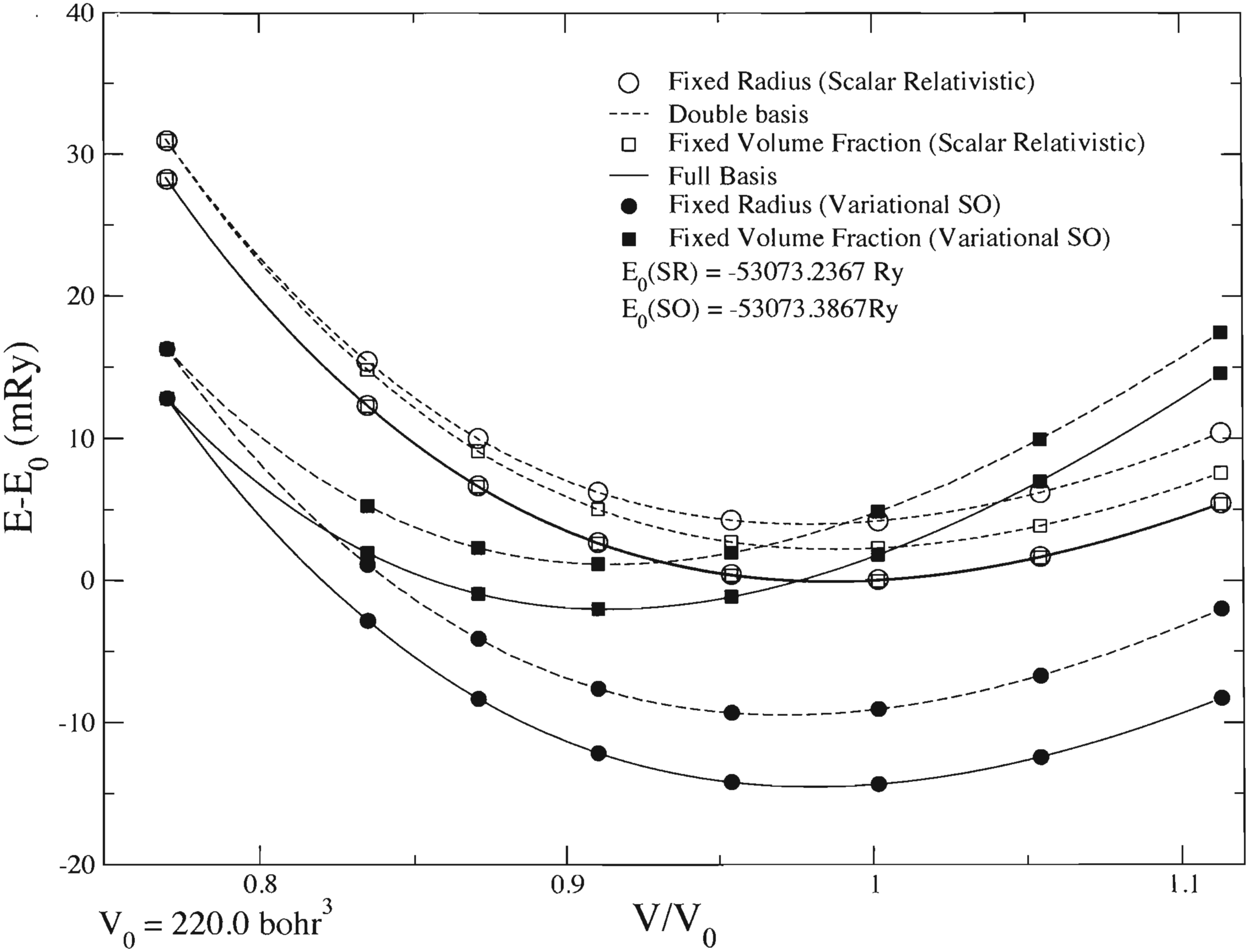
Convergence of the tetrahedron method.

Interstitial volume is a fixed fraction (FF) of the total volume.

PBE exchange/correlation

V_{exp} = 220.00 bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- The $16^3/2$ sampling size is converged, and used in what follows.



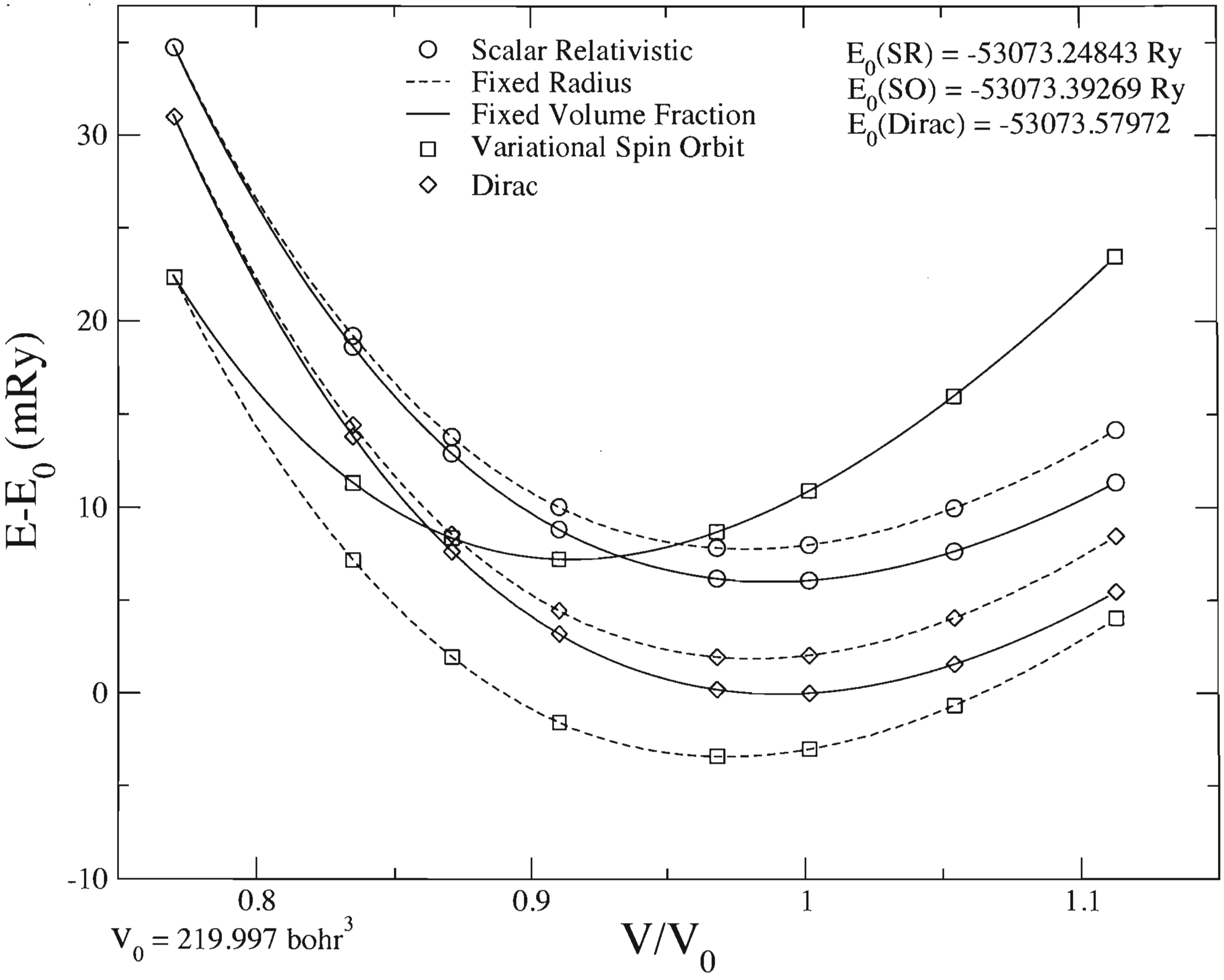
Energy vs Volume for Th using SR and SO.

Comparing fixed radius (FR) and fixed fraction (FF) treatments of the interstitial, and a triple basis with a double basis.

PBE exchange/correlation

V_{exp} = 220.00 bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- Th full (triple) basis: 2(6s6p) 3(7s7p) 2(6d5f); Th double basis: 2(6s6p) 2(7s7p6d5f).
- A full basis in RSPt gives converged results (FF and FR are the same)
- A double basis isn't converged;
- With a double basis the FF method gives the correct shape, and should be used.



Energy vs Volume for Th using a double basis.

Comparing fixed radius (FR) and fixed fraction (FF) treatments of the interstitial using Dirac, SR, and SO.

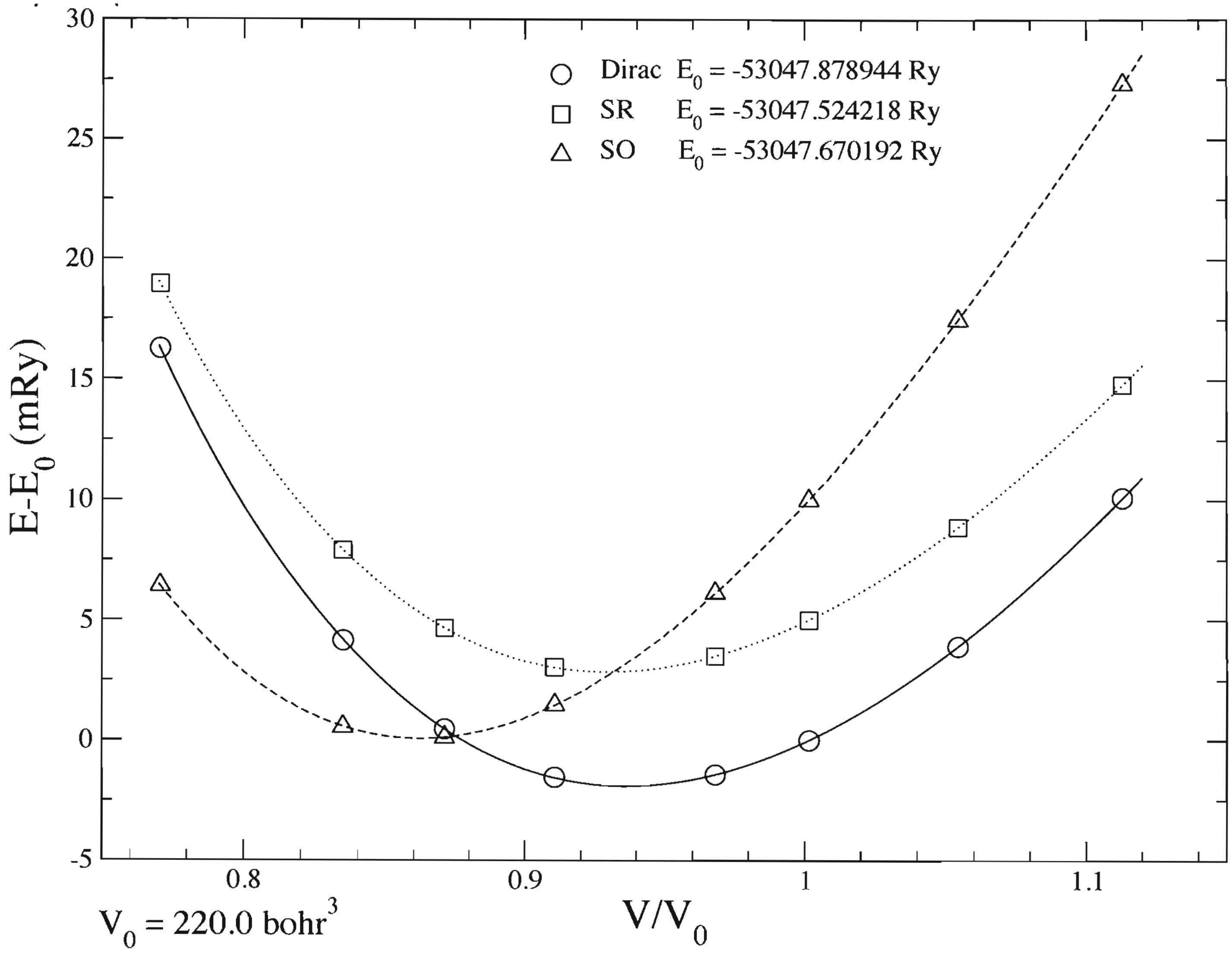
PBE exchange/correlation

V_{exp} = 220.00 bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- SR and Dirac differ considerably in energy, but differ only in detail with respect to shape and minimum energy.
- In contrast, while the SO energy is comparable to Dirac, the shape and minimum volume are very different.

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



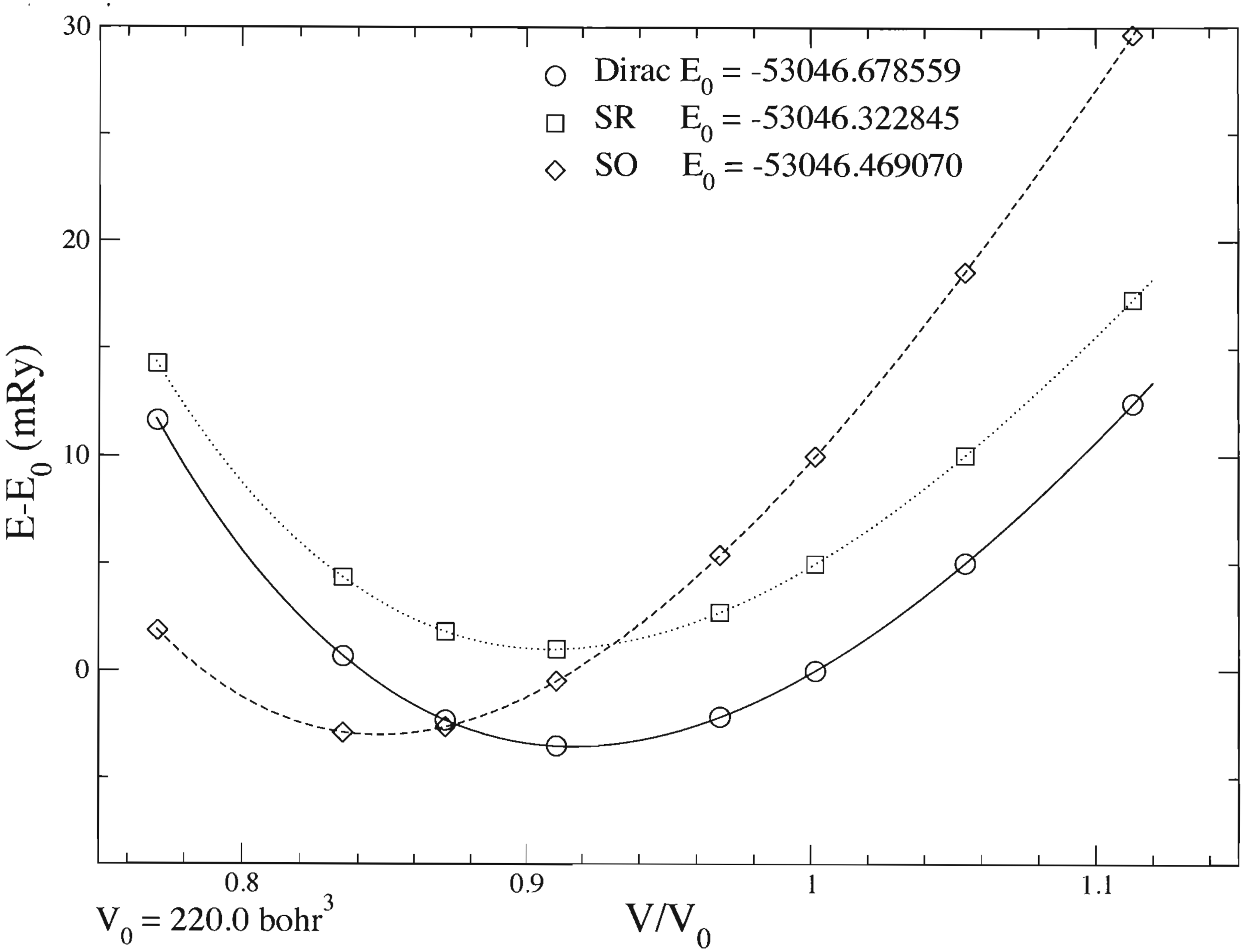
$V_0 = 220.0$ bohr^3

Energy vs Volume for Th using a double basis and the AM05 functional.

Dirac, SR, and SO are compared using a (FF) treatment of the interstitial.

$V_{exp} = 220.00$ bohr^3
$a = 9.583$ bohr $= 5.071$A
(Haas2009)

- The results are summarized in Table 1

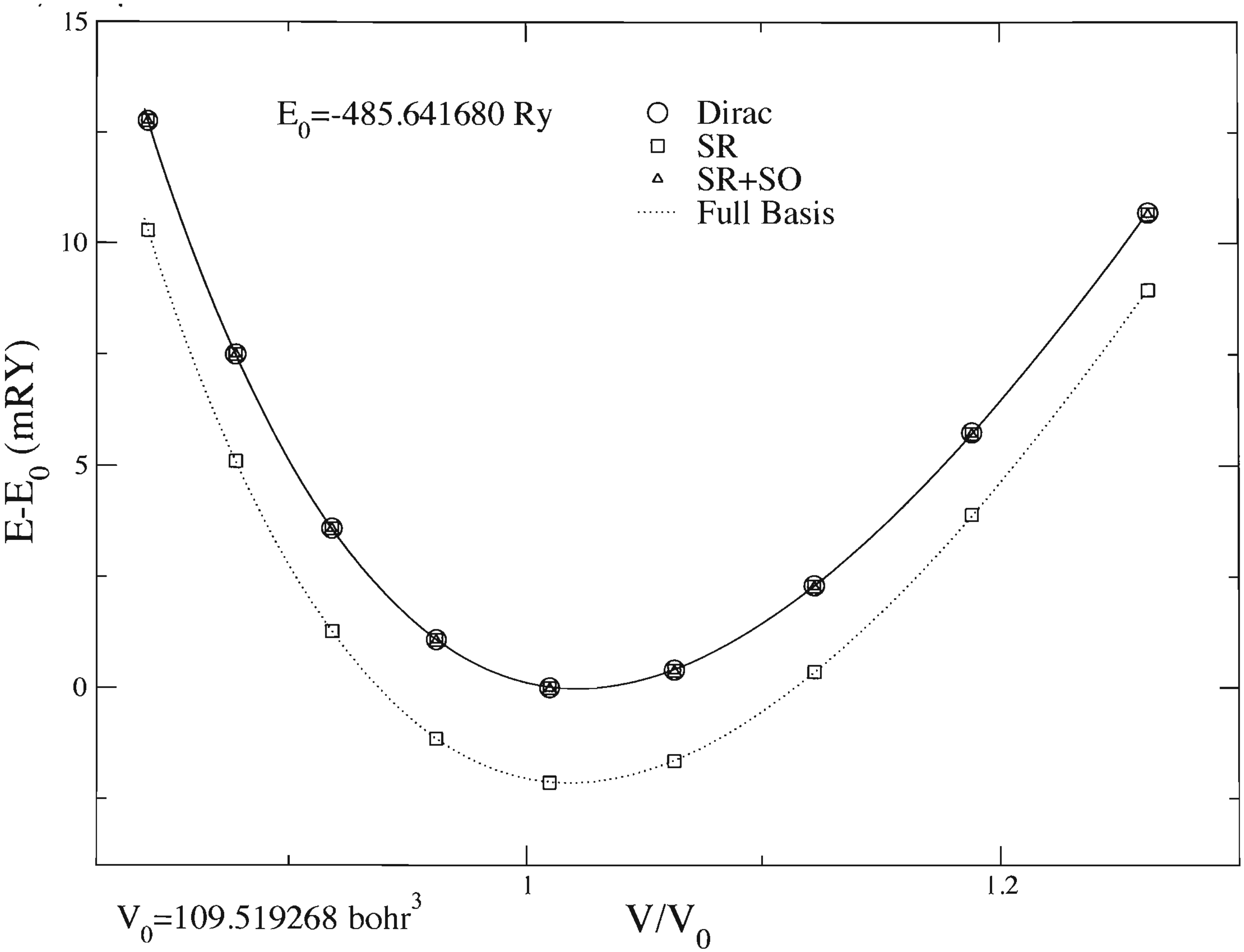


Energy vs Volume for Th using a double basis and the PW functional.

Dirac, SR, and SO are compared using a (FF) treatment of the interstitial.

V_{exp} = 220.00 bohr^3
a = 9.583 bohr = 5.071A
(Haas2009)

- The results are summarized in Table 1



Energy vs Volume for Al using a double basis and the PBE functional.

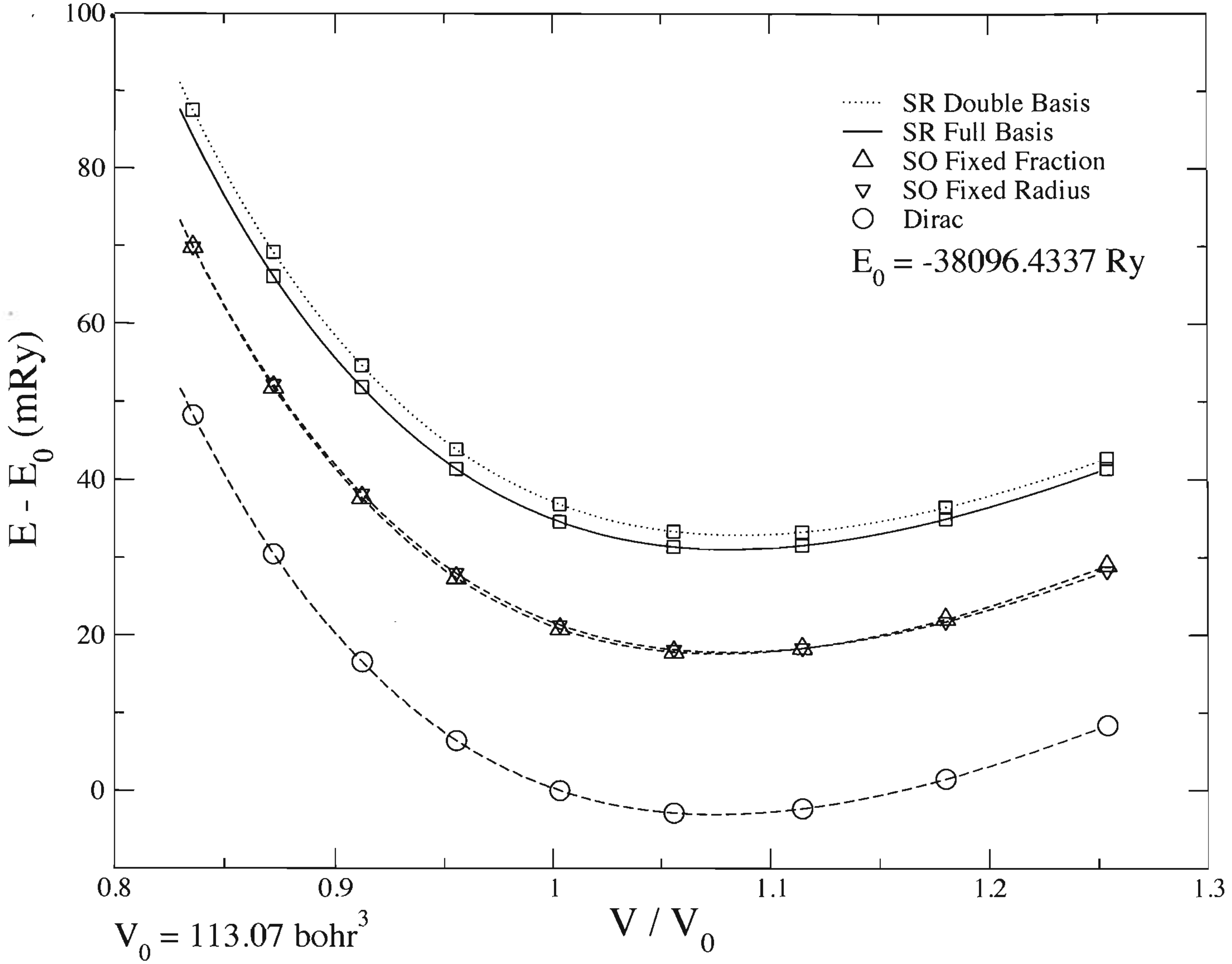
Dirac, SR, and SO are compared using a (FF) treatment of the interstitial.
Full basis results for SR are also shown.

$V_{exp} = 109.52$ bohr^3
a = 7.595 bohr = 4.019 A
(Haas2009)

- As Al os a very non-relativistic element, all methods give the same answer.
- The results show, as expected, that all methods produce energy curves that are essentially identical.
- Also shown is the EV curve for a full basis. Note the similarity in scale of the difference in energy between double and full bases as in Th.

TABLE II: Gold 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 the PBE functional. Results are obtained using a double basis as described in the text. Results for a full basis are also shown for the scalar relativistic method. The zero temperature experimental volume, with zero point motion subtracted, is 113.07 bohr^3[13]. Note the poor agreement with experiments that PBE gives. Reference 13 gives 114.09 for AM05. 120.93 for PBE, and 111.84 for PW.

	V/a_0^3	B (GPa)
Scalar Relativistic	123.07	135
Scalar Relativistic Full Basis	122.39	137
Scalar Relativistic+Spin Orbit	115.46	180
Full Dirac	121.82	141

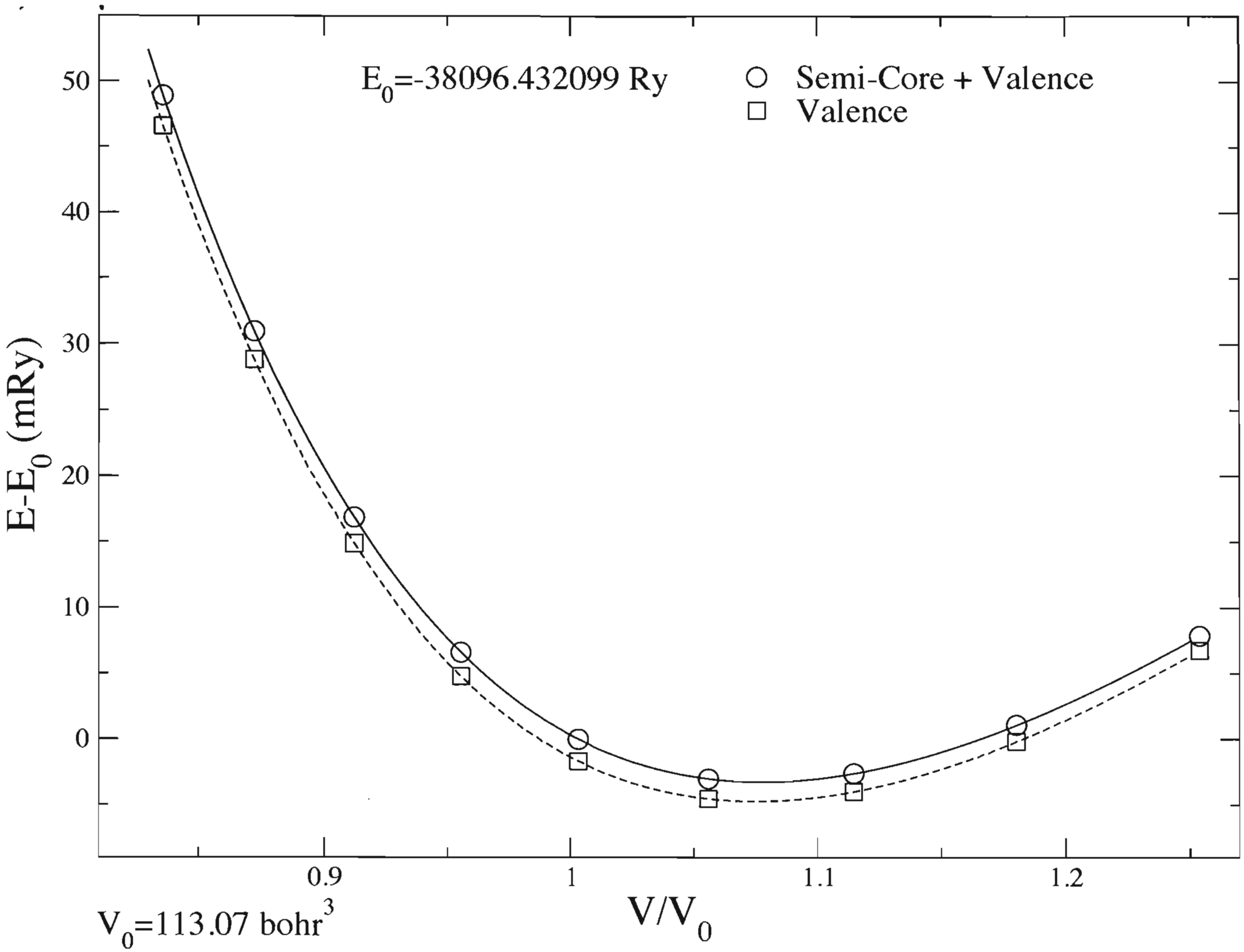


Energy vs Volume for Au with only valence electrons and the semi-core kept in the core, comparing FF and FR and for SO, double and full bases for SR, and a double Dirac basis.

PBE exchange/correlation.

$V_{exp} = 113.07$ bohr^3
a = 7.676 bohr = 4.062A
(Haas2009)

- Confining the semi-core (5s5p) states to the core is a good approximation in Au, since the semi-core and valence states are well separated in energy.
- All curves have a common zero of energy (energy offset).
- The effect of relativity is much larger than the difference in energy between double and full bases.
- Because the difference between FF and FR with SO is small, we concluded that the spin-orbit interaction is a small effect in Au.

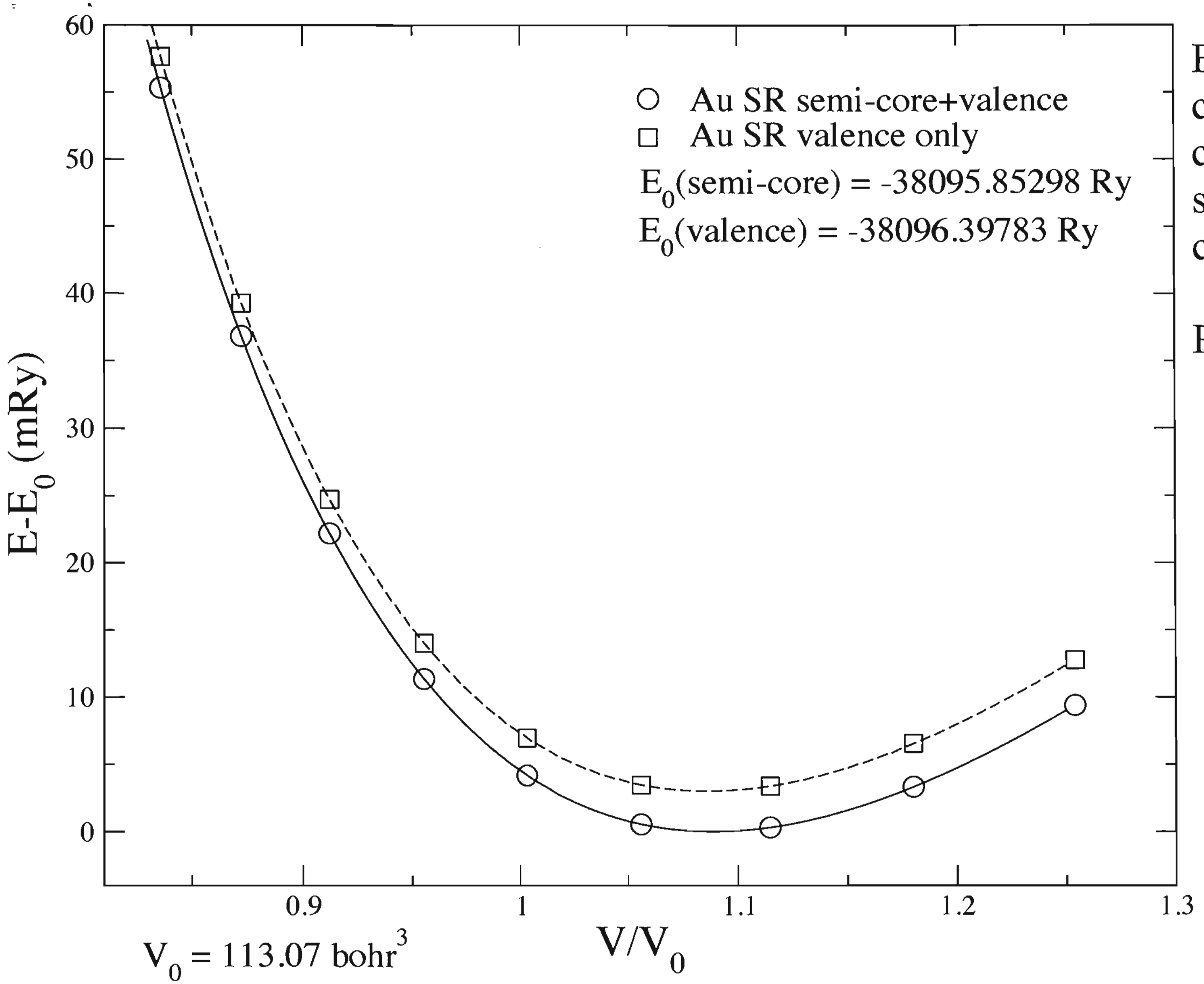


Energy vs Volume for Au calculated with Dirac bases, with valence only and semi-core+valence configurations.

PBE exchange/correlation.

$V_{exp} = 113.07$ bohr^3
$a = 7.676$ bohr $= 4.062$A
(Haas2009)

The small difference in energy, resulting from semi-core/valence hybridization, indicates that the semi-core is well separated from the valence, and there is no difference in shape, between the EV curves predicted by the Dirac method.
In Figure \ref{Au.SR.scValence} we show the same results obtained using the SR method.
There is a large difference in energy, resulting from using a different Hamiltonian on the semi-core states, but
again we find essentially no difference in shape.



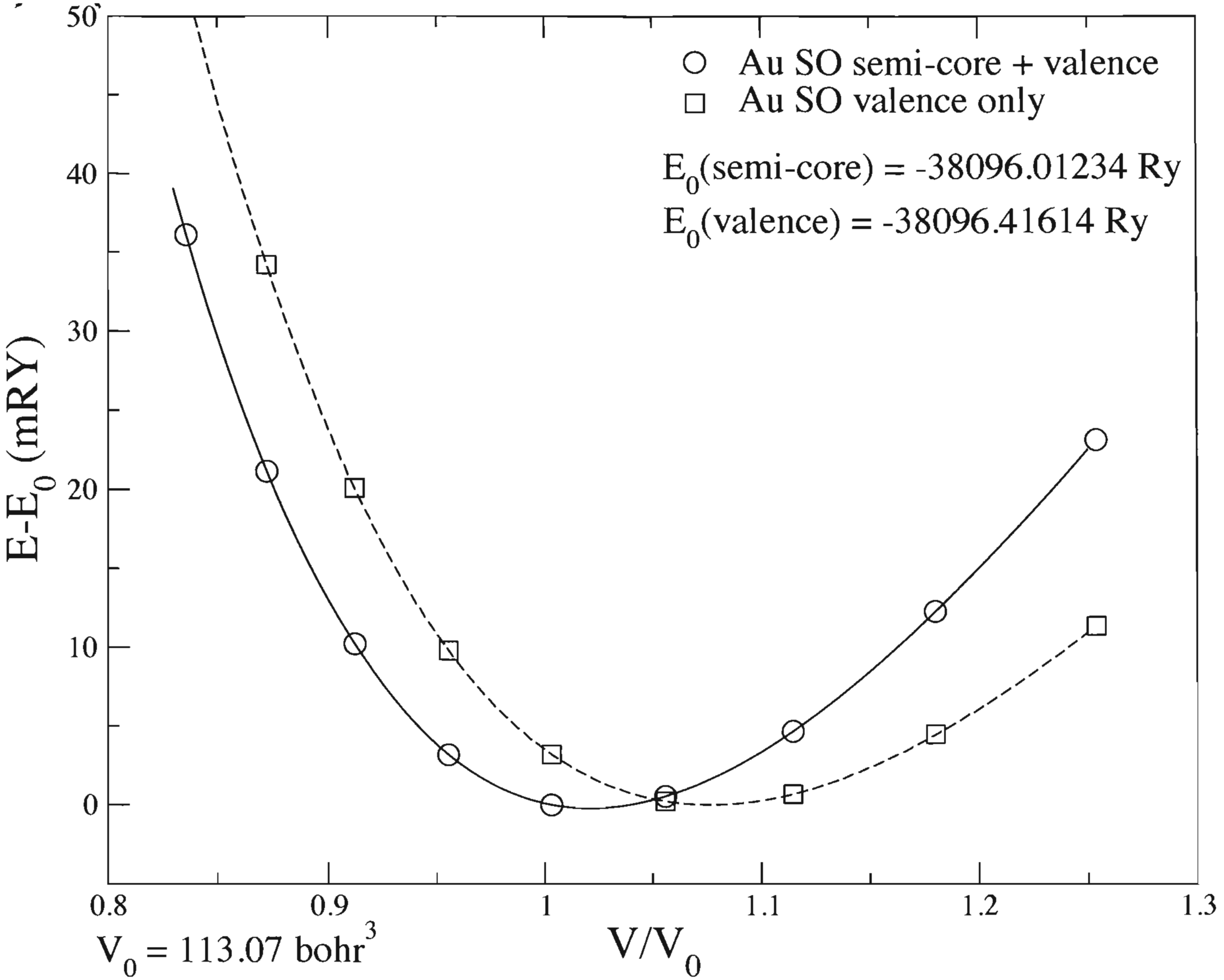
$V_0 = 113.07$ bohr^3

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

PBE exchange/correlation.

$V_{exp} = 113.07$ bohr^3
a = 7.676 bohr = 4.062A
(Haas2009)

- The same results obtained using the SR method show a large difference in energy, resulting from using a different Hamiltonian on the semi-core states, but again we find essentially no difference in shape.



$V_0 = 113.07$ bohr^3

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

PBE exchange/correlation.

$V_{exp} = 113.07$ bohr^3
a = 7.676 bohr = 4.062A
(Haas2009)

- This figure compares a calculation in which the semi-cores states are Dirac states, confined to the core and valence states are perturbed with the spin orbit calculation, with a calculation in which the semi-core and valence are perturbative.
- When there is significant hybridization between semi-core and valence states, the separation breaks down and cannot be accomplished.
- When the spin-orbit interaction is large, as for semi-core p-states, the perturbative treatment always fails.

Conclusions

The most reliable set of calculations in RSPt, or, in general, an all-electron augmented method, comes with using

- linear interpolation on a tetrahedral mesh for reciprocal space integration
- keeping the interstitial volume a fixed fraction of the total volume, especially if the basis is not converged.
- Accuracy requires using the Dirac equation to generate basis functions.
- SO can be used when the spin-orbit interaction is a small effect is small. It can't be used when spin-orbit is a large effect.
- The spin-orbit interaction is essential for describing semi-core p-states.
- To develop accurate functionals dealing with confinement, or to judge the accuracy of DFT+phenomenological methods applied to heavy materials, Dirac bases are essential.