PHYSICAL REVIEW B VOLUME 62, NUMBER 12 15 SEPTEMBER 2000-II

Approximate two-electron spin-orbit coupling term for density-functional-theory DFT calculations using the Douglas-Kroll-Hess transformation

J. C. Boettger
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 21 April 2000)

A simple approximation is developed for the two-electron spin-orbit coupling terms generated by the Douglas-Kroll-Hess transformation, in the context of density-functional theory (DFT). For the special case of an isolated atom, the two-electron spin-orbit matrix element for each pair of basis functions of type l is replaced with the spin-orbit matrix element for a point charge $-Q(l)$ placed at the origin; where $Q(l)=0,2,10,28,\ldots$. Application of this screened-nuclear-spin-orbit (SNSO) approximation to linear combination of Gaussian-type orbital (LCGTO) DFT calculations on Ce, Ta, and Pu atoms yields spin-orbit splittings that agree with results from a numerical solution of the Dirac-Kohn-Sham equations to within about 6%. This is a marked improvement over the nuclear-only spin-orbit approximation, which systematically overestimates spin-orbit splittings; in some cases by as much as 100%. Crystalline LCGTO DFT calculations on the fcc phases of the light-actinide metals Th→Pu, using a multiatom generalization of the SNSO approximation, yield atomic volumes that are in excellent agreement with results from full-potential linear-augmented-plane-wave calculations.

I. INTRODUCTION

The linear combinations of Gaussian type orbitals (LCGTO) method is the most widely used electronic structure technique in existence today, due largely to its range of applicability. At this time, the LCGTO method is routinely used to study such diverse systems as isolated clusters of atoms, one-dimensional (1D) periodic polymer chains, 2D periodic films, and 3D periodic crystals using both *ab initio* and density-functional theory (DFT) models. Until quite recently, however, all-electron LCGTO calculations were generally restricted to the first three rows of the Periodic Table due to the lack of a stable technique for incorporating relativistic effects.[1] That barrier has been overcome during the last decade through the use of ''no pair'' equations generated with the Douglas-Kroll-Hess (DKH) transformation.[2–4] In particular, an incomplete (nuclear-only) DKH transformation[5] can be used to generate a set of scalar-relativistic equations that are no more demanding computationally than their nonrelativistic counterparts, yet produce DFT results for atoms,[6,7] molecules,[8,9] and solids[10–14] that are comparable to results obtained with numerical methods.

Less attention has been paid to the fully relativistic (spin-orbit coupled) DKH equations, largely because the nuclear-only DKH equations seriously overestimate spin-orbit splittings, especially for f states, while inclusion of the two-electron spin-orbit terms would place a prohibitive burden on the computational resources required for calculations. In spite of these serious limitations, several fully relativistic crystalline LCGTO DFT calculations have been carried out for the light-actinide metals[13] (Th→Pu) and their oxides,[14] within the nuclear-only approximation. In fact, those studies explicitly relied on the nuclear-only approximation to provide an upper bound on the effects of spin-orbit coupling. In addition, a few fully relativistic calculations have been carried out with the two-electron spin-orbit coupling terms included within a one-center mean-field approximation, but only for relatively small molecules.[15–17] There remains a need for some intermediate approximation that is more accurate than the nuclear-only approximation, but less demanding than a full DKH calculation.

In this paper, a screened-nuclear-spin-orbit (SNSO) approximation is developed to replace the two-electron spin-orbit coupling terms in the DKH equations; initially for the special case of LCGTO DFT calculations on isolated atoms. The SNSO equations are no more computationally demanding than the fully relativistic nuclear-only DKH equations, and are easily generalized to multiatom systems. Crystalline LCGTO DFT calculations using the SNSO approximation are carried out for the atomic volumes and bulk moduli of the fcc phases of the light-actinide metals Th→Pu, a subject that has recently become controversial.[13,18]

II. DOUGLAS-KROLL-HESS APPROXIMATION

The development of the relativistic LCGTO DFT method used here begins with the four-component Dirac-Kohn-Sham (DKS) equations[19]

$$h_{DKS}^{(4)}\psi_i=[(c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta mc^2)+v_{eff}]\psi_i=\epsilon_i\psi_i, \tag{1}$$

where

$$v_{eff}=v_n+v_e+v_{xc} \tag{2}$$

is the effective one-electron potential formed from the nuclear potential v_n, the classical electronic Coulomb potential v_e, and the DFT exchange-correlation (XC) potential v_{xc}. The eigenvalues of the DKS equations are unbounded, above and below, since they include both electron and positron degrees of freedom. Therefore, any attempt to directly solve the DKS equations variationally will lead to the wellknown ‘‘variational collapse’’ problem, unless the basis set used is restricted in an appropriate fashion.[1] This difficulty can be circumvented by performing a unitary transformation on the DKS equations that approximately decouples the electron and positron states. For example, the DKS equations can be decoupled to arbitrary order in $(\mathbf{p}/mc)^2$ through a series of Foldy-Wouthuysen[20] transformations. Unfortunately, the Foldy-Wouthuysen procedure produces operators that are highly singular at the nucleus, hence, not amenable to an all-electron variational solution.

An alternative approach, which does not generate singular operators, uses the Douglas-Kroll-Hess transformation[2–4] to decouple the DKS equations to second-order in v_{eff}. This procedure yields the two-component DKH equation

$$h_{DKH}^{(2)}\phi_i=\epsilon_i\phi_i ,$$

$$h_{DKH}^{(2)}=E_p+A_p[v_{eff}+R_p v_{eff} R_p]A_p - \frac{1}{2}(E_p W^2+W^2E_p+2WE_pW), \tag{3}$$

where

$$E_p=c(p^2+m^2c^2)^{1/2}, \tag{4}$$

$$A_p=\left[\frac{E_p+mc^2}{2E_p}\right]^{1/2}, \tag{5}$$

$$R_p=K_p\boldsymbol{\sigma}\cdot\mathbf{p}, \tag{6}$$

$$K_p=c/(E_p+mc^2), \tag{7}$$

and W can be expressed in momentum space as

$$W_{p,p'}=A_p(R_p-R_{p'})A_{p'}\left[\frac{v_{eff}(\mathbf{p},\mathbf{p}')}{E_p+E_{p'}}\right], \tag{8}$$

with $v_{eff}(\mathbf{p},\mathbf{p}')$ being the momentum-space representation of v_{eff}.

As expressed, the DKH equations are fully relativistic, in the sense that they include mass-velocity, Darwin, and spin-orbit coupling corrections. If desired, the spin-orbit coupling terms can be separated from the scalar-relativistic terms. All of the spin-orbit coupling effects at first-order in v_{eff} are contained in the term $A_pR_pv_{eff}R_pA_p$. Using the standard properties of the Pauli matrices (σ), this term can be rewritten as

$$A_pR_pv_{eff}R_pA_p=A_pK_p(\mathbf{p}\cdot v_{eff}\mathbf{p}+i\boldsymbol{\sigma}\cdot\mathbf{p}\times v_{eff}\mathbf{p})K_pA_p . \tag{9}$$

The first term on the right-hand side is scalar relativistic, while the second term is a spin-orbit coupling term. The second-order terms in Eq. (3) are somewhat more complicated, but can be decomposed into scalar and spin-orbit terms in a similar fashion.[7]

Analytical evaluation of the GTO matrix elements for the momentum-space operators in Eq. (3) has not proven to be practical thus far. This difficulty can be circumvented by employing a basis set composed of p^2 eigenfunctions.[21] First, the matrix elements of $\mathbf{p}\cdot v_{eff}\mathbf{p}$ and $\mathbf{p}\times v_{eff}\mathbf{p}$ are evaluated along with the traditional nonrelativistic matrix elements. Next the nonrelativistic kinetic-energy matrix is diagonalized to obtain approximate eigenfunctions of p^2 and all of the matrices are transformed to this basis. Since the operators E_p, A_p, and K_p are diagonal in p^2 space, they can be obtained trivially from the p^2 eigenvalues. These basic components are then used to construct the more complicated matrix elements needed, such as $A_pR_pvR_pA_p$. Finally, all of the matrices are back-transformed to the original GTO representation.

The most serious drawback to the procedure described above is that the transformations for the two-electron integrals are computationally intensive. In the case of scalar-relativistic calculations, this difficulty can be avoided through use of a nuclear-only DKH approximation,[5] in which v_{eff} is replaced by v_n in all of the scalar-relativistic correction terms in Eq. (3). Unfortunately, as discussed above, the nuclear-only DKH approximation severely overestimates spin-orbit coupling because it fails to account for the screening effect of the electrons. The remainder of this work will therefore focus on approximately incorporating the two-electron spin-orbit terms in Eq. (3).

III. FULLY RELATIVISTIC LCGTO DFT CALCULATIONS FOR ATOMS

Isolated atoms provide a natural starting point for any investigation of spin-orbit coupling effects, because the high symmetry (and small size) of an atom makes it possible to calculate DFT atomic spin-orbit splittings either by solving the four-component DKS equations numerically[22] or by solving the complete DKH equations using a relatively large GTO basis set. In both cases, the spherical symmetry of v_{eff} allows the spin-orbit matrix elements to be simplified using the standard relationship

$$i\boldsymbol{\sigma}\cdot\mathbf{p}\times v_{eff}\mathbf{p}=2\mathbf{L}\cdot\mathbf{S}\frac{1}{r}\frac{dv_{eff}}{dr}. \tag{10}$$

For this work, an existing scalar-relativistic LCGTO DFT atom code[7] was extended to include spin-orbit coupling. The resulting code (SOATOM) is specifically designed to carry out DKH calculations with each term in the one-electron potential (v_n,v_e, and v_{xc}) treated at a different level of approximation. (The highest level of approximation currently implemented in SOATOM neglects only a few small terms; the scalar terms of the form v_ev_{xc}, all second-order spin-orbit coupling terms involving v_{xc}, and spin-orbit terms that scale as v_e^2.) In addition, SOATOM can use several DFT models, including the Hedin-Lundqvist[23] local density approximation (LDA) and the Perdew-Wang[24] generalized gradient approximation (GGA).

SOATOM was first used here to calculate LDA spin-orbit splittings for the occupied states of Ce, Ta, and Pu atoms, at two levels of approximation; the second-order nuclear-only spin-orbit (nSO) approximation and the second-order nuclear plus electronic spin-orbit (neSO) approximation. In both sets of calculations, all significant scalar-relativistic terms were included and all spin-orbit coupling terms involving v_{xc} were neglected. Basis set effects were minimized by using an exceptionally large $(40s40p33d28f)$ GTO basis set, derived from the universal basis set of Malli *et al.*[25] by removing the

TABLE I. Spin-orbit splittings (Ry) obtained for the orbitals of a Ce atom using the nuclear plus electronic (neSO) and nuclear-only (nSO) DKH approximations are compared with results from numerical Dirac calculations. An estimated effective point charge $Q_{est}(i)$ (defined in the text) is listed for each orbital. The spin-orbit splittings obtained here using the SNSO approximation, and their percentage errors relative to the numerical Dirac results, are given in the last two columns.

Orbital	Dirac	neSO	nSO	$Q_{est}(i)$	SNSO	Error
$2p$	32.7859	33.3094	34.6792	2.29	33.4012	+1.9%
$3p$	6.4409	6.5507	6.8353	2.41	6.5837	+2.2%
$4p$	1.3841	1.4084	1.4710	2.47	1.4170	+2.4%
$5p$	0.1906	0.1940	0.2028	2.52	0.1955	+2.6%
$3d$	1.3852	1.3682	1.6586	10.16	1.3711	−1.0%
$4d$	0.2405	0.2378	0.2906	10.54	0.2403	−0.1%
$5d$	0.0113	0.0111	0.0138	11.35	0.0115	+1.8%
$4f$	0.0205	0.0198	0.0387	28.33	0.0200	−2.4%

seven largest d exponents and 12 largest f exponents. The value of the largest exponent used for the s and p basis sets (roughly 3.4×10^8) implies that the $j=1/2$ states should be accurately represented to a distance of roughly 10^{-14} m from the nucleus. Test calculations using substantially smaller basis sets indicated that the representation of the $j=1/2$ states near the nucleus should not be an issue for any reasonable basis set selection.

The spin-orbit splittings obtained here for Ce, Ta, and Pu atoms, using the nSO and neSO approximations, are compared with results from numerical DKS calculations[22] in Tables I, II, and III, respectively. As noted earlier, the nSO approximation systematically overestimates all of the spin-orbit splittings, with the Ce $4f$ splitting being overestimated by nearly 100%. When the screening effects of v_e are included, the agreement with the numerical results is improved dramatically, with the maximum error being reduced to less than 6%. (Adding in the first-order spin-orbit coupling term involving v_{xc} only slightly reduces this maximum error, which appears to be intrinsic to the DKH approximation.) These results confirm that accurate fully relativistic LCGTO DFT calculations on large systems will require the development of some computationally tractable scheme for approximately incorporating the two-electron spin-orbit coupling terms.

TABLE II. Same as Table I, but for Ta.

Orbital	Dirac	neSO	nSO	$Q_{est}(i)$	SNSO	Error
$2p$	93.2619	96.0127	99.2563	2.39	96.1920	+3.1%
$3p$	20.0717	20.6843	21.4073	2.47	20.7489	+3.4%
$4p$	4.6390	4.7837	4.9572	2.55	4.8041	+3.6%
$5p$	0.6476	0.6682	0.6937	2.68	0.6723	+3.8%
$3d$	4.3752	4.3409	5.0594	10.37	4.3600	−0.3%
$4d$	0.8521	0.8459	0.9956	10.98	0.8578	+0.7%
$5d$	0.0424	0.0422	0.0505	12.00	0.0436	+2.8%
$4f$	0.1459	0.1427	0.2335	28.39	0.1437	−1.5%

TABLE III. Same as Table I, but for Pu.

Orbital	Dirac	neSO	nSO	$Q_{est}(i)$	SNSO	Error
$2p$	313.1508	330.4677	339.7566	2.57	330.4478	+5.5%
$3p$	72.5603	76.5642	78.1398	2.57	76.5848	+5.5%
$4p$	19.1427	20.2126	20.7957	2.64	20.2328	+5.7%
$5p$	4.6761	4.9400	5.0845	2.67	4.9481	+5.8%
$6p$	0.7264	0.7689	0.7904	2.57	0.7705	+6.1%
$3d$	14.5424	14.4913	16.3997	10.94	14.6266	+0.6%
$4d$	3.4939	3.4833	3.9681	11.48	3.5388	+1.3%
$5d$	0.6930	0.6911	0.7909	11.86	0.7059	+1.9%
$6d$	0.0298	0.0298	0.0342	12.11	0.0308	+3.4%
$4f$	0.9276	0.9143	1.3088	28.33	0.9178	−1.1%
$5f$	0.0728	0.0718	0.1064	28.55	0.0752	+3.3%

In the early 1960s, Blume and Watson[26,27] demonstrated that the full spin-orbit operator for the many-electron (*ab initio*) Hamiltonian could be rigorously divided into an effective one-electron operator and a residual two-electron operator, which depends on the particular orbital under consideration. Although this rigorous result is more interesting than useful in the context of large-scale calculations, it led to a commonly used technique for approximately incorporating spin-orbit coupling effects into calculations using effective core potentials. In that approach, the effect of spin-orbit coupling on a given valence shell is approximated by the spin-orbit coupling due to an effective nuclear charge Z_{eff}, which is simply adjusted to match experimental spin-orbit splittings.[28] An approach of this type is particularly appealing within the context of DFT, since the DKS equations are themselves effective one-electron equations. It is in this spirit that the present work will proceed.

Using Eqs. (9) and (10), ignoring v_{xc}, and dropping all second-order terms, which can be shown to have little effect on the atomic spin-orbit splittings, the spin-orbit coupling operator for a spherical potential can be written in the form

$$h_{SO}=A_pK_p(2\mathbf{L}\cdot\mathbf{S})\left[\frac{Z}{r^3}-\frac{Q(r)}{r^3}\right]K_pA_p\,, \tag{11}$$

where

$$Q(r)=\int_0^r \rho(x)x^2dx \tag{12}$$

is the electronic charge contained inside of a sphere of radius r centered on the nucleus. For any given atomic orbital ϕ_i, the spin-orbit operator of Eq. (11) could be replaced with an orbital dependent operator of the form

$$h_{SO}(i)=A_pK_p(2\mathbf{L}\cdot\mathbf{S})\left[\frac{Z}{r^3}-\frac{Q(i)}{r^3}\right]K_pA_p\,, \tag{13}$$

where

$$Q(i)=\frac{\langle i|Q(r)r^{-3}|i\rangle}{\langle i|r^{-3}|i\rangle} \tag{14}$$

is an effective point charge that screens the nuclear charge seen by ϕ_i.

Up to this point, no additional approximations have been made and no time saving has been achieved, since $Q(i)$ must still be calculated for all orbitals at each iteration. Nevertheless, an analysis of the values of $Q(i)$ for Ce, Ta, and Pu may be educational. Although $Q(i)$ could be exactly calculated for any given atomic orbital, such a calculation is not required for the present purpose. Instead, for each atomic orbital listed in Tables I, II, and III, the value of $Q(i)$ is roughly estimated here using the expression

$$Q_{est}(i)=Z\left[\frac{\Delta\epsilon_{nSO}(i)-\Delta\epsilon_{neSO}(i)}{\Delta\epsilon_{nSO}(i)}\right], \tag{15}$$

where $\Delta\epsilon_{nSO}(i)$ and $\Delta\epsilon_{neSO}(i)$ are the spin-orbit splittings obtained for orbital i in the nSO and neSO approximations. [Note that $Q_{est}(i)$ would be exact if ϕ_i was identical for the two approximations.] Values of $Q_{est}(i)$ are given for each atomic orbital in Tables I, II, and III.

Inspection of the $Q_{est}(i)$ in the tables reveals a strong l dependence, with $Q_{est}(i)$ ranging from 2.29→2.68 for p states, 10.16→12.11 for d states, and 28.33→28.55 for f states. This result suggests that the orbital dependent spin-orbit operator in Eq. (11) could be replaced with an effective l-dependent operator of the form

$$h_{SO}(l)=A_pK_p(2\mathbf{L}\cdot\mathbf{S})\left[\frac{Z}{r^3}-\frac{Q(l)}{r^3}\right]K_pA_p, \tag{16}$$

where

$$Q(l)=0,2,10,28,\ldots \tag{17}$$

is the total number of electrons contained in all filled shells with $n\leqslant l$. Given the values of $Q_{est}(i)$ listed in the tables, this model should at least provide a reasonable lower bound to the exact $Q(i)$ and has a rather transparent interpretation. Henceforth, this approximation will be referred to as the SNSO approximation, since the primary effect of $Q(l)$ is to screen the nuclear charge.

Atomic spin-orbit splittings obtained for Ce, Ta, and Pu using the SNSO approximation are listed in Tables I, II, and III. Close inspection of the tables reveals that the SNSO approximation produces results that only differ from the neSO results by a few percent. For example, the SNSO approximation overestimates the splitting of the Ce $4f$ orbital by 1%, relative to the neSO approximation, versus the nearly 100% overestimate produced by the nSO approximation. Comparison of the SNSO results with the nearly exact numerical Dirac results (see the errors listed in the tables) indicates that the maximum error is 6.1% (for the $6p$ orbital of Pu), most of which is actually due to the DKH approximation, not the SNSO approximation. These results suggest that the SNSO approximation should, at least, be reliable for atoms ranging from Ce ($Z=58$) to Pu ($Z=94$), and may prove useful for lighter atoms as well, since the errors appear to shrink as Z is reduced.

IV. EXTENSION TO CRYSTALLINE SOLIDS

In order to develop a computationally tractable method for extending the SNSO approximation to multi-atom systems, it will now be assumed that intersite spin-orbit coupling can be neglected. This assumption is consistent with results from recent DKH calculations on molecules[29] and is no more severe than the spin-orbit coupling approximation that is most commonly used in crystalline calculations, in which the spin-orbit operator is spherically averaged inside of a muffin-tin sphere and is set to zero outside.[30] With this assumption, the SNSO approximation can be implemented in any fully relativistic nuclear-only DKH code by replacing the nuclear-only spin-orbit operator h_{nSO} with a basis-function-dependent operator of the form

$$h_{SNSO}(i,j)=h_{nSO}-\sqrt{\frac{Q(l_i)}{Z_i}}h_{nSO}\sqrt{\frac{Q(l_j)}{Z_j}}, \tag{18}$$

where Z_i is the nuclear charge of the site on which the basis function ϕ_i is centered. It is trivial to show that Eq. (18) reduces to Eq. (16) for an isolated atom. This form of the SNSO approximation has been implemented in the program GTOFF,[31] which is designed to carry out DFT calculations on thin films and crystalline solids using the all-electron linear combinations of Gaussian-type orbital–fitting-function (LCGTO-FF) technique.[32]

The light-actinide metals Th→Pu, in their fcc phases, provide an ideal test for the multi-atomic SNSO approximation, since GTOFF has already been used to study those systems with scalar relativistic and fully relativistic nuclear-only DKH calculations.[13] Moreover, the atomic volumes of the light-actinide metals have recently become controversial.[13,18] The basic issues involved can be illustrated with the case of fully-relativistic GGA calculations on fcc Th. A series of calculations[18] using the full-potential linear muffin-tin orbital (FLMTO) method yielded an atomic volume for Th that is roughly 10% smaller than the experimental volume, an unusually large contraction for a GGA calculation. Subsequent calculations using two distinctly different methods, the LCGTO-FF method in the nuclear-only DKH approximation and the full-potential linear-augmented-plane-wave (FLAPW) method,[13] instead found atomic volumes that agreed with experiment to within about 3%. For the series of metals, Th→Pu, this general outcome was consistently repeated with the LCGTO-FF and FLAPW atomic volumes being in good qualitative agreement with each other (although the spin-orbit induced shifts are larger for the LCGTO-FF method, as expected) and the FLMTO volumes being 3→10% smaller. In each case, the former results were closer to experiment than the latter.[13] Tables IV and V list the atomic volumes and bulk moduli found in those studies for the fcc light-actinide metals using the GGA model.

The large discrepancy between the FLAPW and FLMTO results was particularly perplexing, since those methods use nearly identical approximations. Numerous test calculations on fcc Th (Ref. 33 and 34) ultimately revealed that the source of this discrepancy is an unfortunate coupling between the muffin-tin radius (used in both methods) and the spin-orbit coupling of the $6p$ state. In the FLAPW calculations, the muffin-tin radius was held fixed at a relatively small value throughout each series of calculations, whereas

TABLE IV. Atomic volumes (atomic units) for the fcc phases of the light-actinide metals Th→Pu obtained with the LCGTO-FF method using three DKH approximations [the nuclear-only scalar-relativistic (nSR) approximation, the nuclear-only fully-relativistic (nFR) approximation, and the screened-nuclear spin-orbit (SNSO) approximation] are compared with results from scalar-relativistic (SR) and fully relativistic (FR) FLAPW calculations, and FR-FLMTO calculations. All results are taken from Ref. 13, except the present SNSO results and the FR-FLMTO results (Ref. 18).

	nSR	SR-FLAPW	nFR	SNSO	FR-FLAPW	FR-FLMTO
Th	216.9	219.3	214.8	214.3	218.1	199.9
Pa	171.5	172.3	173.9	173.2	172.8	160.2
U	146.1	147.5	151.5	148.8	148.7	138.6
Np	131.6	131.4	142.2	137.2	137.9	125.8
Pu	121.2	122.3	141.4	133.4	133.4	119.2

the FLMTO calculations used a variable muffin-tin radius constrained to keep the ratio of the sphere volume to the cell volume constant. If the muffin-tin radii were treated the same in both methods, they produced similar results.

Although the reasonable agreement between the FLAPW, LCGTO-FF, and experimental atomic volumes suggests that the fixed-radius method is preferable to the fixed-volume-ratio method, this conclusion is not entirely beyond argument. One difficulty is that there are systematic differences between the LCGTO-FF and FLAPW results. The largest disagreement is for fcc Pu, where the atomic volume found with the LCGTO-FF method is 6% larger than the FLAPW result. While the most likely source for this difference is the nuclear-only DKH approximation, the muffin-tin instability associated with the FLAPW method may also have some residual impact. Thus a significant uncertainty remains in the calculated atomic volumes of the light-actinide metals. This uncertainty can now be reduced with LCGTO-FF calculations using the SNSO approximation.

Since the differences between the various calculations appear to be rooted in the approximations being used for spin-orbit coupling, a brief comparison of the methods is warranted at this time. In the FLAPW and FLMTO methods, the spin-orbit coupling of the core states is treated with a nearly exact numerical method. The spin-orbit coupling of the band states is included via a variational method. First basis functions are obtained by numerically solving the scalar-relativistic one-electron equations for a muffin-tin potential. Those ‘‘scalar-relativistic’’ basis functions are then used to variationally solve the full-potential one-electron equations with a spin-orbit operator that is spherically averaged inside the muffin-tin sphere, and is set to zero outside. A serious drawback to this approach is that the basis functions are forced to be orthogonal to the scalar-relativistic core states, not the fully relativistic core states. This problem is most significant for the p states, because the $j=1/2$ states are very different from the scalar-relativistic p states near the nucleus. This means that the p basis set used is far from complete inside of the muffin-tin sphere, and any small variation in the basis functions can therefore produce large shifts in the energy, and hence the muffin-tin instability.

TABLE V. Same as Table IV, except the entries are bulk moduli (GPa).

	nSR	SR-FLAPW	nFR	SNSO	FR-FLAPW	FR-FLMTO
Th	59	57	63	64	73	62
Pa	102	100	94	93	96	122
U	101	125	110	120	99	148
Np	142	137	112	132	140	161
Pu	170	153	97	85	121	143

TABLE VI. Atomic spin-orbit splittings (eV) obtained for the $6p$ and $5f$ orbitals of Pu using approximations and basis sets consistent with crystalline LCGTO-FF calculations and LASTO calculations (Ref. 35) are compared with splittings from numerical Dirac calculations. Errors relative to the Dirac calculations are also given.

	Dirac	LASTO	Error	LCGTO-FF	Error
$6p$	9.88	7.3	−26%	10.20	+3%
$5f$	0.99	0.98	−1%	0.98	−1%

To assess the impact of using scalar-relativistic basis functions during fully relativistic linearized-augmented Slater-type-orbital (LASTO) calculations on fcc Pu, Fernando *et al.*[35] calculated LDA spin-orbit splittings for the $6p$ and $5f$ states of a Pu atom using a scalar-relativistic LASTO basis set similar to that used for their bulk calculations. To allow a direct comparison, GTOFF has been used to calculate the same splittings with basis sets that are similar to those used in the earlier crystalline LCGTO-FF calculations. These sets of spin-orbit splittings are compared with numerical DKS results in Table VI. The large impact that the scalar-relativistic basis functions used in the LASTO method (and the FLMTO and FLAPW methods) have on the splittings of p states is clearly evidenced in the 26% underestimate of the $6p$ splitting. The excellent agreement between the LCGTO-FF spin-orbit splittings and the numerical results,

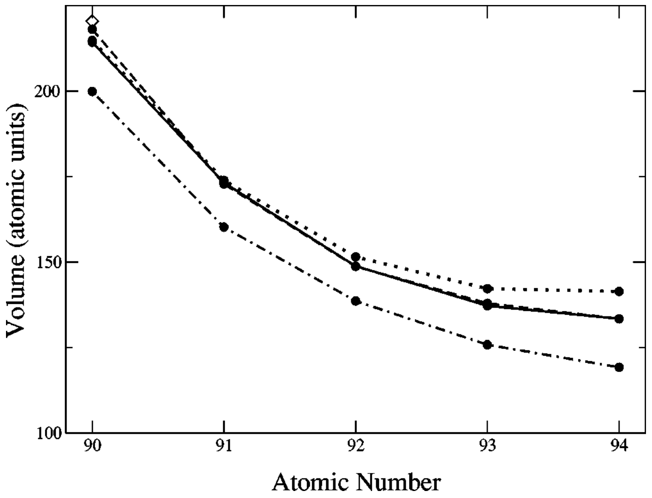

FIG. 1. Atomic volumes for the light-actinide metals Th→Pu obtained with the LCGTO-FF method within the SNSO approximation (solid line) are compared with results from nuclear-only DKH calculations (dotted line; Ref. 13), FLAPW calculations (dashed line; Ref. 13), and FLMTO calculations (dash-dotted line; Ref. 18). An atomic volume for Th obtained with the LCAO method using ZORA is also shown (diamond; Ref. 36).

and the absence of any muffin-tin instability in the LCGTO-FF method, suggests that fully relativistic LCGTO-FF results using the SNSO approximation should be substantially more reliable than results from FLMTO or FLAPW calculations.

Atomic volumes and bulk moduli for the fcc phases of the light-actinide metals Th→Pu were calculated here with GTOFF in the SNSO approximation, with the GGA, using the same basis sets as were used in the earlier LCGTO-FF calculations.[13] Those atomic volumes and bulk moduli are compared in Tables IV and V, and in Fig. 1, with the earlier GGA results[13,18] discussed above. Figure 1 also shows an atomic volume for Th calculated quite recently by Philipsen and Baerends[36] using a linear combinations of atomic orbitals (LCAO) method, with relativistic effects (including spin-orbit coupling) incorporated using the zeroth-order regular approximation (ZORA).[37] The atomic volumes obtained here for Pa→Pu using the SNSO approximation agree with the FLAPW results to within about 0.5%; see Fig. 1. For Th, the difference is somewhat larger (1.8%). Most of that difference, however, also appears in the scalar-relativistic atomic volumes, and cannot be attributed to spin-orbit coupling effects. This excellent agreement clearly indicates that the differences between the earlier LCGTO-FF results and the FLAPW results were due to the use of the nuclear-only DKH approximation, not the muffin-tin instability. It also is clear that the fixed-radius method used in the FLAPW calculations should be preferred to the fixed-volume-ratio method used in the FLMTO calculations. The various theoretical bulk moduli in Table V agree to the extent that can be expected for a derivative quantity determined from a fit to a rather small number of points; typically five or six.

V. SUMMARY

A screened-nuclear-spin-orbit (SNSO) approximation has been developed for the two-electron spin-orbit terms generated by the DKH transformation of the DFT one-electron equations. This approximation is no more computationally demanding than the nuclear-only DKH approximation, and is applicable both to isolated atoms and extended systems. For atoms ranging from Ce through Pu, the SNSO approximation yields spin-orbit splittings that agree with numerical calculations to within about 6%. For the fcc phases of the light-actinide metals, Th→Pu, the SNSO approximation produces atomic volumes that are in excellent agreement with results from recent FLAPW calculations.[13]

ACKNOWLEDGMENTS

Many helpful conversations with R. C. Albers, M. D. Jones, J. D. Johnson, and S. B. Trickey are gratefully acknowledged. This work was supported by the U. S. Department of Energy under Contract No. W-7405-ENG-36. Partial support was provided by the laboratory directed research and development (LDRD) program at Los Alamos National Laboratory.

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