

*Doctoral Thesis*

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**Development of Relativistic Effective Core  
Potential method for  $f$  elements**

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# 1 General Introduction

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## 1.1 General aspect

Recently, accurate quantum computational chemistry has evolved dramatically. The size of molecular systems, which can be studied accurately using molecular theory, is increasing rapidly. Theoretical chemistry has opened up a world of new possibilities and become an integral part of chemistry research.

The chemistry of  $f$  elements has received increasing attention in quantum chemistry. The complex electronic structure of lanthanide and actinide compounds poses a great challenge to both experimental and theoretical work. Due to high angular momentum and spin multiplicity of the low-lying states of lanthanide and actinide atoms with partially filled  $f$  and  $d$  shells, a large number of energetically adjacent molecular electronic states results, which are further split and mixed by a strong spin-orbit interaction. However, although no entirely satisfactory calculations on these systems can be performed at present, the rapid development of computer technology as well as methodology and software made considerable progress in the last decade. It will certainly enable rather accurate investigations of these compounds in the near future. Accurate treatment of these heavy-element systems requires incorporation of both relativistic and electron correlation effects. The relativistic effect in heavy atoms had not been regarded as an important effect for chemical properties so far because the relativistic effects appear primarily in the core region. However, recent studies have revealed the importance of relativistic effects, which play essential and vital roles in the total nature of molecular electronic structure for these systems.

This doctoral thesis presents the development of new relativistic effective core potential molecular theory and efficient computational schemes for treating  $f$  elements and their compounds with reasonable accuracy.

## 1.2 Development of third-order Douglas-Kroll *ab initio* model potential for actinides

Accurate *ab initio* molecular calculation on systems including many heavy atoms is a challenging problem in recent quantum chemistry. In particular, in order to describe accurately the complex electronic structure of such compounds, a large basis sets have to be used. The concomitant increase in the number of integrals to be evaluated and the size of matrices to be manipulated have so far prevented *ab initio* all electron relativistic and electron correlated treatments from becoming routine for polyatomic molecules. The development of computational quantum chemistry as an applicable and useful tool to achieve such realistic calculations has been closely connected with continuing improvement of the relativistic effective core potential methods (RECP). The RECP methods, which are all based on the frozen core approximation, can be grouped into two families: pseudopotential (PP) and model potential (MP) methods. The PP methods originate from Phillips-Kleinman equation and result in nodeless valence pseudoorbitals, while MP methods originate from Huzinaga-Cantu equation and result in valence orbitals, which retain their inner nodal structure. The *ab initio* model potential (AIMP) method has been developed as an extension of MP method and describes correct behavior for the inner nodal structure of valence orbitals. The AIMP method can be applied to different relativistic formulations. Currently, several relativistic AIMPs are available in literature, i.e. Cowan-Griffin AIMP (CG-AIMP), and its spin-orbit extension of Wood and Boring (WB-AIMP), relativistic elimination of small component AIMP (RESC-AIMP), second-order Douglas-Kroll AIMP (DK2-AIMP), third-order Douglas-Kroll AIMP (DK3-AIMP) methods and its spin-orbit extension.

The RECPs significantly reduce computational efforts and allows more rigorous treatment of electron correlation of valence electrons by replacing the chemically inert core electrons with a

potential acting on the valence electrons. By taking advantage of these facts, we have developed the third-order Douglas-Kroll *ab initio* model potential for actinides.

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## **2 Third-order Douglas-Kroll *ab initio* model potential for actinides**

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## 2.1 Third-order Douglas-Kroll *ab initio* model potential for actinides

### Abstract

A relativistic *ab initio* model potential (AIMP) method with the third-order Douglas-Kroll (DK3) approximation has been developed for the whole series of the actinide elements from Th to Lr. Two different cores, i.e., [Xe, 4*f*,5*d*] and [Xe, 4*f*], have been employed and the corresponding valence basis sets, (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*4*f*] and (14*s*10*p*12*d*9*f*)/[6*s*5*p*6*d*4*f*], are presented for all actinides. The mean absolute errors of the AIMP relative to the all-electron results for the atomic SCF valence orbital energies ( $\epsilon$ ) and the radial expectation values ( $\langle r \rangle$ ) are 0.003 (0.001) hartree and 0.004 (0.006) bohr with the small (large) core set. The spectroscopic properties of the  $^1\Sigma^+$  ground state of thorium monoxide, ThO, are calculated at the SCF and complete active space SCF (CASSCF) levels. The DK3-AIMP results again satisfactorily reproduce the all-electron DK3 results. The large core set gives almost the same results as the small set for atomic and molecular calculations, suggesting that the 5*d* electrons can safely be omitted from the valence electrons in actinide chemistry.

### 2.1.1 Introduction

The chemistry of *f* elements, lanthanides and actinides, has received much attention. This is because of their fascinating complexity due to the possible open *f* shells. They pose a great challenge to experimental and theoretical analysis. For actinides, both the electron correlation and relativistic effects have to be fully taken into account in order to get reliable results. The most widely used quantum mechanical method in the chemistry of lanthanides and actinides nowadays is the effective core potential (ECP) approximation.<sup>1-6</sup> In this approximation the core electrons are

modeled using a suitable function, and only the valence electrons are treated explicitly. Part of the relativistic effects, especially the scalar effects, may also be taken into account without having to perform full relativistic calculations.

In many cases it gives reasonable results while reducing computational effort. The *ab initio* model potential (AIMP) method<sup>7,8</sup> has been developed as an extension of the model potential methods<sup>2-6</sup> and describes the correct behavior for the inner nodal structure of the valence orbitals. The AIMP consists of a Coulomb potential, an exchange potential, and a projection operator, and has a clear physical meaning since it represents Coulomb and exchange interactions between a single valence electron and the core electrons. The implementation requires only modification of the one-electron operator in the usual AIMP methods.

Several sets of relativistic pseudopotentials are currently available in the literature.<sup>9-20</sup> However, relativistic effects for the heavy elements such as actinides are very significant and a highly accurate treatment is required even at the scalar relativistic level of theory. The main purpose of this study is to develop highly accurate AIMP for all actinide elements from Th to Lr by means of the third-order Douglas-Kroll (DK3) approximation.<sup>21,22</sup> In order to check the performance of the present AIMP, illustrative calculations on the spectroscopic constants for the  $^1\Sigma^+$  ground state of thorium monoxide, ThO, have been carried out using SCF and complete active space SCF (CASSCF) methods. The results are compared with the corresponding all-electron calculations.

### 2.1.2 AB INITIO MODEL POTENTIALS AND VALENCE BASIS SETS

Relativistic effects were incorporated by the third-order Douglas-Kroll approximation.<sup>21,22</sup> The no-pair DK3 Hamiltonian<sup>22</sup> is given by

$$H_+^{\text{DK3}} = H_+^{\text{DK2}} + \frac{1}{2} \sum_i [W_1(i), [W_1(i), V_{\text{eff}}(i)]], \quad (1)$$

where  $H_+^{\text{DK2}}$  is the second-order Douglas-Kroll (DK2) Hamiltonian<sup>23-25</sup> and can be written as

$$H_+^{\text{DK2}} = \sum_i E_i - mc^2 + \sum_i V_{\text{eff}}(i) + \frac{1}{2} \sum_{i \neq j} V_{\text{eff}}(i, j) - \frac{1}{2} \sum_i [W_1(i), [W_1(i), E_i]_+]_+ \quad (2)$$

with

$$E_i = (p_i^2 c^2 + m^2 c^4)^{1/2}, \quad (3)$$

$$V_{\text{eff}}(i) = A_i [V_{\text{ext}}(i) + (\boldsymbol{\sigma}_i \mathbf{R}_i) V_{\text{ext}}(i) (\boldsymbol{\sigma}_i \mathbf{R}_i)] A_i, \quad (4)$$

$$V_{\text{eff}}(i, j) = A_i A_j \left[ \frac{1}{r_{ij}} + (\boldsymbol{\sigma}_i \mathbf{R}_i) \frac{1}{r_{ij}} (\boldsymbol{\sigma}_i \mathbf{R}_i) + (\boldsymbol{\sigma}_j \mathbf{R}_j) \frac{1}{r_{ij}} (\boldsymbol{\sigma}_j \mathbf{R}_j) \right. \\ \left. + (\boldsymbol{\sigma}_i \mathbf{R}_i) (\boldsymbol{\sigma}_j \mathbf{R}_j) \frac{1}{r_{ij}} (\boldsymbol{\sigma}_i \mathbf{R}_i) (\boldsymbol{\sigma}_j \mathbf{R}_j) \right] A_i A_j, \quad (5)$$

$$A_i = \left( \frac{E_i + mc^2}{2E_i} \right)^{1/2}, \quad (6)$$

$$\mathbf{R}_i = \frac{c \mathbf{p}_i}{E_i + mc^2}, \quad (7)$$

where  $V_{\text{ext}}$  is the external potential,  $m$  is the mass,  $c$  is the speed of light,  $\mathbf{p}_i$  is the momentum operator, and  $\boldsymbol{\sigma}_i$  denotes the vector of three Pauli  $2 \times 2$  spin matrices. Here,  $W_1(i)$  is an integral operator with kernel,

$$W_1(\mathbf{p}_i, \mathbf{p}_i') = A_i (\mathbf{R}_i - \mathbf{R}_i') A_i' \frac{V_{\text{ext}}(\mathbf{p}_i, \mathbf{p}_i')}{E_i + E_i'}, \quad (8)$$

and  $[a, b]_+$  and  $[a, b]$  denote the anti-commutator and the commutator, respectively. For light elements, the DK2 approximation in Eq. (2) is sufficient. However, for heavy elements, with  $Z$  larger than 80, the DK3 approximation is indispensable for an accurate description of relativistic effects.

In this study, the spin-free part of the DK3 Hamiltonian was used and the spin-dependent

term was not considered. The relativistic kinematics correction to the two-electron integrals was ignored, since the effects of two-electron integrals have been shown to be small. Modification of the one-electron integrals for the third-order relativistic correction with the DK3 Hamiltonian is not expensive in comparison with the DK2 Hamiltonian. The speed of light in a vacuum was taken to be 137.0359895 a.u.

The spin-free valence-only DK3-AIMP Hamiltonian with approximations described above is given as

$$H^{DK3-AIMP} = \sum_{i=1}^{N_v} \left\{ E_i - mc^2 + V_{eff}(i) - \frac{1}{2} [W_1(i), [W_1(i), E_i]_+] + \frac{1}{2} [W_1(i), [W_1(i), V_{eff}(i)]]_+ \right. \\ \left. + \sum_{\mu} \left[ \frac{Z_{\mu}^{core}}{|r_i - R_{\mu}|} + V_{\mu}^{DK3-AIMP} \right] + \sum_{i>j=1}^{N_v} \frac{1}{r_{ij}} + \sum_{\mu>\nu} \frac{Z_{\mu}^{eff} Z_{\nu}^{eff}}{|R_{\mu} - R_{\nu}|} \right\} \quad (9)$$

where the first four terms are identical to the all-electron terms in Equations (1) and (2) and with

$$V_{\mu}^{DK3-AIMP} = V_{Coul}^{\mu,MP} + V_{Exch}^{\mu,MP} + P_{core}^{\mu} \quad (10)$$

The  $V_{Coul}$  operator represents the Coulomb interactions of one valence electron with the  $Z_{core}$  electrons and the same number of protons located at the nucleus. It is convenient to fit  $V_{Coul}$  with a linear combination of Gaussian functions

$$V_{Coul}(i) = -\frac{Z_{core}}{r_i} + 2 \sum_c^{core} J_c(i) \approx V_{Coul}^{MP}(i) = \sum_j C_j \frac{e^{-\alpha_j r_i^2}}{r_i} \quad (11)$$

In the same way, the  $V_{exch}$  operator represents the exchange interaction between one valence electron and the core electrons. Its spectral representation operator replaces this operator

$$V_{exch}(i) = -\sum_c^{core} K_c(i) \approx V_{exch}^{MP}(i) = \sum_l \sum_{m=-l}^l \sum_{a,b} |a; lm\rangle A_{l,ab} \langle b; lm| \quad (12)$$

where  $a$  and  $b$  are arbitrary Gaussian functions.  $A_{l,ab}$  is an element in the following matrix:

$$A = S^{-1} K S^{-1} \quad \text{where } K_{ij} = \langle i | V_{exch} | j \rangle \text{ and } S_{ij} = \langle i | j \rangle \quad (13)$$

By using these operators, all of the one-electron exchange integrals become those of the all-electron calculation, if  $\langle i|$  and  $|j\rangle$  belong to the  $\{a;lm\}$  and  $\{b;lm\}$  basis functions. The operator  $P(i)$  is obtained by the core-valence orthogonality, and consists of the core orbitals,  $\phi_c$ , and the core orbital energies,  $\varepsilon_c$ . The nodal structures of the valence orbitals are ensured through this operator.

$$P(i) = -\sum_c^{core} 2\varepsilon_c |\phi_c\rangle\langle\phi_c| \quad (14)$$

In this way, the direct relativistic effects on the valence electrons are handled with the no-pair relativistic operators of kinetic (and rest mass) energy and nuclear attraction and the indirect relativistic effects on the valence electrons brought about by the core electrons are considered by means of the core AIMP.

### 2.1.3 RESULTS

#### A. Atomic results

The valence configuration  $6s^2 6p^6 5f^l 6d^2 7s^1$  for Th,  $6s^2 6p^6 5f^{n+1} 6d^1 7s^1$  for Pa, Am and  $6s^2 6p^6 5f^n 6d^1 7s^2$  for U to Pu and Cm to Lr, where  $n$  stands for the position number of the respective atom in the actinide series (Pa = 2 to Lr = 14), were chosen as the reference states. The all-electron SCF calculations with the scalar relativistic DK3 were performed on these reference states with the relativistic uncontracted GTO.<sup>26</sup> The orbitals and the orbital energies from these reference calculations were adopted in the present AIMP method to describe the inner core orbitals.

According to its basic approximations, the AIMP method should work when the frozen-core approximation itself works. Furthermore, the accuracy improves systematically with the quality of the valence basis set. It has been found that the AIMP perform best with all-electron basis sets. We examined the partitioning of the core and valence orbitals. Numerical experience suggests two cores, i.e., the large [Xe, 4f, 5d] and the small [Xe, 4f] cores. That is, the 6s, 6p, 5f, 6d, and 7s electrons are treated as the valence electrons in the large core set while keeping 78 electrons

as the core electrons. In the case of the small cores, the 5*d* electrons are also treated as valence electrons and 68 electrons are treated as the core electrons.

The core 78 or 68 electrons were replaced with the potential. The linear combination of the 14 and 15 terms of the Gaussian-type functions were fitted to the Coulombic potentials calculated from the reference core orbitals. The exponents of the valence basis sets were optimized for the respective reference states by means of the minimization of the DK3 valence SCF total energies. The high quality of the inner part of the AIMP valence orbitals requires the use of basis sets with a relatively large number of primitive functions as compared with the nodeless pseudopotentials. This fact, however, does not represent a real increment in the computing time in molecular calculations. The computational cost depends on the number of contracted functions rather than on the length of their expansion. The number of basis functions (contracted functions) in AIMP molecular calculations is more or less the same as in corresponding pseudopotential calculations. *The bonus of the inner quality of the valence orbitals should be expected in calculations of valence correlation energies and in spin-orbit effects.*

The valence basis sets were contracted using the DK3 SCF valence orbital coefficients, and the outermost four *s*-type, four *p*-type, four *d*-type and three *f*-type primitives were augmented to give more flexibility to the orbitals in the molecular calculations. The resulting valence basis sets for Th to Lr are (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*4*f*] for a large core [Xe, 4*f*,5*d*] and (14*s*10*p*12*d*9*f*)/[6*s*5*p*6*d*4*f*] for a small core, i.e., [Xe, 4*f*].

The atomic valence properties, the orbital energies ( $\varepsilon$ ) and radial expectation values ( $\langle r \rangle$ ) are calculated with the present AIMP and a valence basis set in a fully uncontracted manner. The results with a large core are given in Table I and those with a small core are shown in Table II. The present DK3-AIMP results with small and large cores are very similar and both results reproduce the all-electron calculation to high accuracy. The mean absolute errors (MAE) for the small and large core sets are 0.003 and 0.001 hartree for the orbital energies and 0.004 and 0.006

bohr for the radial expectation values. Note that the fitting of the valence orbitals is not included in the optimization procedure for either the core potentials or the valence basis sets. Nevertheless, the present AIMP satisfactorily reproduces the valence orbitals to an excellent accuracy in the atomic calculations. The  $r^2R(r)^2$  functions for the valence orbitals of the Th atom are plotted in Figure 1. The difference between the AIMP and all-electron results is too small to be visible for the entire  $r$  range on the scale of the figure.

Both small and large cores give almost identical values for all actinide atoms. We assume that the  $5d$  electrons are not valence electrons, and thus can be safely frozen into the core. That is, the  $6s$ ,  $6p$ ,  $5f$ ,  $6d$ , and  $7s$  electrons are expected to play an active role in actinide chemistry.

## B. Molecular calculations on ThO

The spectroscopic properties, namely the dissociation energy  $D_e$ , the rotational constant  $B_e$ , the vibrational wave number  $\omega_e$ , and the bond length  $r_e$ , were calculated for the  $^1\Sigma^+$  ground state of thorium monoxide, ThO, using the SCF and CASSCF methods. To obtain the bond length  $r_e$ , the total energy was calculated for several Th-O distances, differing by 0.05 a.u. Then the minimum has been obtained by fitting a third-degree polynomial to the eight points of lowest energy. The same potential has been used to calculate  $\omega_e$  and  $B_e$ . The dissociation energy  $D_e$  was subtracted from the corresponding atomic ground states of the Th  $6d^27s^2\ ^3F$ , O  $2p^4\ ^3P$  and molecular calculations of the  $^1\Sigma^+$  ground state of ThO, Th $^{2+} 7s^2 O^{2-} 2p^6$ , respectively.

Our calculations were carried out in  $C_2$  symmetry, using the program system MOLCAS 5<sup>27</sup> modified for the inclusion of the DK3-AIMP. The active space in CASSCF was chosen to include eight electrons distributed over nine orbitals ( $7s$  and  $6d$  of thorium,  $2p$  of oxygen) while the  $2s$  orbital of oxygen was kept doubly occupied.

We used two different cores for the thorium atom, the large core [Xe, 4*f*,5*d*] with the (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*4*f*] valence basis set and the small core [Xe, 4*f*] with the (14*s*10*p*12*d*9*f*)/[6*s*5*p*6*d*4*f*] valence basis set. For the oxygen atom we have produced the same kind of DK3-AIMP, i.e., a [He] core with the (6*s*7*p*1*d*)/[3*s*4*p*1*d*] basis set. The linear combination of the twelve terms of the Gaussian-type functions was fitted to the Coulomb potential, and the (6*s*6*p*) valence basis set was optimized in the oxygen <sup>3</sup>P ground state. The valence basis set was contracted into the atomic DK3 SCF valence orbitals, and the outermost two *s*-type and three *p*-type primitives were added. This basis set was further augmented by one *p*-type Gaussian primitive with the exponent 0.059,<sup>28</sup> and one *d*-type Gaussian primitive with the exponent 1.154,<sup>29</sup> representing the diffuse and the polarization functions, resulting in a (6*s*7*p*1*d*)/[3*s*4*p*1*d*] basis set. The basis sets employed in all-electron DK3 calculations were the relativistic GTO basis sets taken from reference 26, and augmented in the same way in the valence region: (12*s*9*p*1*d*)/[4*s*4*p*1*d*] for oxygen and (35*s*26*p*18*d*13*f*)/[11*s*9*p*8*d*5*f*] for thorium.

The calculated results are listed in Table III. The previous calculations and experimental data are also listed for comparison. Careful examination of the table shows that the AIMP satisfactorily reproduces the all-electron results and there is no significant difference in the quality between the AIMP with a small core and that with a large core.

The AIMP-SCF with a large core, [Xe, 4*f*,5*d*] gives a bond length of 1.833 Å and the AIMP-CASSCF yields  $r_e = 1.879$  Å. The SCF calculation yields a bond length slightly shorter, while the CASSCF calculation gives a longer bond length relative to experiment. However, AIMP reproduces the all-electron bond length at both levels of theory. The difference is only 0.001 Å and 0.002 Å at the SCF and CASSCF levels, respectively. The AIMP gives vibrational frequencies that are close to the all-electron values. The difference between AIMP and all-electron calculations is 14 cm<sup>-1</sup> (SCF) and 10 cm<sup>-1</sup> (CASSCF). This is also true for the rotational constant. The difference between AIMP and all-electron calculations is only 0.001 cm<sup>-1</sup>. The observed

dissociation energy is 9.00 eV for ThO. The SCF  $D_e$  is very poor compared with the experimental value. However, the AIMP-SCF  $D_e$  of 5.96 eV is close to the all-electron SCF  $D_e$  of 5.82 eV. The CASSCF improves the deficiency of the SCF and gives a value close to the observed one. Again, the AIMP-CASSCF value of 9.14 eV is close to the all-electron value of 9.01 eV. The present calculations show that the AIMP with a large core, [Xe, 4f,5d] works well at the SCF and CASSCF levels.

As expected, spectroscopic properties calculated by AIMP with a small core [Xe, 4f] are very close to the all-electron values. The AIMP values agree with the all-electron ones within 0.001 Å in  $r_e$ , 8 cm<sup>-1</sup> in  $\omega_e$  and 0.001 cm<sup>-1</sup> in  $B_e$ . The dissociation energy reproduces the all-electron value with an error of less than 0.14 eV.

The present calculations confirm that the DK3-AIMP works quite well, and that the errors relative to the all-electron calculations are acceptable. In addition, the large core gives a similar accuracy to the small core, leading to the conclusion that the 5d electrons can be treated as core electrons in actinide chemistry.

The table also lists the previous results calculated with the Cowan-Griffin AIMP<sup>30</sup> and the relativistic energy-adjusted pseudopotential.<sup>12</sup> The Cowan-Griffin AIMP employs the same core-valence partitioning as the present large core while the energy-adjusted pseudopotential uses a smaller core than the present treatment. It is difficult to discuss the quality of these ECPs from the limited data. However, all calculations show very similar tendencies for the spectroscopic properties of ThO. The table also includes the all-electron Dirac-Hartree-Fock results.<sup>31</sup> Dirac-Hartree-Fock includes the spin-dependent effect such as the spin-orbit effect, which is not considered in the present treatment. Comparison with our AIMP-SCF results suggests that the spin-orbit effect is significant, particularly on the bond length and the dissociation energy of ThO.

#### 2.1.4 CONCLUSION

We have developed the AIMP for the actinide series from Th to Lr. Two different cores, large [Xe, 4*f*,5*d*] and small [Xe, 4*f*] cores have been employed and the corresponding valence basis sets, (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*4*f*] and (14*s*10*p*12*d*9*f*)/[6*s*5*p*6*d*4*f*], were optimized by minimizing the valence SCF total energies. The relativistic effect was considered through the scalar relativistic DK3 approximation. The present AIMP, and the valence basis sets, were tested for the atoms and ThO. The atomic and molecular results are in excellent agreement with all-electron calculations. These illustrative calculations confirm that the present AIMP is of sufficient accuracy throughout the actinide series. The large core set gives almost the same results as the small set for atomic and molecular calculations, suggesting that the 5*d* electrons could safely be omitted from the valence electrons in actinide chemistry.

The present AIMP can easily be combined with highly accurate relativistic effect and correlation treatments, both of which are vital for the actinides. While in this study we neglected the effect of spin-orbit coupling which is important for 5*f* elements, the spin-orbit effects may be included by means of mean-field and AIMP-based spin-orbit methods.<sup>33</sup> Thus, the entire field of actinide chemistry is now open for an accurate theoretical treatment.

The present DK3-AIMP core and valence basis sets are available on AIP Document E-PAPS files.<sup>34</sup>

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***Figure caption***

Figure 1. The  $r^2R(r)^2$  functions for the  $5d$ ,  $6s$ ,  $6p$ ,  $5f$ ,  $6d$ ,  $7s$  orbitals for the corresponding small and large core sets of the excited state of ( $^5I$ ) Th. The solid and dotted lines denote the AIMP and the all-electron (AE) results, respectively.

Table I. The spin-free relativistic valence orbital energies ( $\varepsilon$ ) and radial expectation values ( $\langle r \rangle$ ) both in the DK3-AIMP and all-electron (AE) calculations. The DK3-AIMP calculations correspond to a large [Xe, 4*f*,5*d*] core and a 6*s*, 6*p*, 5*f*, 6*d*, and 7*s* valence.

Configuration				AIMP		AE	
				$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)	$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)
Th	$5f^4 6d^2 7s^1$	$^5I$	6 <i>s</i>	-1.907	1.589	-1.912	1.585
			6 <i>p</i>	-0.964	1.931	-0.968	1.923
			5 <i>f</i>	-0.180	1.723	-0.180	1.713
			6 <i>d</i>	-0.168	3.501	-0.167	3.502
			7 <i>s</i>	-0.187	4.643	-0.187	4.635
Pa	$5f^3 6d^1 7s^1$	$^6L$	6 <i>s</i>	-1.897	1.563	-1.902	1.558
			6 <i>p</i>	-0.925	1.914	-0.928	1.906
			5 <i>f</i>	-0.176	1.672	-0.174	1.666
			6 <i>d</i>	-0.120	4.060	-0.118	4.073
			7 <i>s</i>	-0.178	4.783	-0.178	4.755
U	$5f^3 6d^1 7s^2$	$^5L$	6 <i>s</i>	-2.123	1.501	-2.126	1.499
			6 <i>p</i>	-1.069	1.829	-1.072	1.824
			5 <i>f</i>	-0.397	1.438	-0.390	1.441
			6 <i>d</i>	-0.229	2.978	-0.228	2.969
			7 <i>s</i>	-0.196	4.389	-0.196	4.391
Np	$5f^4 6d^1 7s^2$	$^6L$	6 <i>s</i>	-2.203	1.466	-2.206	1.464
			6 <i>p</i>	-1.098	1.791	-1.102	1.786
			5 <i>f</i>	-0.451	1.356	-0.443	1.359
			6 <i>d</i>	-0.234	2.910	-0.233	2.902
			7 <i>s</i>	-0.199	4.335	-0.199	4.331
Pu	$5f^6 6d^1 7s^2$	$^7K$	6 <i>s</i>	-2.297	1.431	-2.298	1.431
			6 <i>p</i>	-1.138	1.752	-1.142	1.749
			5 <i>f</i>	-0.501	1.278	-0.491	1.283
			6 <i>d</i>	-0.184	3.170	-0.183	3.170
			7 <i>s</i>	-0.208	4.230	-0.208	4.227
Am	$5f^7 6d^1 7s^1$	$^{10}D$	6 <i>s</i>	-2.205	1.422	-2.210	1.420
			6 <i>p</i>	-1.034	1.761	-1.039	1.755
			5 <i>f</i>	-0.374	1.288	-0.368	1.291
			6 <i>d</i>	-0.106	4.252	-0.105	4.241
			7 <i>s</i>	-0.194	4.467	-0.195	4.475
Cm	$5f^7 6d^1 7s^2$	$^9D$	6 <i>s</i>	-2.441	1.374	-2.447	1.371
			6 <i>p</i>	-1.183	1.692	-1.188	1.687
			5 <i>f</i>	-0.600	1.186	-0.592	1.188
			6 <i>d</i>	-0.212	2.901	-0.210	2.894
			7 <i>s</i>	-0.210	4.147	-0.210	4.138

Table I. (Continued)

Configuration				AIMP		AE	
				$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)	$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)
Bk	$5f^8 6d^1 7s^2$	$^8\text{H}$	6s	-2.534	1.344	-2.541	1.341
			6p	-1.218	1.661	-1.223	1.655
			5f	-0.610	1.151	-0.602	1.153
			6d	-0.191	2.990	-0.190	2.983
			7s	-0.216	4.065	-0.216	4.060
Cf	$5f^9 6d^1 7s^2$	$^7\text{K}$	6s	-2.624	1.317	-2.633	1.314
			6p	-1.252	1.630	-1.257	1.626
			5f	-0.639	1.113	-0.627	1.116
			6d	-0.173	3.114	-0.172	3.115
			7s	-0.222	3.986	-0.223	3.979
Es	$5f^{10} 6d^1 7s^2$	$^6\text{L}$	6s	-2.712	1.290	-2.720	1.287
			6p	-1.279	1.603	-1.285	1.599
			5f	-0.666	1.082	-0.655	1.085
			6d	-0.169	3.106	-0.168	3.118
			7s	-0.226	3.925	-0.227	3.920
Fm	$5f^{11} 6d^1 7s^2$	$^5\text{L}$	6s	-2.799	1.265	-2.808	1.262
			6p	-1.305	1.578	-1.312	1.573
			5f	-0.692	1.053	-0.679	1.055
			6d	-0.165	3.115	-0.164	3.113
			7s	-0.231	3.865	-0.231	3.862
Md	$5f^{12} 6d^1 7s^2$	$^4\text{K}$	6s	-2.889	1.240	-2.899	1.237
			6p	-1.332	1.553	-1.339	1.548
			5f	-0.716	1.026	-0.704	1.028
			6d	-0.161	3.132	-0.159	3.131
			7s	-0.235	3.811	-0.236	3.800
No	$5f^{13} 6d^1 7s^2$	$^3\text{H}$	6s	-2.978	1.217	-2.992	1.213
			6p	-1.358	1.530	-1.366	1.525
			5f	-0.744	1.000	-0.732	1.002
			6d	-0.156	3.153	-0.155	3.166
			7s	-0.240	3.752	-0.241	3.746
Lr	$5f^{14} 6d^1 7s^2$	$^2\text{D}$	6s	-3.070	1.195	-3.085	1.191
			6p	-1.382	1.509	-1.391	1.503
			5f	-0.775	0.976	-0.766	0.978
			6d	-0.151	3.189	-0.149	3.203
			7s	-0.245	3.695	-0.246	3.688

Table II. The spin-free relativistic valence orbital energies ( $\varepsilon$ ) and radial expectation values ( $\langle r \rangle$ ) both in the DK3-AIMP and all-electron (AE) calculations. The DK3-AIMP calculations correspond to a large [Xe, 4f] core and a  $5d$ ,  $6s$ ,  $6p$ ,  $5f$ ,  $6d$ , and  $7s$  valence.

Configuration			AIMP		AE		
			$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)	$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)	
Th	$5f^4 6d^2 7s^1$	$^5I$	$5d$	-3.642	0.934	-3.639	0.933
			$6s$	-1.911	1.588	-1.912	1.585
			$6p$	-0.965	1.928	-0.968	1.923
			$5f$	-0.185	1.708	-0.180	1.713
			$6d$	-0.167	3.500	-0.167	3.502
			$7s$	-0.187	4.644	-0.187	4.635
			Pa	$5f^3 6d^1 7s^1$	$^6L$	$5d$	-3.754
$6s$	-1.900	1.562				-1.902	1.558
$6p$	-0.925	1.912				-0.928	1.906
$5f$	-0.180	1.662				-0.174	1.666
$6d$	-0.119	4.076				-0.118	4.073
$7s$	-0.178	4.784				-0.178	4.755
U	$5f^3 6d^1 7s^2$	$^5L$				$5d$	-4.159
			$6s$	-2.123	1.501	-2.126	1.499
			$6p$	-1.069	1.829	-1.072	1.824
			$5f$	-0.397	1.438	-0.390	1.441
			$6d$	-0.229	2.977	-0.228	2.969
			$7s$	-0.196	4.389	-0.196	4.391
			Np	$5f^4 6d^1 7s^2$	$^6L$	$5d$	-4.387
$6s$	-2.204	1.466				-2.206	1.464
$6p$	-1.098	1.791				-1.102	1.786
$5f$	-0.450	1.356				-0.443	1.359
$6d$	-0.234	2.906				-0.233	2.902
$7s$	-0.199	4.334				-0.199	4.331
Pu	$5f^5 6d^1 7s^2$	$^7K$				$5d$	-4.623
			$6s$	-2.294	1.432	-2.298	1.431
			$6p$	-1.137	1.753	-1.142	1.749
			$5f$	-0.498	1.280	-0.491	1.283
			$6d$	-0.184	3.173	-0.183	3.170
			$7s$	-0.208	4.228	-0.208	4.227
			Am	$5f^7 6d^1 7s^1$	$^{10}D$	$5d$	-4.644
$6s$	-2.206	1.422				-2.210	1.420
$6p$	-1.034	1.761				-1.039	1.755
$5f$	-0.374	1.288				-0.368	1.291
$6d$	-0.106	4.244				-0.105	4.241
$7s$	-0.194	4.481				-0.195	4.475
Cm	$5f^7 6d^1 7s^2$	$^9D$				$5d$	-5.064
			$6s$	-2.441	1.374	-2.447	1.371
			$6p$	-1.183	1.692	-1.188	1.687
			$5f$	-0.600	1.186	-0.592	1.188
			$6d$	-0.211	2.904	-0.210	2.894
			$7s$	-0.210	4.143	-0.210	4.138

Table II. (Continued)

Configuration				AIMP		AE	
				$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)	$\varepsilon$ (Hartree)	$\langle r \rangle$ (Bohr)
Bk	$5f^8 6d^1 7s^2$	$^8\text{H}$	$5d$	-5.305	0.793	-5.302	0.792
			$6s$	-2.535	1.344	-2.541	1.341
			$6p$	-1.218	1.661	-1.223	1.655
			$5f$	-0.610	1.150	-0.602	1.153
			$6d$	-0.191	2.993	-0.190	2.983
			$7s$	-0.216	4.063	-0.216	4.060
Cf	$5f^9 6d^1 7s^2$	$^7\text{K}$	$5d$	-5.541	0.777	-5.540	0.776
			$6s$	-2.626	1.316	-2.633	1.314
			$6p$	-1.250	1.631	-1.257	1.626
			$5f$	-0.635	1.114	-0.627	1.116
			$6d$	-0.173	3.121	-0.172	3.115
			$7s$	-0.223	3.973	-0.223	3.979
Es	$5f^{10} 6d^1 7s^2$	$^6\text{L}$	$5d$	-5.773	0.762	-5.772	0.761
			$6s$	-2.713	1.290	-2.720	1.287
			$6p$	-1.278	1.604	-1.285	1.599
			$5f$	-0.662	1.083	-0.655	1.085
			$6d$	-0.169	3.115	-0.168	3.118
			$7s$	-0.227	3.926	-0.227	3.920
Fm	$5f^{11} 6d^1 7s^2$	$^5\text{L}$	$5d$	-6.005	0.747	-6.004	0.747
			$6s$	-2.801	1.264	-2.808	1.262
			$6p$	-1.305	1.578	-1.312	1.573
			$5f$	-0.688	1.054	-0.679	1.055
			$6d$	-0.165	3.132	-0.164	3.113
			$7s$	-0.231	3.862	-0.231	3.862
Md	$5f^{12} 6d^1 7s^2$	$^4\text{K}$	$5d$	-6.239	0.733	-6.237	0.733
			$6s$	-2.889	1.240	-2.899	1.237
			$6p$	-1.331	1.554	-1.339	1.548
			$5f$	-0.713	1.026	-0.704	1.028
			$6d$	-0.161	3.137	-0.159	3.131
			$7s$	-0.236	3.809	-0.236	3.800
No	$5f^{13} 6d^1 7s^2$	$^3\text{H}$	$5d$	-6.472	0.720	-6.471	0.720
			$6s$	-2.980	1.217	-2.992	1.213
			$6p$	-1.357	1.531	-1.366	1.525
			$5f$	-0.741	1.001	-0.732	1.002
			$6d$	-0.156	3.158	-0.155	3.166
			$7s$	-0.240	3.757	-0.241	3.746
Lr	$5f^{14} 6d^1 7s^2$	$^2\text{D}$	$5d$	-6.705	0.707	-6.703	0.707
			$6s$	-3.073	1.194	-3.085	1.191
			$6p$	-1.382	1.509	-1.391	1.503
			$5f$	-0.776	0.976	-0.766	0.978
			$6d$	-0.150	3.194	-0.149	3.203
			$7s$	-0.245	3.694	-0.246	3.688

Table III. Spectroscopic constants for the  $^1\Sigma^+$  ground state of thorium monoxide, ThO, using the DK3-AIMP and corresponding all-electron DK3 (AE-DK3) methods.

	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
This work				
AIMP-SCF <sup>a</sup>	1.833	945	0.335	5.96
AIMP-CASSCF <sup>a</sup>	1.879	856	0.319	9.14
AIMP-SCF <sup>b</sup>	1.832	951	0.336	5.96
AIMP-CASSCF <sup>b</sup>	1.878	861	0.320	9.14
AE-SCF <sup>c</sup>	1.832	959	0.336	5.82
AE-CASSCF <sup>c</sup>	1.877	866	0.320	9.01
Previously				
AIMP-SCF <sup>d</sup>	1.819	956		5.99
AIMP-CASSCF <sup>d</sup>	1.886	865		9.15
PP-SCF <sup>e</sup>	1.829	943		6.07
PP-CASSCF <sup>e</sup>	1.882	876		8.92
AE-DFR <sup>f</sup>	1.873	930	0.321	7.67
Expt. <sup>g</sup>	1.840	896	0.333	9.00

<sup>a</sup> This work. A core [Xe, 4*f*,5*d*] and a (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*4*f*] basis set.

<sup>b</sup> This work. A core [Xe, 4*f*] and a (14*s*10*p*12*d*9*f*)/[6*s*5*p*6*d*4*f*] basis set.

<sup>c</sup> This work. A (35*s*26*p*18*d*13*f*)/[11*s*9*p*8*d*5*f*] basis set.

<sup>d</sup> Reference 30. A [Xe, 4*f*,5*d*] core and a (14*s*10*p*11*d*9*f*)/[6*s*5*p*5*d*5*f*] Cowan-Griffin basis set.

<sup>e</sup> Reference 12. Relativistic energy-adjusted pseudopotential calculation corresponding to a [Kr, 4*d*,4*f*] core and a (12*s*11*p*10*d*8*f*)/[8*s*7*p*6*d*4*f*] basis set.

<sup>f</sup> Reference 31. All electron Dirac-Fock-Roothaan calculations with a (24*s*19*p*16*d*8*f*)/[8*s*7*p*7*d*5*f*] basis set.

<sup>g</sup> Reference 32.

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# **3 Third-order Douglas-Kroll *ab initio***

## **model potential based spin-orbit**

## **method**

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## 3.1 Relativistic and correlated calculations on the ground and excited states of ThO

### Abstract

We report on the performance of the third-order Douglas-Kroll *ab initio* model potential (DK3-AIMP) method-based electron-correlated spin-orbit calculations. Our treatment assumes that the problem can be separated into a spin-free correlation treatment and a spin-orbit calculation. The correlation effects were calculated using the multistate complete active space second-order perturbation (MS-CASPT2) method, and the spin-orbit effects were treated by means of the restricted active space state interaction spin-orbit (RASSI-SO) method, where the spin-orbit effects were approximated by the Douglas-Kroll type of atomic mean-field spin-orbit (DK-AMFI-SO) method. We used our method for illustrative calculations on the ground and low-lying electronic states of thorium monoxide. For a proper description of the inner core region in the spin-orbit calculations, an auxiliary spin-orbit basis set was introduced. The DK3-AIMP-based electron-correlated spin-orbit calculations on ThO yield good agreement with corresponding all-electron results and with the available experimental data. This confirms that the DK3-AIMP method can be easily combined with highly accurate correlation treatments and relativistic effects, both of which are vital for studying the actinides. To our knowledge, the literature contains no references to AIMP calculations on the low-lying states of ThO.

### 3.1 Introduction

Correlation and relativistic effects have a significant impact, both quantitatively and qualitatively, on the description of systems containing heavy elements. The most commonly used quantum mechanical method in the chemistry of heavy elements is the relativistic effective core

potential (RECP) approximation.<sup>1-6</sup> In this approximation, the core electrons are modeled using a suitable function, and only the valence electrons are treated explicitly. Some relativistic effects, and in particular, scalar effects are taken into account without having to perform full relativistic calculations. In many cases, this approach gives reasonable results and at the same time, reduces the computational effort. The *ab initio* model potential (AIMP) method<sup>7, 8</sup> has been developed as an extension of the RECP method,<sup>2-6</sup> and describes the correct behavior for the inner nodal structure of the valence orbitals. The AIMP consists of a Coulomb potential, an exchange potential, and a projection operator, and has a clear physical meaning, since it represents the Coulomb and exchange interactions between a single valence electron and the core electrons. In a previous paper, we have developed the third-order Douglas-Kroll *ab initio* model potential (DK3-AIMP) method, and have successfully applied it to actinide elements.<sup>9</sup> The DK3-AIMP method is expected to be a useful tool in the study of actinide chemistry. The relativistic spin-free effects were considered by means of the third-order Douglas-Kroll (DK3) approximation<sup>10, 11, 12</sup> while for simplicity, the spin-dependent effects were neglected in the orbital optimization process. Nevertheless, spin-orbit effects can be easily included during the later calculation stages, *e.g.* in molecular calculations, this can be performed by means of the atomic mean-field and the AIMP-based spin-orbit methods<sup>13</sup>. Therefore, by assuming that the problem can be separated into a spin-free correlation treatment and a spin-orbit correlation treatment, we can successfully include spin-orbit effects. In the DK3-AIMP-based spin-orbit-correlated calculations, the spin-orbit splittings are not only dependent on the spin-orbit coupling between the states of a spin-free Hamiltonian, but also on the electron correlation effects that determine the relative energies between those states. This implies that a high quality of the spin-orbit calculations can only be achieved using calculations that do not show any deficiency in the treatment of the spin-free effects. This is particularly so for calculations of the correlation, since any incorrect values for the spin-orbit

splitting could be otherwise due to an insufficient treatment of the correlation rather than to the quality of the spin-orbit operator.

The main purpose of this study was to demonstrate that the DK3-AIMP method could easily be combined with highly accurate electron correlation treatments and relativistic effects, both of which are vital for studying the actinides. As an illustration, calculations were performed on the low-lying states of thorium monoxide (ThO). The correlation effects were determined using the multistate complete active space second-order perturbation (MS-CASPT2) method.<sup>14</sup> The spin-orbit effects were treated by means of the restricted active space state interaction spin-orbit (RASSI-SO) method,<sup>15</sup> in which the spin-orbit effects were approximated by a Douglas-Kroll-type atomic mean-field spin-orbit (DK-AMFI-SO) method.<sup>13</sup> For a proper description of the inner core region in the spin-orbit calculations, an auxiliary spin-orbit basis set was introduced. Furthermore, the all-electron spin-orbit mean field integrals were adjusted to be used with the AIMP wavefunction. Thus, the emphasis of the present approach is more focused on computational savings, while keeping a reasonably high level of accuracy.

The following section provides a theoretical background. The computational details are described in Section III, and the calculated results along with the available experimental data are given in Section IV. The final section provides our conclusions to the work, along with possible future developments in this area.

## **3.2. THEORETICAL BACKGROUND**

### **A. The DK3-AIMP method**

In the section, we will provide a brief summary of the DK3-AIMP method in which relativistic effects are incorporated by using the third-order Douglas-Kroll approximation.<sup>10, 11, 12</sup>

The no-pair DK3 Hamiltonian is described by

$$H_+^{\text{DK3}} = H_+^{\text{DK2}} + \frac{1}{2} \sum_i [W_1(i), [W_1(i), V_{\text{eff}}(i)]] \quad (1)$$

where  $H_+^{\text{DK2}}$  is the second-order Douglas-Kroll (DK2) Hamiltonian,<sup>16-18</sup> and this can be written as

$$H_+^{\text{DK2}} = \sum_i E_i - mc^2 + \sum_i V_{\text{eff}}(i) + \frac{1}{2} \sum_{i \neq j} V_{\text{eff}}(i, j) - \frac{1}{2} \sum_i [W_1(i), [W_1(i), E_i]_+]_+ \quad (2).$$

The spin-free valence-only DK3-AIMP Hamiltonian<sup>9</sup> is

$$H^{\text{DK3-AIMP}} = \sum_{i=1}^{N_v} \left( E_i - mc^2 + V_{\text{eff}}(i) - \frac{1}{2} [W_1(i), [W_1(i), E_i]_+]_+ + \frac{1}{2} [W_1(i), [W_1(i), V_{\text{eff}}(i)]]_+ \right. \\ \left. + \sum_{\mu} \left[ \frac{Z_{\mu}^{\text{core}}}{|r_i - R_{\mu}|} + V_{\mu}^{\text{DK3-AIMP}} \right] + \sum_{i>j=1}^{N_v} \frac{1}{r_{ij}} + \sum_{\mu>\nu} \frac{Z_{\mu}^{\text{eff}} Z_{\nu}^{\text{eff}}}{|R_{\mu} - R_{\nu}|} \right) \quad (3),$$

where the first four terms are identical to the all-electron terms in Equations (1) and (2), with

$$V_{\mu}^{\text{DK3-AIMP}} = V_{\text{Coul}}^{\mu, \text{MP}} + V_{\text{Exch}}^{\mu, \text{MP}} + P_{\text{core}}^{\mu} \quad (4)$$

$$V_{\text{Coul}}(i) = -\frac{Z_{\text{core}}}{r_i} + 2 \sum_c^{\text{core}} J_c(i) \approx V_{\text{Coul}}^{\text{MP}}(i) = \sum_j C_j \frac{e^{-\alpha_j r_i^2}}{r_i} \quad (5)$$

$$V_{\text{exch}}(i) = -\sum_c^{\text{core}} K_c(i) \approx V_{\text{exch}}^{\text{MP}}(i) = \sum_l \sum_{m=-l}^l \sum_{a,b} |a; lm\rangle A_{l,ab} \langle b; lm| \quad (6)$$

and

$$P(i) = -\sum_c^{core} 2\varepsilon_c |\phi_c\rangle\langle\phi_c| \quad (7).$$

In this way, direct relativistic effects on the valence electrons are handled by the no-pair relativistic operators of the kinetic (and rest mass) energy and nuclear attraction, and the indirect relativistic effects on the valence electrons brought about by the core electrons are considered by means of the core AIMP. References 9-12 provide further details.

## B. Breit-Pauli and Douglas-Kroll types of the spin-orbit operator

One of the most important spin-dependent relativistic effects is the spin-orbit interaction. The full Breit-Pauli spin-orbit operator contains both one-electron and two-electron parts

$$\mathbf{H}_{SO} = \frac{\alpha^2}{2} \left[ \sum_{i,K} \frac{\mathbf{l}_{iK} \cdot \mathbf{s}_i}{r_{iK}^3} - \sum_{i,j} \frac{\mathbf{l}_{ij} \cdot (\mathbf{s}_i + 2\mathbf{s}_j)}{r_{ij}^3} \right] \quad (8),$$

where  $i$  and  $K$  refer to the electrons and the nuclei, respectively. The quantity  $\alpha$  is the fine-structure constant, and the angular momenta are defined as

$$\begin{aligned} \mathbf{l}_{iK} &= -i\mathbf{r}_{iK} \times \nabla_i, \\ \mathbf{l}_{ij} &= -i\mathbf{r}_{ij} \times \nabla_i. \end{aligned} \quad (9).$$

The Douglas-Kroll type spin-orbit operator may be derived by following the work of Sucher.<sup>19</sup> On collecting terms, rearranging, and introducing explicitly the Coulomb potential of the nuclei, an expression for a variationally stable no-pair spin-orbit operator can be deduced

$$\begin{aligned}
H_{SO}^+ &= \sum_i \sum_\alpha c^2 Z_\alpha \frac{A_i}{E_i + mc^2} \boldsymbol{\sigma}_i \left( \frac{\mathbf{r}_{i\alpha}}{r_{i\alpha}^3} \times \mathbf{p}_i \right) \frac{A_i}{E_i + mc^2} - \\
&- c^2 \sum_{i \neq j} \frac{A_i A_j}{E_i + mc^2} \left( \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \cdot (\boldsymbol{\sigma}_i + 2\boldsymbol{\sigma}_j) \frac{A_i A_j}{E_i + mc^2}
\end{aligned} \tag{10}$$

The Breit-Pauli spin-orbit of Equation (8) and the corresponding no-pair operators of Equation (10) have the same structure. The only difference between them is the presence of kinematic factors in the no-pair form, which regularize the spin-orbit interaction for small values of  $r$ . Starting from Equations (8) or (10), Hess *et al.*<sup>20</sup> derived a Fock-type generalization of the spin-orbit operator of the form

$$\begin{aligned}
H_{ij}^{SO-mf} &= \langle i | H^{SO}(1) | j \rangle + \\
&+ \frac{1}{4} \sum_M^{mf-orbs.} occ(M) \left[ \begin{aligned}
&\langle iM_\alpha | H^{SO}(1,2) | jM_\alpha \rangle + \langle iM_\beta | H^{SO}(1,2) | jM_\beta \rangle - \\
&-\langle iM_\alpha | H^{SO}(1,2) | M_\alpha j \rangle - \langle iM_\beta | H^{SO}(1,2) | M_\beta j \rangle - \\
&-\langle M_\alpha i | H^{SO}(1,2) | jM_\alpha \rangle - \langle M_\beta i | H^{SO}(1,2) | jM_\beta \rangle
\end{aligned} \right]
\end{aligned} \tag{11}$$

where  $occ(M)$  denotes the occupation number of orbital  $M$ ,  $i$  and  $j$  denote the spin-orbitals, and  $M_s$  denotes the partially occupied orbitals with which the electronic charge distribution interacts. The computational cost and disk requirements are significantly reduced by taking into account only the one-electron two-center/two-electron one-center spin-orbit integrals, and this is known as the mean-field spin-orbit approximation.

### C. Auxiliary AIMP-SO basis set

If the one- and two-electron spin-orbit integrals are calculated within the AIMP approximation, then the M-orbitals in the Coulomb and exchange terms of Equation (11) must always be expressed in the all-electron basis set.<sup>13</sup> The  $r^{-3}$  dependency of the spin-orbit operator makes the demand on the quality of the inner part of the AIMP orbitals exceedingly high. This problem can be circumvented by calculating the spin-orbit integrals in the all-electron basis set, and then transforming these integrals with an AIMP wavefunction. This approximation necessitates a close correspondence between the all-electron and the AIMP core and valence basis sets. In principle, the AIMP is capable of fulfilling these demands.

To obtain the matrix representation of the spin-orbit operator in the DK3-AIMP basis set, the effective one-electron integrals of Equation (11) were first calculated from the auxiliary spin-orbit basis set

$$\mathbf{V}_{\text{AE}}^{\text{SO}} = \mathbf{S}_{\text{AE}} \sum_i \sum_j \{C_i H_{ij}^{mf-\text{SO}} C_j^T\} \mathbf{S}_{\text{AE}} \quad (12).$$

In the AIMP basis set, the spin-orbit integral matrix is then given by

$$\mathbf{V}_{\text{AIMP}}^{\text{SO}} = (\mathbf{R}_{\text{AE}}^{\text{AIMP}})^T \mathbf{S}_{\text{AE}}^{-1} \mathbf{V}_{\text{AE}}^{\text{SO}} \mathbf{S}_{\text{AE}}^{-1} \mathbf{R}_{\text{AE}}^{\text{AIMP}} \quad (13).$$

Here,  $\mathbf{R}_{\text{AE}}^{\text{AIMP}}$  is the rectangular overlap matrix between the all-electron and the AIMP basis functions. Finally, the matrix representation of the spin-orbit Hamiltonian in the AIMP basis set is

$$H_{\text{AIMP}}^{\text{SO}} = \sum_{\mu} \sum_{\nu} |\chi_{\mu}\rangle (\mathbf{S}_{\text{AIMP}}^{-1} \mathbf{V}_{\text{AIMP}}^{\text{SO}} \mathbf{S}_{\text{AIMP}}^{-1})_{\mu\nu} \langle \chi_{\nu} | \quad (14).$$

### III. COMPUTATIONAL DETAILS

Our calculations were carried out assuming  $C_2$  symmetry, using the software program MOLCAS 5<sup>21</sup> that had been modified for the inclusion of the DK3-AIMP and DK-AMFI codes. To obtain a proper description of the inner core region in the molecular calculations, and to take into account the discussion in Section II.C, we employed an auxiliary spin-orbit basis set. The auxiliary spin-orbit basis set chosen was the all electron third-order Douglas-Kroll (AE-DK3) basis set taken from Reference 22. This was re-optimized and augmented in the valence part to properly match with the AIMP’s valence part, *i.e.* the  $(14s11p1d)/[4s4p1d]$  orbitals for oxygen, and the  $(39s30p22d16f)/[11s9p8d5f]$  orbitals for thorium. This auxiliary spin-orbit basis set corresponds to the DK3-AIMP core and valence basis set,<sup>9</sup> and this was also employed without augmentation in the DK3-AE calculations, *i.e.* the  $(12s9p1d)/[4s4p1d]$  orbitals for oxygen, and the  $(35s26p18d13f)/[11s9p8d5f]$  orbitals for thorium. In the DK3-AIMP calculations for the thorium atom, a large  $[Xe,4f,5d]$  core with the  $(14s10p11d9f)/[6s5p5d4f]$  valence basis set was used. For the oxygen atom, we produced the same type of DK3-AIMP, *i.e.*, a  $[He]$  core with a  $(6s7p1d)/[3s4p1d]$  basis set. The valence basis set was contracted into the atomic DK3 SCF valence orbitals, and the outermost two  $s$ -type and three  $p$ -type primitives were added. This basis set was further augmented by a single  $p$ -type Gaussian primitive with an exponent of 0.059,<sup>23</sup> and a single  $d$ -type Gaussian primitive with an exponent of 1.154.<sup>24</sup> These represented the diffuse and polarization functions, and resulted in a  $(6s7p1d)/[3s4p1d]$  basis set.

## IV. RESULTS

### A. Spin-free correlated calculations

The relativistic spin-free effects were considered by using the third-order Douglas-Kroll (DK3) approximation, and handled the same as the effects of electron correlation. For each geometry, we first performed a SCF calculation, and then the resulting wavefunction was further optimized by using the state-averaged CASSCF<sup>25-27</sup> and MS-CASPT2 methods<sup>14</sup> with a G2 type of Fock operator.<sup>28</sup> For comparative analysis, we carried out both the spin-free DK3-AIMP and DK3-AE-based calculations to check the quality of the DK3-AIMP-based results. To our knowledge, presently, there are no AIMP calculations available in the literature on the low-lying states of ThO.

The ground state of ThO, *i.e.* the  $^1\Sigma^+$  state, may be simply denoted as  $\text{Th}^{2+}(7s^2) \text{O}^{2-}(2p^6)$ , the  $^1,^3\Sigma^+$ ,  $^1,^3\Pi$  and  $^1,^3\Delta$  low-lying states arise mainly from the  $\text{Th}^{2+}(7s^1 6d^1) \text{O}^{2-}(2p^6)$  configuration, and the  $^3\Sigma^-$  and  $^3\Phi$  states from the  $\text{Th}^{2+}(6d^2) \text{O}^{2-}(2p^6)$  configuration. The corresponding  $\Omega$  values for these states are  $0^-$ ,  $0^+$ , 1, 2, and 3, respectively. The  $\Omega = 0^+$  states arise from the interaction of the  $^1\Sigma^+$  and the  $^3\Pi$  states, the  $\Omega = 0^-$  states from the  $^3\Sigma^+$  and the  $^3\Pi$  states, the  $\Omega = 1$  states from the  $^3\Sigma^+$ ,  $^3\Sigma^-$ ,  $^3\Pi$ ,  $^1\Pi$ ,  $^3\Delta$  and the  $^3\Phi$  states, and the  $\Omega = 2$  states from the  $^3\Pi$ ,  $^3\Delta$ ,  $^1\Delta$  and the  $^3\Phi$  states. Only the  $\Omega = 3$  state arises from the  $^3\Delta$  and  $^3\Phi$  states. The states that arise from  $\text{Th}^{2+}(7s^1 5f^1) \text{O}^{2-}(2p^6)$ ,  $\text{Th}^{2+}(5f^2) \text{O}^{2-}(2p^6)$ ,  $\text{Th}^{2+}(7s^1 7p^1) \text{O}^{2-}(2p^6)$ , and  $\text{Th}^{2+}(7p^2) \text{O}^{2-}(2p^6)$  configurations lie at energies higher than  $32,198 \text{ cm}^{-1}$ ,<sup>30</sup> and thus, do not contribute to, nor interact with the low-lying states. This is because the  $5f$  orbitals have much stronger relativistic destabilizations, and lie at much higher energies, making them unavailable for interaction with the lower-lying states. Therefore, these configurations were neglected in the present work. In addition, we considered the influence of quintet states arising from possible  $\text{Th}^+\text{O}^-$  configurations. Following the work of Küchle *et al.*,<sup>30</sup> the active space in the state-averaged CASSCF calculations was chosen to include only eight electrons distributed over nine orbitals, *i.e.* the  $7s$  and  $6d$  orbitals of thorium, and the  $2p$  orbitals of oxygen with the  $2s$  orbitals of oxygen kept doubly occupied. This active space was taken as the

reference space for the subsequent MS-CASPT2 calculations for single, triple, and quintet excitations. In particular, these results had a qualitative character, and served as a good guidance in later calculations. An analysis of the DK3-AIMP calculations with the corresponding DK3-AE-based results showed that the doubly occupied  $6p$  orbitals of thorium play an active role in the valence part, and could not be omitted from the active space. Neglecting these had a direct influence on the triplet states, and in the later spin-orbit calculations. Thus, an active space that included eight electrons over nine orbitals was correct only for singlets, while a proper active space for triplets had to contain the  $6p$  orbitals of Th, *i.e.* 14 electrons distributed over 12 orbitals. In this way, all the spin-free states generated by the AE calculations were very well reproduced at the AIMP level. Insufficient or rather limited electron correlation was most probably the reason why Küchle *et al.*<sup>30</sup> could not qualitatively achieve good accuracy for their excited states. Therefore, in next step, the active space in the state-averaged CASSCF and subsequent MS-CASPT2 methods was chosen to include 14 electrons distributed over 12 orbitals, *i.e.* the  $7s$ ,  $6d$ , and  $6p$  orbitals of thorium and the  $2p$  orbitals of oxygen, while keeping the  $2s$  orbital of oxygen doubly occupied. In this way, singlets, triplets, and also quintet states could be included. For each irreducible representation (IR) and spin multiplicity we considered the following number of CI roots. For IR  $A$  and spin multiplicity 1, 3 and 5 we considered 9, 6 and 1 CI roots. For IR  $B$  and spin multiplicity 1, 3 and 5 we considered 8, 8 and 2 CI roots. After the relativistic spin-free electron-correlated treatment, we performed DK-AMFI-based RASSI-SO<sup>15</sup> calculations to treat the spin-orbit coupling.

In our previous paper<sup>9</sup>, we performed spin-free DK3-AIMP and DK3-AE-based SCF and state-specific CASSCF calculations on the  $^1\Sigma^+$  ground state of ThO, even though there had been a number of previous studies devoted to the  $^1\Sigma^+$  ground state of ThO.<sup>29, 30, 34, 35</sup> However, none of these had thoroughly investigated the effect of spin-orbit coupling along with effect of electron

correlation on the derived molecular properties. In the present work, we have focused on both the effect of electron correlation and of spin-orbit coupling upon the spectroscopic properties of the  $^1\Sigma^+$  ground state of ThO. In our DK3-AIMP-based MS-CASPT2 calculations, the  $^1\Sigma^+$  ground state of ThO is well separated (by 0.69 eV) from the first low-lying excited state 1 (H), and under the effect of spin-orbit coupling, the molecular valence energy of the ground state remains almost unchanged. The spin-free DK3-AIMP calculations bond length,  $r_e$ , resulted in a value of  $r_e = 1.862 \text{ \AA}$ , which is longer by  $0.022 \text{ \AA}$  from the experimentally observed value of  $r_e = 1.840 \text{ \AA}$ . The vibrational wave number,  $\omega_e$ , was underestimated by 40 wavenumbers, and the rotational constant,  $B_e$ , was underestimated by  $0.008 \text{ cm}^{-1}$ . From the DK3-AIMP-based spin-orbit calculations (Table I) we obtained nearly same results for the values of  $r_e$ ,  $\omega_e$ , and  $B_e$  of the  $^1\Sigma^+$  ground state of ThO. We supposed that the effect of spin-orbit coupling on the ground state was negligible for small  $r_e$ ,  $\omega_e$ , and  $B_e$ , but that it was the dynamical correlation that had a significant impact upon their values. This is not true for the dissociation energy,  $D_e$ , because the spin-orbit coupling lowers the ground states of the atomic Th ( $^3F$ ) and O ( $^3P$ ) states. Our spin-free AE calculated dissociation energy resulted in 8.43 eV, and the spin-orbit corrected value in 8.10 eV. Again the AIMP results very well reproduced AE at the spin-free and spin-orbit frameworks, resulted in the dissociation energies of 8.43 eV and 8.09 eV. Note that the experimental dissociation energy of 9.00 eV is an upper bound to the exact value of 8.86 or 8.79 eV. Then our spin-free and spin-orbit corrected results yield good agreement for the value  $D_e$  with both DK3-AIMP and AE based calculations (Table I). This is also obvious from our previous state-specific DK3-AE based CASSCF calculations on the  $^1\Sigma^+$  ground state of ThO, where the core electrons representing the largest core [ $Xe, 4f, 5d$ ] in the AE calculations were kept inactive rather than frozen, and resulted in the value of  $D_e = 9.01 \text{ eV}$ .

Table I also lists previous results calculated using a relativistic adjusted pseudopotential (PP)<sup>30</sup> and a Cowan-Griffin AIMP.<sup>35</sup> It is difficult to discuss the quality of these ECPs from the limited data available. Table I also includes four-component all-electron Dirac-Hartree-Fock results<sup>36</sup>, in which spin-dependent terms are included, but only at the SCF level. However, all the calculations show reasonable results for the calculated spectroscopic properties of ThO.

In general, we concluded that the overestimation of bond lengths and the underestimation of the vibrational wave numbers by the spin-free DK3-AIMP and DK3-AE-based MS-CASPT2-correlated calculations is due to the uncorrelated core and valence basis sets employed in the calculations. The spectroscopic properties could be marginally corrected by inclusion of *g*-functions into the basis set for better correlation of the *6d* orbitals, and also by including the *2s* orbitals of oxygen and the *6s* and *5f* orbitals of thorium into the active space. However, this dramatically increases the computational effort.

## B. Spin-orbit calculations

In this work, the spin-orbit coupling was considered by means of a Douglas-Kroll-type atomic mean-field (AMFI) approximation using the RASSI-SO method<sup>15</sup> with respect to the low-lying spin-free states. In the spin-orbit calculations, the matrix which was diagonalized, contained in the diagonal the MS-CASPT2 energies. The spin-orbit coupling terms computed by the AMFI approach were evaluated in the basis of the first-order wavefunction of the MS-CASPT2 method and added to the matrix with the MS-CASPT2 energies. These spin-free states, *i.e.* singlets, triplets, and quintets obtained from the MS-CASPT2 interact with each other, resulting in spin-coupled states. The present calculation evaluated 74 spin-orbit states in total.

The spectroscopic constants, *i.e.*,  $r_e$ ,  $\omega_e$ , and  $B_e$ , and also the term energies,  $T_e$ , were calculated relative to the  $^1\Sigma^+$  ground state of ThO for the low-lying states, *i.e.* the  $^{1,3}\Sigma^+$ ,  $^{1,3}\Pi$  and  $^{1,3}\Delta$  states arising mainly from the  $\text{Th}^{2+}(7s^16d^1) \text{O}^{2-}(2p^6)$  configuration, and the  $^3\Phi$  and  $^3\Sigma^-$  states from the  $\text{Th}^{2+}(6d^2) \text{O}^{2-}(2p^6)$  configuration. Note that the quintet states arising from  $\text{Th}^+\text{O}^-$  configurations were included, but they did not make a substantial contribution.

The calculated DK3-AIMP-based results are listed in Table II, the DK3-AE-based results are listed in Table III, and the available experimental data<sup>29-33</sup> compared with the DK3-AIMP results and our preliminary calculations are listed in Table IV. The previous preliminary spin-orbit calculations<sup>30</sup> that have been carried out on ThO are also briefly discussed in Table IV.

In proper calculations, 14 electrons were correlated in 12 orbitals. The results obtained from the AIMP were very well reproduced at the AE level. The bond lengths of the AE calculations were longer by less than 0.005 Å, with exception of the 1 (D) spin-coupled states, *i.e.* 0.021 Å. The term energies of the AE calculations for the spin-coupled states, 1 (H), 2 (Q), 3 (W) and 1 (C) were underestimated by 51, 85, 201 and 20 cm<sup>-1</sup>, respectively, while the other excited states, 0<sup>+</sup>(A), 1 (B), 1 (D), 0<sup>+</sup>(E) and 2 (G) were overestimated by 172, 136, 387, 231 and 128 cm<sup>-1</sup>, respectively. The rotational constants of the AE calculations were underestimated by less than 0.002 cm<sup>-1</sup>, with exception of the 1 (D) state, which had a deviation of 0.006 cm<sup>-1</sup>. The vibrational wavenumbers were overestimated by less than 13 cm<sup>-1</sup>, with the spin-coupled 1 (D) state being overestimated by 34 cm<sup>-1</sup>. These deviations demonstrate that the present AIMP method reproduced the AE method results to a high accuracy.

The spin-orbit calculations of the AIMP method for the first seven low-lying states yielded satisfactory results when compared to available experimental data (see Table I). For the ground state of ThO, *i.e.* the  $^1\Sigma^+$  state, the calculated  $r_e$  value was  $r_e = 1.862$  Å, and this is 0.022 Å longer than the experimental value of  $r_e = 1.840$  Å. The ground state is dominantly determined by the  $^1\Sigma^+$

state, which corresponds to  $0^+$  in relativistic notation. The effect of spin-orbit coupling on the bond length of the ground state is negligible, which is in contrast to the dynamical correlation, which plays a significant role on the value of  $r_e$ . The spin-coupled 1 ( $H$ ), 2 ( $Q$ ), and 3 ( $W$ ) states are dominantly determined by the  $^3\Delta$  state, with negligible contribution from the  $^3\Pi$  and  $^1\Pi$  states in case of 1 ( $H$ ), and the  $^1\Delta$  and  $^3\Pi$  states in case of 2 ( $Q$ ). These contributions are due to  $\text{Th}^{2+}(7s^16d^1) \text{O}^{2-}(2p^6)$  configuration. However, the present results are in significantly better agreement with experimental data than the preliminary calculations of Küchle *et al.*<sup>30</sup>, *i.e.* using spin-orbit CI calculations based on the quasi-relativistic energy-adjusted pseudopotential that employed an even a smaller core of  $[\text{Kr}, 4d, 4f]$ . The absolute errors,  $\delta$ , for the  $T_e$  of the 1 ( $H$ ), 2 ( $Q$ ), 3 ( $W$ ),  $0^+$  ( $A$ ), 1 ( $B$ ) and 1 ( $C$ ) spin-coupled states are only 283, 650, 9, 385, 84 and 358  $\text{cm}^{-1}$ , respectively, while the corresponding Küchle values are 451, 500, 387, 727, 1123 and 2666  $\text{cm}^{-1}$ , respectively. The composition of the  $0^+$  ( $A$ ) and 1 ( $B$ ) spin-coupled states is dominantly determined by the  $^3\Pi$  state with a small mixture of the  $^1\Sigma^+$  state in the case of  $0^+$  ( $A$ ), and the  $^1\Pi$ ,  $^3\Sigma^+$ ,  $^3\Delta$ , and  $^3\Phi$  states in the case of 1 ( $B$ ). While the  $0^+$  ( $A$ ) and 1 ( $B$ ) states only arise from the  $\text{Th}^{2+}(7s^16d^1) \text{O}^{2-}(2p^6)$  configuration, the 1 ( $C$ ), 1 ( $D$ ),  $0^+$  ( $E$ ) and 2 ( $G$ ) states are mixtures of the  $\text{Th}^{2+}(7s^16d^1) \text{O}^{2-}(2p^6)$  and  $\text{Th}^{2+}(6d^2) \text{O}^{2-}(2p^6)$  configurations. The 1 ( $C$ ) spin-coupled state from both the AIMP and AE calculations is in very good agreement with experimental data, and is a mixture of the dominant  $^1\Pi$  state, with a small contribution from the  $^3\Pi$ ,  $^3\Phi$ ,  $^3\Delta$ ,  $^3\Sigma^+$  and  $^3\Sigma^-$  states. The systematic overestimation of  $r_e$  by 0.02 Å is common in the results for all the first four low-lying states, *i.e.* the  $0^+$  ( $X$ ), 1 ( $H$ ), 2 ( $Q$ ), and 3 ( $W$ ) states. We assume that the systematic overestimation of the bond length is due to the uncorrelated core, and to the valence basis sets that were employed in the DK3-AIMP-based MS-CASPT2-correlated RASSI-SO calculations, and also to the non-inclusion of g-functions into the basis sets that can improve the correlation of the  $6d$  orbitals. As for  $\omega_e$ , the maximum absolute error was  $\delta \leq 40 \text{ cm}^{-1}$ , and for  $B_e$ , was  $B_e \leq 0.008 \text{ cm}^{-1}$ .

<sup>1</sup>. For the  $0^+$  (*A*), 1 (*B*), and 1 (*C*) spin-coupled states, the bond lengths were overestimated by less than 0.04 Å, and  $\omega_e$  by less than 76 cm<sup>-1</sup>. Furthermore, in accordance with Küchle, we have found another four theoretical states, two with  $\Omega = 0^-$ , and two with  $\Omega = 2$ . However, the two theoretical states with  $\Omega = 2$  are exchanged, when compared to the results of Küchle (for more details see Table IV). The spin-coupled states calculated for energies above 15,000 cm<sup>-1</sup> yielded poorer results when compared to available experimental data, even though the present results are in better agreement than those calculated by Küchle. The bond lengths for the 1 (*D*),  $0^+$  (*E*), and 2 (*G*) coupled states were overestimated by less than 0.036 Å. Absolute errors for  $\omega_e$  were  $\delta = 172, 52,$  and 50 cm<sup>-1</sup>, respectively. The error of the 1 (*D*) state in the present and in previous calculations is due to an insufficient correlation of the *6d* orbitals. More accurate results for the 1 (*D*) spin-coupled state and for states lying above 20,000 cm<sup>-1</sup>, would require the inclusion of the *2s* orbitals of oxygen, and the *6s* and *5f* orbitals of thorium into the active space, and would require reducing the core from [*Xe, 4f, 5d*] to [*Kr, 4d, 4f*]. However, this would raise the computational effort dramatically, and is outside the aims of our work.

In general, the DK3-AIMP- and DK3-AE-based electron-correlated spin-orbit calculations overestimate the bond lengths and underestimate the vibrational wave numbers and rotational constants. In contrast, the results obtained from quasi-relativistic energy-adjusted pseudopotential-based spin-orbit CI calculations underestimate the bond lengths and overestimate the vibrational wavenumbers. Therefore, as is clearly observed from both calculated results, the experimental data lay in between the results of these two calculation methods. It is interesting to note that two completely different methods, *i.e.* the quasi-relativistic energy-adjusted pseudopotential-based spin-orbit CI employing a smaller [*Kr, 4d, 4f*] core and the DK3-AIMP-based MS-CASPT2-correlated RASSI spin-orbit calculations employing a larger [*Xe, 4f, 5d*] core exhibited the same qualitative trends.

Nevertheless, from our results it is obvious that the present DK3-AIMP method is an efficient tool for studying actinide chemistry, and is capable of describing qualitatively and quantitatively the ground and excited states to a certain level of accuracy. However, further theoretical and computational developments are required for a higher level of accuracy to model the available experimental data. One such progressive step would be to correlate the core and valence basis sets. This is of particular interest, and further developments along these lines are in progress.

For comparative study, it would be mandatory to perform four-component electron-correlated calculations on the low-lying states of ThO. This is of particular interest to our research group at the University of Tokyo.

## V. CONCLUSIONS

We have successfully tested the performance of the Douglas-Kroll third-order *ab initio* model potential method (DK3-AIMP) in correlated spin-orbit calculations. The correlation effects were determined using a multistate complete active space second-order perturbation (MS-CASPT2) method. The spin-orbit effects were treated by means of the restricted active space state interaction spin-orbit (RASSI-SO) method, in which the spin-orbit effects were approximated by a Douglas-Kroll type atomic mean-field spin-orbit (DK-AMFI-SO) method. Illustrative calculations were performed on ThO.

The DK3-AIMP method easily reproduced the corresponding DK3-AE-calculated values very well, and yielded good agreement with the available experimental data for ThO. Moreover, we assumed that by using correlated orbitals instead of SCF orbitals in the DK3-AIMP method, the core and valence basis set would improve the accuracy of calculated results. Further work along this line of enquiry is in progress.

The DK3-AIMP-based method combined with high correlation treatments and spin-orbit effects has been shown to be a reliable tool for obtaining accurate quantum chemical calculations on the chemistry of the *5f* elements. Thus, the entire field of actinide chemistry is now open for an accurate theoretical treatment on compounds larger than ThO.

The DK3-AIMP basis sets with the auxiliary spin-orbit basis sets for actinides are available in MOLCAS 5.4 versions<sup>38</sup>, for UTChem,<sup>39,40</sup> and in AIP Document E-PAPS files.<sup>41</sup>

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<sup>39</sup> In a new release of the UTChem Program package developed at the University of Tokyo.

<sup>40</sup> See <http://www.chem.t.u-tokyo.ac.jp/appchem/labs/hirao/student/paulovic/paulovic.html>.

<sup>41</sup> See E-PAPS Document No. E-JCPSA6-118-309325 for the DK3-AIMP and auxiliary spin-orbit basis sets for actinides. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>), or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for further information.

Table I. Spectroscopic constants for the  $^1\Sigma^+$  ground state of thorium monoxide ThO from the DK3-AIMP and corresponding DK3-AE calculations using the  $[Xe,4f,5d]$  core sets for Th and a  $[He]$  core set for O. Previous calculations along with available experimental data are listed also.

	$r_e(\text{\AA})$	$\omega_e(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})$	$D_e(\text{eV})$
This work				
DK3-AIMP SCF <sup>[a]</sup>	1.833	945	0.335	5.96
DK3-AIMP CASSCF <sup>[a,b]</sup>	1.879	856	0.319	9.14
DK3-AIMP MS-CASPT2 <sup>[c]</sup>	1.862	856	0.325	8.43
DK3-AIMP MS-CASPT2 RASSI-SO <sup>[c,d]</sup>	1.862	856	0.325	8.09
DK3-AE SCF <sup>[a]</sup>	1.832	959	0.336	5.82
DK3-AE CASSCF <sup>[a,b]</sup>	1.877	866	0.320	9.01
DK3-AE MS-CASPT2 <sup>[c,e]</sup>	1.866	856	0.324	8.43
DK3-AE MS-CASPT2 RASSI-SO <sup>[c,d,e]</sup>	1.866	856	0.324	8.10
Previously				
CG-AIMP SCF <sup>[f]</sup>	1.819	956		5.99
CG-AIMP-CASSCF <sup>[f]</sup>	1.886	865		9.15
PP SCF <sup>[g]</sup>	1.829	943		6.07
PP CASSCF <sup>[g]</sup>	1.882	876		8.92
PP CASSCF MRCI(SD) SCC (2g) <sup>[g,h]</sup>	1.862	867		8.87
				8.45 <sup>[i]</sup>
AE-DFR <sup>[j]</sup>	1.873	930	0.321	7.67
Expt. <sup>[k]</sup>	1.840	896	0.333	9.00

<sup>[a]</sup> Ref. 9.

<sup>[b]</sup> State-specific CASSCF with inactive core electrons.

<sup>[c]</sup> This work. 14 electrons correlated in 12 orbitals.

<sup>[d]</sup> Spin-orbit basis set  $(39s30p22d16f)[11s9p8d5f]$  for thorium and  $(14s11p1d)[4s4p1d]$  for oxygen.

<sup>[e]</sup> Electrons representing core are frozen.

<sup>[f]</sup> Reference 35. A  $[Xe,4f,5d]$  core and a  $(14s10p11d9f)[6s5p5d5f]$  Cowan-Griffin basis set.

<sup>[g]</sup> Reference 30. Relativistic energy-adjusted pseudopotential calculation corresponding to a  $[Kr,4d,4f]$  core and a  $(12s11p10d8f)[8s7p6d4f]$  basis set.

<sup>[h]</sup> SCC is the size consistency correction of Davidson and Langhoff.

<sup>[i]</sup> Spin-orbit corrected.

<sup>[j]</sup> Reference 36. All electron Dirac-Fock-Roothaan calculations with a  $(24s19p16d8f)[8s7p7d5f]$  basis set.

<sup>[k]</sup> Reference 37. The upper bound to the exact value.

Table II.

Table III.

Table IV.

# References

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## **4** General Conclusion

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In this dissertation, the development of the relativistic effective core potential (RECP) for  $f$  elements and its spin-orbit extension was presented.

Finally we expect that our new DK3-AIMP based methods will open up a world in the relativistic *ab initio* molecular orbital calculation for the large polyatomic systems including many heavy atoms.

## List of Publications

1. Third-order Douglas-Kroll *ab initio* model potential for actinide elements.  
J. Paulovič, T. Nakajima, K. Hirao, L. Seijo, J. Chem. Phys. **117**, 3597 (2002).
2. Relativistic and correlated calculations on the ground and excited states of ThO.  
J. Paulovič, T. Nakajima, K. Hirao, R. Lindh, P. Å. Malmqvist, J. Chem. Phys. **119**, 798 (2003).
3. The mechanism of ferromagnetic coupling in Cu(II)-Gd(III) complexes.  
J. Paulovič, F. Cimpoesu, M. Ferbinteanu, K. Hirao, J. Am. Chem. Soc., submitted.
4. The gas-phase chemiionization reaction between samarium and oxygen atoms: a theoretical study.  
J. Paulovič, L. Gagliardi, J. M. Dyke, K. Hirao, J. Chem. Phys., submitted.
5. A theoretical study of the ground and excited states of YbO.  
J. Paulovič, R. Lindh, P. Å. Malmqvist, B. O. Roos, K. Hirao, J. Chem. Phys., to be submitted.

## Other Publications

6. Qualitative intermolecular trends generated through population analysis schemes.  
J. Paulovič, K. Hirao, R. K. Roy, J. Chem. Phys., to be submitted.

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