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# Generalized Relativistic Effective Core Potentials for Actinides

Nikolai S. Mosyagin,<sup>\*,[a,b]</sup> Andrei V. Zaitsevskii,<sup>[a,c]</sup> Leonid V. Skripnikov,<sup>[a,b]</sup> and Anatoly V. Titov<sup>[a,b]</sup>

Actinide compounds are very intriguing objects for the quantum chemistry because, on the one hand, these compounds are of great scientific and technological interest and, on the other hand, quantitative first principle based modeling of their electronic structure is extremely difficult because of strong relativistic effects and complicated electron correlation pattern. The efficiency of high-level all-electron relativistic methods in applications to complex actinide systems of practical interest is questionable and more economical but sufficiently accurate approaches to the studies of such systems are preferable. Recently, generalized relativistic effective core

potentials (GRECPs) have been generated for actinides to perform accurate calculations of electronic structure and properties of their compounds with moderate computational cost. The accuracy of different GRECP versions is analyzed in atomic calculations and their applications to molecular and cluster calculations are reviewed. The results are compared with available experimental data and other theoretical studies. © 2015 Wiley Periodicals, Inc.

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## Introduction

Actinide-containing compounds are on the forefront of the modern quantum chemistry because, on the one hand, these compounds are of great scientific and technological interest and, on the other hand, calculations of their electronic structure to a great extent are challenging because they are largely at the limit of the current capabilities of modern quantum chemistry being extremely sophisticated and time-consuming.<sup>[1]</sup> Many properties of actinide compounds are unique because of nontrivial valence forms (due to variable valency in a wide range) and particular importance of the relativistic effects. The radionuclides resulting from operation of nuclear facilities and forming a basis of high-level waste, represent a serious threat to the environment and human health. Efficient immobilization of the actinide fraction of the high-level waste, diagnosis and prediction of degradation of immobilizing matrices, assessment of possibility for transition of the actinides to solution and especially to the gas phase, as well as detection of (super) small amounts in components of the environment are among the most important and difficult tasks of environmental protection. Reliable information about properties of gas-phase actinide-containing formations, both neutral and charged (including molecular and cluster anions), is necessary for correct interpretation of the results of study of ecosystem objects by destructive methods (laser ablation etc.), development of modern mass-spectrometric techniques. Knowledge about properties of the most important gas-phase and plasma formations containing actinides (except uranium and, to some degree, plutonium) is still fragmentary.

Practical study of complex, especially heterophase and nanostructured systems based on actinide compounds, which simulate matrices of high-level waste during their radiation damage, is hampered by lack of reliable theoretical data to

interpret the results of the most universal nondestructive experimental methods. These methods, including measurements of chemical shifts of X-ray emission spectra and Mössbauer spectra, hyperfine structure and spectra of nuclear quadrupole resonance, are capable to give information about physical-chemical states of atoms beyond the surface layers. An experimental study of chemical and spectroscopic properties of actinides, especially transuranium elements, is essentially hampered by their radioactive decay and radioactive emissions that cause chemical changes in the studied systems. Therefore, accurate relativistic calculations on actinide compounds with a high level of accounting for the electronic correlation are necessary for proper understanding their chemistry, mechanisms of physical-chemical processes, especially, for prediction and study of new properties. Computer simulations and the corresponding numerical experiments facilitate a creation of new materials and technologies, complementing and increasingly replacing real experimental studies with increasing economic effect. Understanding the chemical state (effective configuration) of actinides at atomic

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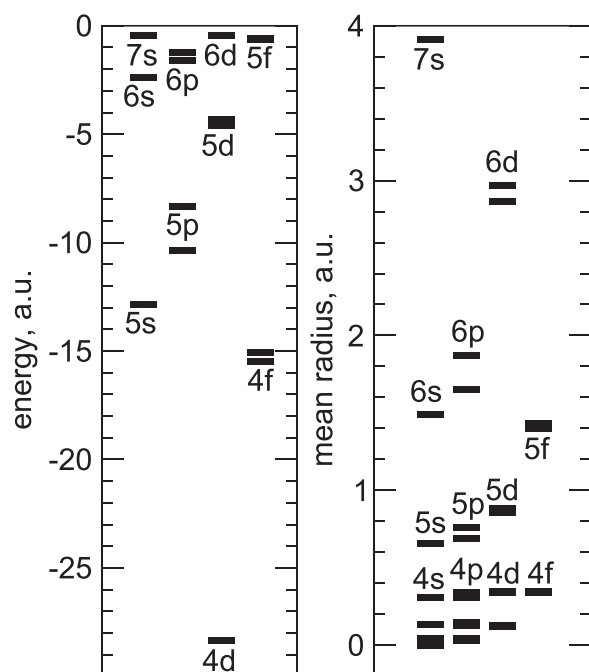
**Table 1.** Transition energies (TE, in  $\text{cm}^{-1}$ ) between the relativistic terms and the states averaged over the nonrelativistic and relativistic configurations of the Bk atom from numerical Dirac-Fock-Breit (DFB) calculations and the corresponding absolute errors of their reproducing in the different versions of all-electron calculations. DF + B means Dirac-Fock (DF) calculations with taking into account for the Breit (+B) interactions in the framework of the perturbation theory.

	TE	Absolute errors			
	DFB A = 247 Fermi	DFB A = 0 Point	DF+B A = 247 Fermi	DF A = 247 Fermi	HF A = 247 Fermi
Nonrel.aver. ... $5f^9 7s^2 \rightarrow$					
... $5f^9 7s^1 7p^1$	16,885	104	0	19	-7030
... $5f^9 7s^1 6d^1$	20,655	127	0	64	-15,645
... $5f^8 7s^2 6d^1$	14,771	-156	-1	-801	56,355
... $5f^8 7s^2 7p^1$	19,436	-224	-1	-899	72,595
... $5f^{10} 7s^1$	36,166	240	3	648	-62,733
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^3 7s_{1/2}^2 \rightarrow$					
... $5f_{5/2}^5 5f_{7/2}^4 7s_{1/2}^2$	18,097	-10	1	318	-9528
... $5f_{5/2}^4 5f_{7/2}^5 7s_{1/2}^2$	31,599	-19	2	622	-19,606
... $5f_{5/2}^3 5f_{7/2}^6 7s_{1/2}^2$	40,478	-25	2	911	-30,202
... $5f_{5/2}^1 5f_{7/2}^8 7s_{1/2}^2$	44,295	-34	3	1440	-52,850
... $5f_{5/2}^2 5f_{7/2}^7 7s_{1/2}^2$	44,714	-30	3	1184	-41,290
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 6d_{3/2}^1 \rightarrow$					
... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 6d_{5/2}^1$	6893	-21	0	65	-2712
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{1/2}^1 \rightarrow$					
... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{3/2}^1$	6542	4	0	57	-6291
... $5f_{5/2}^6 5f_{7/2}^3 7s_{1/2}^2 (J=7.5) \rightarrow$					
... (J=4.5)	7082	-3	0	-79	985
... (J=5.5)	11,915	-5	0	-81	1678
... (J=1.5)	12,725	-6	0	-127	1792
... (J=2.5)	25,412	-12	0	-166	3680
... (J=3.5)	32,455	-16	0	-198	4961

level, the processes of forming relatively small molecular clusters containing actinides, in particular, their oxidation state plays an important role. *Ab initio* modeling is of vital importance to create fundamentally new products and technologies in absence of analogues, because the reliability of *ab initio* predictions depends on belonging of the research object to a particular class in the least degree.

The actinide compounds are very difficult objects for accurate quantum chemical calculations. Computational difficulties are caused by huge relativistic effects, high density of low-lying electronic states, and complexity of electronic structure of actinides that cause extremely high demands on both the computing resources and effectiveness of computational methods, computer codes. The relativistic effects are sometimes neglected or taken into account in the framework of the perturbation theory at the last stage of calculations on light element compounds. However, these effects are rapidly increased with the nuclear charge  $Z$ . The relativistic effects are so huge in the case of actinides (see the errors in the last column of Tables 1 and 3) that they should be taken into account in accurate calculations from the very beginning and not as some kind of *posteriori* corrections. The difference between

the one-electron energies of the valence  $7s_{1/2}$  spinors and the  $5f_{5/2}$ ,  $5f_{7/2}$  ones for actinides is not too high as one can see from Figure 1. (Below for brevity, the  $n l_j = |l-1/2|$  and  $n l_j = |l+1/2|$  pair will be sometimes designated as just  $n l$ , where  $n$ ,  $l$ , and  $j$  are the principal, orbital, and total quantum numbers. The  $n l$ ,  $n l'$ , and  $n l''$  sets will be further designated by the  $n l l' l''$  indices, etc.) Therefore, the energies of excitations from (and into) the  $5f$  shell are rather low; this leads to appearance of the states with different occupation numbers of the  $5f$  shell among the ground and low-lying excited states for the actinide atoms and ions. The large number of low-lying states results in strong static correlation effects between the states of the same symmetry which have to be taken into account in accurate calculations. Most actinides have open  $5f$  shells in the ground states of their atoms and ions. Therefore, the  $5f$  spinors should be considered as valence ones, accounting also for their small one-electron energies. However, the  $5f$  shells are localized in the same spatial region as the  $5spd$  and  $6sp$  shells (see the average radii in Fig. 1), which have relatively large negative one-electron energies and should be considered as core-like states, whereas the  $7sp$  shells are valence. Low-energy excitations from the  $5f$  shell will lead to its



**Figure 1.** DFB one-electron energies and mean spinor radii for the uranium atom.

non-negligible relaxation and will also affect the outercore  $5spd$  and  $6sp$  shells. Like lanthanides and unlike the other light elements, the core  $(n-2)sp$  and  $(n-1)sp$  shells cannot be “frozen” in accurate calculations to reduce the computational efforts (the valence shells are  $nsp$  and  $n = 7$  for actinides).

There are several options to perform actinide compound calculations. The straightforward way is to use the Dirac-Coulomb(-Breit) Hamiltonians,<sup>[2–6]</sup> which are nominally most accurate from known relativistic Hamiltonians. In particular, four-component all-electron calculations with these Hamiltonians are made in Refs. [7,8]. The computational efforts in quantum chemical calculations using basis set expansions of one-electron spinors very rapidly increase with the number of basis functions. The application of four-component Dirac spinors requires the use of significantly larger primitive (usually Gaussians) basis sets (to describe properly their small components) as compared with the one- and two-component quasirelativistic approaches. The latter calculations exploiting the Douglas-Kroll-Hess Hamiltonian<sup>[9,10]</sup> are reviewed in paper.<sup>[11]</sup> Still, too large set of primitive basis functions is required to describe accurately a large number of the radial oscillations, which valence spinors have in the all-electron calculation due to their orthogonality to the core spinors.

The relativistic effective core potential (RECP) or pseudopotential method is widely used in calculations on molecules containing heavy atoms<sup>[12,13]</sup> because it reduces drastically the computational cost at the integral generation, self-consistent field (SCF) calculation and integral transformation stages. Different RECP versions are available for actinides in the literature.<sup>[14–17]</sup> They have been applied in practical calculations.<sup>[18–21]</sup> It was shown in papers<sup>[22–24]</sup> that the conventional radially-local (semilocal) form of the RECP operator (used by many groups up to now but proposed and first applied 50 years ago by Abarenkov and Heine<sup>[25,26]</sup> to nonrelativistic calculations of solids) is limited in

accuracy and some nonlocal corrections to the RECP operator were suggested<sup>[22,24,27,28]</sup> which have already allowed one to improve significantly the RECP accuracy.<sup>[23,24,29,30]</sup> The new generation of the RECPs is able to provide the accuracy as that attainable in the most advanced four-component approaches at many times smaller computational cost. Accordingly, it is possible to use modeling techniques for essentially more complex actinide compounds. Recently, the generalized relativistic effective core potentials (GRECPs) have been generated for actinides to perform calculations of electronic structure and properties of their compounds economically but with very high accuracy. These GRECPs have been analyzed in atomic calculations and then have been applied in series of molecular and cluster calculations.

## The Scheme of the GRECP Generation

The GRECP generation technique<sup>[22,23,31,32]</sup> is based on the RECP construction scheme proposed in Refs. [33–38]. The principal distinctive features of the GRECP technique are (a) generation of the GRECP components for both the valence and outercore electrons with different  $n$  but with the same  $lj$  pair and (b) addition of nonlocal (separable) terms to the conventional semilocal RECP operator. Below, these GRECP components will be also called the potentials. There are also some modifications<sup>[23,24,39]</sup> in respect to the spinor smoothing procedure<sup>[33]</sup> and the procedure of Gaussian approximation of the numerical potentials.<sup>[38,40]</sup> The main steps of the GRECP generation scheme are:

1. The numerical all-electron relativistic calculation of a generator state is performed for an atom under consideration. For this purpose, we use the modern Dirac-Fock-Breit (DFB) version of the atomic Dirac-Fock (DF) code.<sup>[41]</sup> Fermi nuclear charge distribution is used in the all-electron calculations in the present paper (unless otherwise explicitly stated). As a result, the radial parts of the large  $P_{nlj}(r)$  and small  $Q_{nlj}(r)$  components of the four-component DFB spinors and their  $\varepsilon_{nlj}$  one-electron energies are obtained. In this article for the case of actinides, the spinors with  $n \leq 4$  will be excluded from the GRECP calculations as innercore ones (the 60 electron core), the  $5spd$ ,  $6sp$  and  $7sp$ ,  $6d$ ,  $5fg$  ones will be considered as the outercore and valence ones, respectively.
2. The radial parts of the numerical pseudospinors  $\tilde{\varphi}_{nlj}(r)$  are constructed of that of the large components of both the valence and outercore DFB spinors so that the innermost pseudospinors for each  $lj$  pair have no radial nodes (nodeless), the next pseudospinors have one radial node, and so forth. Further, the node will mean the radial node. These pseudospinors satisfy the following conditions:

$$\tilde{\varphi}_{nlj}(r) = \begin{cases} P_{nlj}(r), & r \geq R_c, \\ f(r) = r^\gamma \sum_{i=0}^5 a_i r^i, & r < R_c, \end{cases} \quad (1)$$

$$l=0, 1, \dots, L, \quad j=|l \pm 1/2|, \quad n=n_{c1}, n_{c2}, \dots, n_{cN}, n_v,$$

where  $n=n_{c1}, n_{c2}, \dots, n_{cN}$  and  $n_v$  are the principal quantum numbers of outercore and valence electrons,

respectively,  $L$  is one more than the highest orbital angular momentum of the innercore spinors, and  $r$  is the radial variable. The leading power  $\gamma$  in the polynomial  $f(r)$  is typically chosen to be close to  $L$  to ensure a sufficient ejection of the valence and outercore electrons from the innercore region. The  $a_i$  coefficients are determined by the following requirements:

- $\tilde{\varphi}_{nlj}$  are normalized;
- $\tilde{\varphi}_{nclj}, \tilde{\varphi}_{nc2lj}, \dots, \tilde{\varphi}_{ncnlj}$ , and  $\tilde{\varphi}_{nclj}$  are orthogonal with a high degree of accuracy;
- $f$  and its first four derivatives match  $P_{nlj}$  and its derivatives;
- $f$  is a smooth and nodeless function;
- $\tilde{\varphi}_{nlj}$  ensure a sufficiently smooth shape of the corresponding potential ( $U_{nlj}$ , see the next item)

$R_c$  is chosen near such an extremum of the spinor that the corresponding pseudospinor has the defined above number of nodes. In practice, the  $R_c$  radii for the different spinors should be chosen close to each other to generate smooth potentials. Below, the pseudospinors will be sometimes also called the spinors.

3. The numerical potentials  $U_{nlj}$  are derived for each  $lj$  pair for the valence and outercore pseudospinors so that the  $\tilde{\varphi}_{nlj}$  are solutions of the nonrelativistic-type Hartree-Fock (HF) equations in the  $jj$ -coupling scheme for a "pseudoatom" with the removed innercore spinors

$$U_{nlj}(r) = \tilde{\varphi}_{nlj}^{-1}(r) \left[ \left( \frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \frac{l(l+1)}{2r^2} + \frac{Z^*}{r} - \tilde{J}(r) + \tilde{K}(r) \right. \right. \\ \left. \left. + \varepsilon_{nlj} \right) \tilde{\varphi}_{nlj}(r) + \sum_{n' \neq n} \varepsilon_{n'nlj} \tilde{\varphi}_{n'lj}(r) \right], \quad (2)$$

where  $Z^* = Z - N_{\text{ice}}$  is the effective innercore charge,  $Z$  is the nuclear charge,  $N_{\text{ice}}$  is the number of the InnerCore Electrons,  $\tilde{J}$  and  $\tilde{K}$  are the Coulomb and exchange operators calculated with the valence and outercore pseudospinors, and  $\varepsilon_{n'nlj}$  are the off-diagonal Lagrange multipliers. In the case of the pseudospinor with nodes, the potential is singular because the zeros of the denominator and numerator do not coincide. However, these zeros are close to each other in practice as it had been demonstrated in Ref. [42] and the most appropriate solution of this problem is the interpolation of the potential in a vicinity of the pseudospinor node. The error of reproducing the one-electron energy due to such an interpolation can be made small enough (because the pseudospinors are small in the vicinity of the node and the node position is not virtually changed at forming chemical bond and low-lying excitations). It does not exceed the errors of the GRECP approximation caused by smoothing the spinors and the approximate treatment of the interaction with the innercore electrons.<sup>[22]</sup> Then, one

can write the GRECP as a Hermitian operator in the spinor representation (corresponding to the  $jj$ -coupling scheme)

$$\hat{U}^{\text{GRECP}} = U_{nclj}(r) + \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} [U_{nclj}(r) - U_{nclj}(r)] \hat{P}_{lj} \\ + \sum_{n_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} \{ [U_{nclj}(r) - U_{nclj}(r)] \tilde{P}_{nclj} \\ + \tilde{P}_{nclj} [U_{nclj}(r) - U_{nclj}(r)] \} \\ - \sum_{n_c, n'_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} \tilde{P}_{nclj} \left[ \frac{U_{nclj}(r) + U_{n'_clj}(r)}{2} - U_{nclj}(r) \right] \tilde{P}_{n'_clj}, \\ \hat{P}_{lj} = \sum_{m_j=-j}^j |ljm_j\rangle \langle lj m_j|, \\ \tilde{P}_{nclj} = \sum_{m_j=-j}^j |n_c \widetilde{ljm_j}\rangle \langle n_c \widetilde{ljm_j}|, \quad (3)$$

where  $|ljm_j\rangle \langle lj m_j|$  is the projector on the two-component spin-angular eigenfunction  $\chi_{ljm_j}(\phi, \sigma)$  of the operators of the square  $j^2$  and projection  $j_z$  of the one-electron total momentum  $\hat{j}$ ,  $|n_c \widetilde{ljm_j}\rangle \langle n_c \widetilde{ljm_j}|$  is the projector on the two-component outercore pseudospinors  $\tilde{\varphi}_{nclj}(r) \chi_{ljm_j}(\phi, \sigma)$  (which are functions of the radial  $r$ , angular  $\phi$ , and spin  $\sigma$  variables),  $m_j$  is the quantum number of the total momentum projection, and  $J = L + 1/2$ .

Thus, the many-electron Dirac-Coulomb(-Breit) Hamiltonian is replaced by the effective Hamiltonian with the GRECP

$$\hat{H}^{\text{Ef}} = \sum_p [\hat{h}^{\text{Schr}}(\tau_p) + \hat{U}^{\text{GRECP}}(\tau_p)] + \sum_{p>p'} \frac{1}{r_{pp'}} \quad (4)$$

written only for valence and outercore electrons denoted here by composite indices  $p \equiv (n, l, j, m_j)$ , where  $\tau \equiv (r, \phi, \sigma)$  and  $r_{pp'}$  is the distance between the electrons  $p$  and  $p'$ . The GRECP operator  $\hat{U}^{\text{GRECP}}$  simulates interactions of the explicitly treated (outercore and valence) electrons with those which are excluded from the GRECP calculation. In Eq. (4),  $\hat{h}^{\text{Schr}}$  is the nonrelativistic one-electron Schrödinger operator for a point-charge Coulomb field

$$\hat{h}^{\text{Schr}} = -\frac{1}{2} \nabla^2 - \frac{Z^*}{r}, \quad (5)$$

where  $\nabla$  is the gradient operator. Contrary to the four-component (relativistic) wave function used in Dirac-Coulomb(-Breit) calculations, the pseudowave function in the GRECP case can be both two- and one-component (see the next item).

4. With a view to be used in molecular calculations with Gaussian basis sets, the numerical potentials taken in the form

$$U_{n_v L}^{\text{AREP}}(r)r^2,$$

$$[U_{n_v l}^{\text{AREP}}(r) - U_{n_v L}^{\text{AREP}}(r)]r^2, \quad l=0, 1, \dots, L-1,$$

$$\Delta U_{n_v l}(r)r^2, \quad l=1, 2, \dots, L,$$

$$[U_{n_c l j}(r) - U_{n_v l j}(r)]r^2, \quad n_c = n_{c1}, n_{c2}, \dots, n_{cN}, \quad l=0, 1, \dots, L, \\ j = |l \pm 1/2|, \quad (6)$$

where

$$U_{n_v l}^{\text{AREP}}(r) = \frac{l+1}{2l+1} U_{n_v l+}(r) + \frac{l}{2l+1} U_{n_v l-}(r), \quad (7)$$

$$\Delta U_{n_v l}(r) = U_{n_v l+}(r) - U_{n_v l-}(r) \quad (8)$$

for the valence electrons and  $l \pm \equiv (l, j = l \pm 1/2)$  are usually fitted by Gaussian functions. The latter functions are ordinarily written as

$$\sum_i c_i r^{k_i} \exp(-\alpha_i r^2), \quad (9)$$

where  $\alpha_i > 0$  and  $c_i$  are real parameters,  $k_i$  is equal to 0, 1, or 2. The numerical pseudospinors are fitted by Gaussians in the form

$$\tilde{\varphi}_{n l j}(r) = r^l \sum_i c_i M_i \exp(-\alpha_i r^2), \quad (10)$$

where  $M_i$  are the standard normalization factors.

For application of the GRECP to molecular calculations with the spin-orbital basis sets which are used in most existing quantum-chemical codes, the GRECP operator (3) should be transformed to the spin-orbital representation (which corresponds to the *LS*-coupling scheme) following work.<sup>[37]</sup> The components of the spin-averaged part of the GRECP operator are called the averaged relativistic effective potentials (AREP) and are written in form (7) for the valence electrons and

$$\hat{U}_{n c l}^{\text{AREP}}(r) = \frac{l+1}{2l+1} \hat{V}_{n c n_v l+}(r) + \frac{l}{2l+1} \hat{V}_{n c n_v l-}(r), \\ \hat{V}_{n c n_v l j}(r) = [U_{n c l j}(r) - U_{n_v l j}(r)] \tilde{P}_{n c l j}(r) + \tilde{P}_{n c l j}(r) [U_{n c l j}(r) - U_{n_v l j}(r)] \\ - \sum_{n'_c} \tilde{P}_{n c l j}(r) \left[ \frac{U_{n c l j}(r) + U_{n'_c l j}(r)}{2} - U_{n_v l j}(r) \right] \tilde{P}_{n'_c l j}(r) \quad (11)$$

for the outercore electrons, where  $\tilde{P}_{n c l j}(r)$  is the radial projector on the outercore pseudospinors  $\tilde{\varphi}_{n c l j}(r)$ . Obviously, these components may be used instead of the nonrelativistic generalized effective core potential (ECP) components in the above-

mentioned codes to take into account the scalar relativistic effects.

The operator of the effective spin-orbit interaction can also be derived following paper.<sup>[37]</sup> Its components are called the effective spin-orbit potentials (ESOP) and can be written as [see also Eq. (8)]

$$\Delta \hat{U}_{n c l}(r) = \hat{V}_{n c n_v l+}(r) - \hat{V}_{n c n_v l-}(r), \\ \hat{U}_{n l}^{\text{ESOP}} = \frac{2\Delta \hat{U}_{n l}(r)}{2l+1} \hat{P}_l \hat{\mathbf{l}} \hat{\mathbf{s}}, \quad (12) \\ \hat{P}_l = \sum_{m_l=-l}^l |l m_l\rangle \langle l m_l|,$$

where  $|l m_l\rangle \langle l m_l|$  is the angular projector on the spherical function  $Y_{l m_l}(\phi)$ ,  $m_l$  is the quantum number of the orbital momentum projection,  $\hat{\mathbf{l}}$  and  $\hat{\mathbf{s}}$  are the operators of orbital and spin momenta.

Neglecting the difference between  $U_{n_v L}^{\text{AREP}}$  and  $U_{n_v L}$  for virtual pseudospinors with  $l > L$ , the GRECP operator (3) is rewritten in the form

$$\hat{U}^{\text{GRECP}} \simeq U_{n_v L}^{\text{AREP}}(r) + \sum_{l=0}^{L-1} [U_{n_v l}^{\text{AREP}}(r) - U_{n_v L}^{\text{AREP}}(r)] \hat{P}_l \\ + \sum_{n_c} \sum_{l=0}^L \hat{U}_{n c l}^{\text{AREP}}(r) \hat{P}_l + \sum_{l=1}^L [\hat{U}_{n_v l}^{\text{ESOP}} + \sum_{n_c} \hat{U}_{n c l}^{\text{ESOP}}] \hat{P}_l, \quad (13)$$

where the following identities for the  $\hat{P}_{l j}$  projectors were used:

$$\hat{P}_{l \pm}(\phi, \sigma) = \frac{1}{2l+1} \left[ \left( l + \frac{1}{2} \pm \frac{1}{2} \right) \hat{P}_l(\phi) \pm 2\hat{P}_l(\phi) \hat{\mathbf{l}} \hat{\mathbf{s}} \hat{P}_l(\phi) \right]. \quad (14)$$

## The Main Features of the GRECP Method

- The “core-type” properties (or properties of *atoms in compounds*<sup>[43]</sup>) such as electronic densities near heavy nuclei, hyperfine constants, and matrix elements (ME) of the other operators singular on heavy nuclei (i.e., the spatial localization rather than the orbital subspace partitioning is taken into account) can be calculated reliably via the one-center restoration of four-component wavefunction in the vicinity of heavy nuclei from the smoothed pseudospinors.<sup>[44,45]</sup> Some examples are given in subsection “GRECP/coupled cluster calculations of T,P-odd effects in diatomic molecules.”
- As well as standard small-core pseudopotentials, GRECPs leave both outercore and valence electrons. However, in contrast to the conventional semilocal models, different potentials (GRECP components) act on the outercore and valence electrons with the same *lj* pairs (see e.g., Fig. 2). The outercore (nodeless) pseudospinors together with valence (nodal) pseudospinors are used for constructing the GRECP components (see the third item in section “The scheme of the GRECP generation”). This is essential



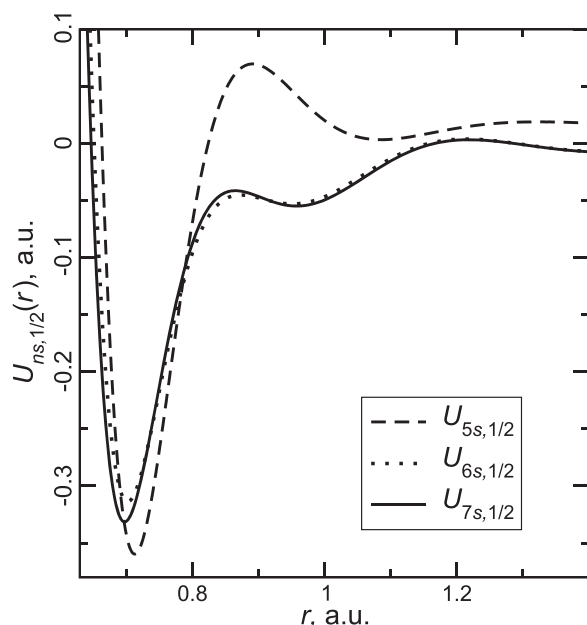


Figure 2. The GRECP components for the valence ( $7s_{1/2}$ ) and outercore ( $5s_{1/2}$ ,  $6s_{1/2}$ ) subshells of uranium.

for accurate description of properties associated with processes in a rather wide range of energies.

- The most common GRECP operators can be represented by simple combinations of semilocal<sup>[33,46]</sup> [see the first line in Eq. (3) or the terms containing  $U_{nv}$  in Eq. (13)] and separable<sup>[47,48]</sup> [the 2–4 lines in Eq. (3) or the terms containing  $U_{nc}$  in Eq. (13)] operators. For some particular cases, Huzinaga-type<sup>[49,50]</sup> terms (see the next item) can also be incorporated into the GRECP operator. Therefore, a very high accuracy of the model, significantly superior to that of contemporary correlation methods, does not require much additional computational efforts compared with conventional pseudopotential models.
- Both two-component spinors (i.e., the  $\tilde{\varphi}_{nlj}(r)\chi_{ljm_j}(\phi, \sigma)$  basis functions) and conventional one-component spin-orbitals (the  $\tilde{\varphi}_{nl}(r)Y_{lm_l}(\phi)\Upsilon_{m_s}(\sigma)$  basis functions where  $\Upsilon_{m_s}$  is the spin function and  $m_s$  is the quantum number of the spin projection) can be used in molecular GRECP calculations. The former case was implemented in the GRECP/RCCSD program package.<sup>[29,51]</sup> The latter case was used in the GRECP/SODCI codes.<sup>[52]</sup> The number of Coulomb two-electron integrals can be significantly decreased in the latter case due to the spin symmetry. It should be emphasized that the innercore shells are explicitly excluded from GRECP calculations just as spinors at the stage of the GRECP generation (see the first item in section “The scheme of the GRECP generation”). Moreover, the outercore shells can also be “frozen” as spinors in GRECP calculations with the spin-orbit basis sets when the level-shift terms of  $B_{nc,lj}\tilde{P}_{nc,lj}$  Huzinaga-type (where  $B_{nc,lj} \gg |\varepsilon_{nc,lj}|$ ) are transformed to the spin-orbital representation using Eq. (14) and are then added to GRECP operator (13).<sup>[24,52]</sup>

- Breit interactions and other quantum electrodynamics effects<sup>[31,32]</sup> as well as the effects of finite nuclear size are readily and efficiently incorporated into the GRECP model. That allows one to perform high-level relativistic calculations with computationally simple Coulomb electron-electron interaction operator (one can see that the results of the DFB calculations with Fermi nuclear charge distribution and the corresponding GRECP calculations with Hamiltonian (4) agree well in Tables 2 and 4).
- As it was discussed in the Introduction, the  $5f$  shells in actinides have both the valence and outercore features. That leads to either the larger number of explicitly treated electrons or essentially lower accuracy in (G)RECP calculations of actinide compounds in comparison with that of the main group elements. The similar situation is observed for the  $4f$  shells in lanthanides and in a less degree for  $d$ -shells in transition metal elements. The GRECP model described above is readily extended to include other terms such as the “self-consistent” and “term-splitting” corrections for economical but accurate treatment of  $d$ - and  $f$ -elements.<sup>[24,28]</sup> (Note meantime that the GRECP “term-splitting” correction is equivalent in essence to the well-known Hubbard “+U” correction actively exploited in the density functional theory (DFT) studies of systems with open localized  $d$  and  $f$  shells.<sup>[53]</sup>) The correlations with the core shells can be approximately taken into account with the help of “correlated” GRECP versions.<sup>[54]</sup> The decrease in the number of explicitly correlated electrons will reduce dramatically the computational expenses in challenging correlation calculations.

## Atomic Tests of GRECP Accuracy

The generated GRECPs were tested in atomic SCF calculations which are largely sufficient to analyze the quality of different (G)RECP versions. These calculations are numerical (finite-difference), this allows one to exclude the errors due to incompleteness of the basis sets and compare the “pure” errors inherent to different GRECP versions. In the framework of the atomic SCF approach, one can easily perform the reference all-electron calculations with the Dirac-Coulomb-Breit Hamiltonian. The errors appearing already in the atomic one-configuration GRECP studies as compared with the DFB ones are, obviously, inherent for the corresponding GRECP. These errors will be added to the errors appearing in the following correlation and molecular calculations with this GRECP. Therefore, the atomic one-configurational calculations give upper limits on the accuracy of the tested GRECP versions. The all-electron calculations were performed using the modern DFB version of the numerical atomic DF code.<sup>[41]</sup> The GRECP calculations were performed with the help of the numerical atomic two-component HF code in the  $jj$ -coupling scheme.<sup>[22]</sup> The results of the DFB calculations are presented in the second column of Tables 1–4, whereas the errors of their reproducing in the different all-electron and GRECP calculations are given in the following columns.

**Table 2.** Transition energies (TE, in  $\text{cm}^{-1}$ ) between the relativistic terms and the states averaged over the nonrelativistic and relativistic configurations of the Bk atom from numerical DFB calculations and the corresponding absolute errors of their reproducing in calculations with different GRECP versions.

	TE	Absolute errors				
	DFB A = 247 Fermi	Original GRECP (num.)	Original GRECP (gauss.)	Valence GRECP	Core GRECP 6spd, 5fg	Core GRECP 5spdfg
Nonrel.aver. ... $5f^9 7s^2 \rightarrow$						
... $5f^9 7s^1 7p^1$	16,885	−1	−1	2	−98	−2324
... $5f^9 7s^1 6d^1$	20,655	−1	−1	8	−98	−1976
... $5f^8 7s^2 6d^1$	14,771	567	573	655	677	−485
... $5f^8 7s^2 7p^1$	19,436	577	583	667	704	−1038
... $5f^{10} 7s^1$	36,166	−539	−542	−523	−653	−1879
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^3 7s_{1/2}^2 \rightarrow$						
... $5f_{5/2}^5 5f_{7/2}^4 7s_{1/2}^2$	18,097	415	413	498	496	306
... $5f_{5/2}^4 5f_{7/2}^5 7s_{1/2}^2$	31,599	609	607	772	769	410
... $5f_{5/2}^3 5f_{7/2}^6 7s_{1/2}^2$	40,478	581	578	819	813	308
... $5f_{5/2}^1 5f_{7/2}^8 7s_{1/2}^2$	44,295	−146	−150	227	217	−516
... $5f_{5/2}^2 5f_{7/2}^7 7s_{1/2}^2$	44,714	329	325	637	629	−1
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 6d_{3/2}^1 \rightarrow$						
... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 6d_{5/2}^1$	6893	−9	−7	−9	−5	97
Rel.aver. ... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{1/2}^1 \rightarrow$						
... $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{3/2}^1$	6542	−4	−3	0	9	−460
... $5f_{5/2}^6 5f_{7/2}^3 7s_{1/2}^2 (J=7.5) \rightarrow$						
... ( $J=4.5$ )	7082	250	250	259	259	218
... ( $J=5.5$ )	11,915	484	484	500	500	431
... ( $J=1.5$ )	12,725	463	463	480	480	406
... ( $J=2.5$ )	25,412	1020	1021	1054	1055	906
... ( $J=3.5$ )	32,455	1253	1253	1295	1296	1100

To estimate contribution from the relativistic effects, the DFB calculations with the light velocity increased in 1000 times were performed. These calculations are excellent approximation of the nonrelativistic HF ones in the *jj*-coupling scheme (except perhaps the nuclear model). Their errors are presented in the last column of Tables 1 and 3. One can see that the relativistic effects are huge for actinides and have to be accounted for in reliable calculations. The contribution from the finite size of the nucleus is rather small and can be neglected for the level of the “chemical accuracy” ( $\sim 1$  kcal/mol or  $350 \text{ cm}^{-1}$ ). The largest error due to neglecting the Breit interactions (which are the relativistic corrections to the Coulomb interelectronic interactions) is  $1500 \text{ cm}^{-1} \approx 4.5$  kcal/mol (see the ...  $5f^8 7s^2 7p^1 \rightarrow \dots 5f^{10} 7s^1$  transition in Table 1) that is larger than the “chemical accuracy” level. One can also see that the differences between accounting for Breit interactions in the framework of the perturbation theory and by self-consistent manner are small.

As it was noted in the Introduction, open *5f* shells in actinides, on the one hand, are close in one-electron energies to the valence *7sp* shells and, on the other hand, are spatially close to the outercore *5sp* and *6spd* shells. That leads to advisability to include all the electrons with the principal quantum numbers  $n \geq 5$  explicitly in GRECP calculations.

Thus, the 60-electron inner cores are used in the presented GRECP versions for actinides. The valence and core GRECP versions were derived from the original GRECP version by neglecting the differences between the outercore and valence potentials. Thus, the valence GRECP operator is semilocal one with the *7s*, *7p*, *6d*, *5f*, and *5g* components of the original GRECP version [i.e., the first line in Eq. (3) or the terms containing  $U_{n_v}$  in Eq. (13)]. The main difference of the valence GRECP from the conventional RECPs is that the components of the former were constructed for nodal valence pseudospinors. Thus, these are the valence potentials (not the outercore or somehow averaged ones) which act on the valence electrons in this GRECP version. Two different core GRECP operators contain the *6spd*, *5fg*, and *5spdfg* components, respectively.

It should be emphasized that the *5f* pseudospinors are nodeless that can result in essential errors (e.g., see splitting into terms in Table 2). The one potential per each *lj* pair acts on the *f* shells of actinides in the present GRECP version unlike, for example, the three *5s*, *6s*, and *7s* potentials for the *s* shell. Thus, the GRECP for the *f* shells resembles the conventional semilocal RECP and it is not surprising that the accuracy of the different nonlocal original and semilocal (valence and core) GRECP versions for transitions with the



**Table 3.** The  $\langle r^2 \rangle$  ME (in a.u.) obtained with the spinors from numerical DFB calculations of the state averaged over the nonrelativistic  $5f^8 7s^2 7p^1$  configuration (which differs from the generator state by the occupation number of the  $5f$  shell) of the Bk atom and the corresponding relative errors (in %) of their reproducing in different versions of all-electron calculations.

	ME	Relative errors (in %)		
	DFB A = 247 Fermi	DFB A = 0 Point	DF A = 247 Fermi	HF A = 247 Fermi
$5s_{1/2}$	0.410832	-0.211	-0.268	30.579
$5p_{1/2}$	0.442487	-0.023	-0.406	31.326
$5p_{3/2}$	0.555741	0.015	-0.236	4.563
$5d_{3/2}$	0.686152	0.020	-0.189	3.515
$5d_{5/2}$	0.734351	0.020	-0.098	-3.279
$5f_{5/2}$	1.55976	0.064	0.188	-14.338
$5f_{7/2}$	1.65332	0.069	0.377	-19.186
$6s_{1/2}$	1.99991	-0.257	-0.286	36.381
$6p_{1/2}$	2.45085	-0.026	-0.467	39.410
$6p_{3/2}$	3.33916	0.043	-0.242	2.323
$7s_{1/2}$	16.2517	-0.312	-0.215	33.954
$7p_{1/2}$	27.8947	0.084	-0.337	20.498
$7p_{3/2}$	37.4487	0.185	-0.106	-10.244

change of the  $5f$  shell occupation number is close. To increase the accuracy, one can include the  $4f$  electrons in the GRECP calculations that leads to the  $5f$  pseudospinors with one node and the two  $4f$  and  $5f$  potentials. It is obviously that it also leads to a large increase in computational expenses. Alternatively, one can apply the self-consistent and term-splitting corrections to the GRECP operator<sup>[24,28]</sup> that also leads to the different potentials acting on the  $f$  electrons. However, the present GRECP versions should be suitable for reliable calculations of actinide compounds at the level of accuracy of order of  $1000 \text{ cm}^{-1} \approx 3 \text{ kcal/mol}$ . Of course, if the  $5f$  shell occupation number is not changed in the studied cases, the accuracy will be significantly higher. The original GRECP version errors are quite small for the transitions where the  $5f$  spinors are not directly involved, for example,  $5f^9 7s^2$

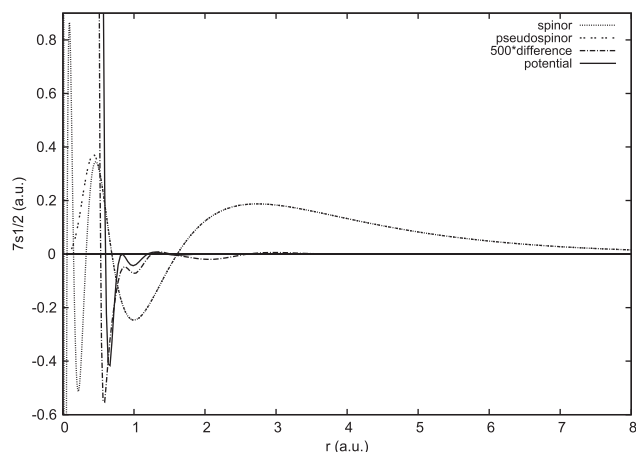
$\rightarrow 5f^9 7s^1 7p^1$  and  $5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{1/2}^1 \rightarrow 5f_{5/2}^6 5f_{7/2}^2 7s_{1/2}^2 7p_{3/2}^1$  ones in Table 2.

The  $\langle r^2 \rangle$  ME characterize the wavefunction in the outermost region. They are reproduced in the GRECP calculations with high accuracy for the case of the nodal  $7sp$  pseudospinors and notably worse for the nodeless  $5f$  ones as one can see in Table 4. The errors in reproducing  $\langle r^2 \rangle$  for the  $7sp$  spinors are essentially increased for the semilocal (valence and especially core) GRECP versions. One can also see from Figure 3 that the shape of the  $7s$  spinor is very well reproduced in the outercore and valence region with the help of the GRECP. It should be emphasized that the state used in these calculations (Table 4 and Fig. 3) differs from the generator state by the occupation number of the  $5f$  shell. One can also see from comparison of the third and fourth columns in Tables 2 and 4 that the accuracy of Gaussian approximation of the numerical GRECP components is high.

There is the large number of articles<sup>[16,55–71]</sup> where the parameters of the energy-consistent (or energy-adjusted) pseudopotentials (ECPs) are presented. Unlike the GRECP, the ECPs are generated by direct fitting the transition energies between multitude of different valence states for a considered atom and its ions and use the conventional semilocal RECP operator. These ECPs are included in many quantum chemical packages and widely used in calculations. In our studies,<sup>[23,29,32]</sup> (one can also compare also the excitation energies for the superheavy element 120 atom in Refs. [72–76]), the ECP accuracy was found notably lower than the GRECP one. Later such a drawback of the ECPs was attributed to the used Wood-Boring approximation<sup>[77]</sup> instead of the Dirac-Coulomb(-Breit) Hamiltonian, the small number of Gaussians in ECP expansions, and using the two-step fitting procedure for the scalar-relativistic and spin-orbit ECP parts instead of the one-step procedure at the two-component level<sup>[78–80]</sup> and the new more accurate ECPs were generated. Unfortunately, the parameters of the new and allegedly accurate ECP for the Hg atom<sup>[78]</sup> were not provided for our analysis and are not published elsewhere.<sup>[81]</sup>

**Table 4.** The  $\langle r^2 \rangle$  ME (in a.u.) obtained with the spinors from numerical DFB calculations of the state averaged over the nonrelativistic  $5f^8 7s^2 7p^1$  configuration (which differs from the generator state by the occupation number of the  $5f$  shell) of the Bk atom and the corresponding relative errors (in %) of their reproducing in calculations with different GRECP versions.

	ME	Relative errors (in %)				
	DFB A = 247 Fermi	Original GRECP (num.)	Original GRECP (gauss.)	Valence GRECP	Core GRECP $6spd, 5fg$	Core GRECP $5spdfg$
$5s_{1/2}$	0.410832	2.813	2.824	3.290	3.387	2.839
$5p_{1/2}$	0.442487	2.544	2.542	3.024	3.042	2.569
$5p_{3/2}$	0.555741	2.499	2.498	2.959	2.980	2.554
$5d_{3/2}$	0.686152	1.980	1.978	2.101	2.108	2.119
$5d_{5/2}$	0.734351	1.882	1.882	1.997	2.003	2.028
$5f_{5/2}$	1.55976	0.627	0.623	0.333	0.339	1.295
$5f_{7/2}$	1.65332	0.570	0.566	0.302	0.306	1.293
$6s_{1/2}$	1.99991	0.096	0.098	0.080	0.040	-1.371
$6p_{1/2}$	2.45085	0.069	0.070	0.034	0.026	-0.633
$6p_{3/2}$	3.33916	0.047	0.047	0.044	0.033	-0.535
$7s_{1/2}$	16.2517	-0.002	0.001	-0.025	0.116	2.884
$7p_{1/2}$	27.8947	-0.011	-0.016	-0.029	-0.080	-2.104
$7p_{3/2}$	37.4487	-0.015	-0.017	-0.009	-0.069	-5.397



**Figure 3.** The radial parts for the  $\tilde{\varphi}_{7s1/2}$  pseudospinor and the  $P_{7s1/2}$  large component of the spinor from numerical DFB calculation of the state of the Bk atom averaged over the nonrelativistic  $\dots 5f^8 7s^2 6d^1$  configuration (which differs from the generator state by the occupation number of the  $5f$  shell), their difference multiplied by 500, and the  $U_{7s1/2}$  potential.

## Molecular Calculations

### GRECP/coupled cluster calculations of T,P-odd effects in diatomic molecules

The GRECP method can be applied to accurate calculation of special type of parameters of actinide (heavy atom) containing molecules such as hyperfine structure and closely related parameters that are required for planning and interpretation of experiments toward the search for effects of violation of fundamental symmetries and variation of fundamental “constants.” It was found since 1960th<sup>[82–88]</sup> that extremely sensitive experiments toward the search of effects of violation of time-reversal (T) and/or space-parity (P) symmetries in fundamental interactions can be performed on molecules containing heavy atoms. One of such effects is the electric dipole moment (EDM) of electron (eEDM),  $d_e$ . The Standard model predicts that the eEDM value is less than  $10^{-38} e \cdot \text{cm}$ .<sup>[87]</sup> However, its popular extensions predict about ten orders of magnitude higher value.<sup>[89]</sup> Therefore, the search of eEDM can be considered as the search of the New physics beyond the Standard model.

The common feature of the molecular experiments toward the search of eEDM is that interpretation of their result requires knowledge of the internal effective electric field (see below for definition) which cannot be measured and have to be calculated. Experiment gives only interaction energy of the field with eEDM. The current limit,  $|d_e| < 9 \times 10^{-29} e \cdot \text{cm}$ , was set with a molecular beam of thorium monoxide (ThO) molecules in the metastable electronic  $H^3\Delta_1$  state.<sup>[90]</sup> The interpretation of the experiment required the value of effective electric field obtained in Ref. [91]. There is a number of systems on which experiments to search for T,P-odd effects have already been conducted or suggested and which are investigated theoretically and experimentally (HfF<sup>+</sup>,<sup>[92–98]</sup> YbF,<sup>[99–106]</sup> ThO,<sup>[90,91,107–111]</sup> ThF<sup>+</sup>,<sup>[93,112]</sup> TaN,<sup>[113,114]</sup> WC,<sup>[115,116]</sup> PbF,<sup>[117–119]</sup> RaO,<sup>[120,121]</sup> RaF,<sup>[122,123]</sup> PtH<sup>+</sup>,<sup>[96,124]</sup> etc.). Here, we consider our recent calculations of the electronic structure of ThO and

ThF<sup>+</sup> molecules.<sup>[91,109,110,112]</sup> The systems are of great interest for experiments due to rather high effective electric field acting on electrons (see below) and a number of experimental advantages such as existing of low-lying metastable or ground electronic  $^3\Delta_1$  state. The state contains close  $\Omega$ -doublet levels, which allow one full polarization in a small electric field and cancelation of many systematic errors due to opposite signs of the effects on the doublet components,<sup>[125,126]</sup> very small magnetic moment due to cancelation of the orbital and spin contributions<sup>[96]</sup> and long lifetime of  $^3\Delta_1$  electronic state.<sup>[113]</sup> The experiments on the molecules are in progress.<sup>[90,92,93]</sup>

It was mentioned above that to interpret the results of the molecular eEDM experiment in terms of the eEDM one should know the parameter usually called “the effective electric field on electron,”  $E_{\text{eff}}$ , which cannot be measured.  $E_{\text{eff}}$  actually relevant to only the spin-polarized electrons. It can be evaluated as an expectation value of the T,P-odd operator (see Refs. [127–129]):

$$W_d = \frac{1}{\Omega} \left\langle \Psi \left| \sum_p \frac{H_d(p)}{d_e} \right| \Psi \right\rangle, \quad (15)$$

where  $\Psi$  is the many-electron wave function of the considered state of ThO and ThF<sup>+</sup>,  $\Omega = \langle \Psi | \mathbf{J} \cdot \mathbf{n} | \Psi \rangle$ ,  $\mathbf{J}$  is the total electronic momentum,  $\mathbf{n}$  is the unit vector along the molecular axis  $\zeta$  directed from Th to light atom ( $\Omega = 1$  for the considered  $^3\Delta_1$  state of ThO/ThF<sup>+</sup>),

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma E \end{pmatrix}, \quad (16)$$

$\mathbf{E}$  is the inner molecular electric field, and  $\sigma$  are the Pauli matrices. In these designations  $E_{\text{eff}} = W_d / \Omega$ .

In addition to interaction (16), there is a T,P-odd interaction defined by pseudoscalar–scalar electron–nucleus neutral currents that is given by the following operator (see<sup>[130]</sup>):

$$H_{T,P} = i \frac{G_F}{\sqrt{2}} Z k_{T,P} \gamma_0 \gamma_5 \rho_N(\mathbf{r}), \quad (17)$$

where  $k_{T,P}$  is the dimensionless constant of the interaction,  $G_F$  is the Fermi constant,  $\gamma_0$  and  $\gamma_5$  are the Dirac matrixes and  $\rho_N(\mathbf{r})$  is the nuclear density normalized to unity.  $k_{T,P}$  constant can be extracted from the ThO or ThF<sup>+</sup> experiment if one knows an electronic structure factor,  $W_{T,P}$ , on the Th nucleus:

$$W_{T,P} = \frac{1}{\Omega} \left\langle \Psi \left| \sum_p \frac{H_{T,P}(p)}{k_{T,P}} \right| \Psi \right\rangle. \quad (18)$$

Similarly to  $E_{\text{eff}}$ , the parameter can to be obtained only theoretically.

Finally, using  $^{229}\text{Th}$  isotope one can search for T,P-odd interaction of  $^{229}\text{Th}$  nuclear magnetic quadrupole moment (MQM) with electrons in  $^{229}\text{ThO}$  and  $^{229}\text{ThF}^+$  molecules.<sup>[109,112,113]</sup> The T,P-odd electromagnetic interaction is described by the Hamiltonian<sup>[86,127]</sup>

$$H^{\text{MQM}} = -\frac{M}{2I(2I-1)} \sum_{p,q} T_{pq} \frac{3}{2} \frac{[\alpha \times \mathbf{r}]_p r_q}{r^5}, \quad (19)$$

where  $\alpha$  are the  $4 \times 4$  Dirac matrices,  $\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$ ,  $\mathbf{r}$  is the displacement of the electron from the Th nucleus,  $I$  is the nuclear spin,  $M$  is the nuclear MQM,

$$M_{p,q} = \frac{3M}{2I(2I-1)} T_{p,q} \quad (20)$$

$$T_{p,q} = I_p I_q + I_p I_q - \frac{2}{3} \delta_{p,q} I(I+1). \quad (21)$$

In the subspace of  $\pm\Omega$  states Hamiltonian (19) is reduced to the following effective molecular Hamiltonian<sup>[84]</sup>:

$$H_{\text{eff}}^{\text{MQM}} = -\frac{W_M M}{2I(2I-1)} \hat{\mathbf{S}} \cdot \hat{\mathbf{n}}, \quad (22)$$

where  $\mathbf{S}$  is the effective electron spin,<sup>[131]</sup>  $S = |\Omega| = 1$ .  $W_M$  parameter can be evaluated by the following ME<sup>[113]</sup>:

$$W_M = \frac{3}{2\Omega} \left\langle \Psi \left| \sum_p \left( \frac{\alpha_p \times \mathbf{r}_p}{r_p^5} \right) r_{\zeta} \right| \Psi \right\rangle. \quad (23)$$

In the MQM search one can obtain limits on the strength constants of T,P-odd nuclear forces, neutron EDM, quantum chromodynamics (QCD) vacuum angle  $\theta$ , quark EDM, and chromo-EDM.<sup>[109,113]</sup>

To verify (indirectly)  $E_{\text{eff}}$ ,  $W_{T,P}$ , and  $W_M$  values one can compute and compare with experiment value of hyperfine structure constant which is closely connected to the considered parameters.<sup>[132]</sup> To obtain  $A_{||}$  on  $^{229}\text{Th}$  in the  $^{229}\text{ThO}$  and  $^{229}\text{ThF}^+$  the following ME can be computed:

$$A_{||} = \frac{\mu_{\text{Th}}}{\Omega} \left\langle \Psi \left| \sum_p \left( \frac{\alpha_p \times \mathbf{r}_p}{r_p^3} \right) r_{\zeta} \right| \Psi \right\rangle, \quad (24)$$

where  $\mu_{\text{Th}}$  is magnetic moment of an isotope of  $^{229}\text{Th}$  nucleus having spin  $I$ .

For the preparation and conduction of the experiment, the value of  $g$ -factor of the considered molecule is of interest. It is defined as

$$G_{||} = \frac{1}{\Omega} \left\langle \Psi \left| \hat{\mathbf{L}}_{\hat{n}}^e - g_S \hat{\mathbf{S}}_{\hat{n}}^e \right| \Psi \right\rangle, \quad (25)$$

where  $\hat{\mathbf{L}}^e$  and  $\hat{\mathbf{S}}^e$  are the electronic orbital and electronic spin momentum operators, respectively;  $g_S = -2.0023$  is a free-electron  $g$ -factor. For  $^3\Delta_1$  state, the value of  $G_{||}$  is zero in nonrelativistic limit (with free electron  $g$ -factor set to  $-2.000$ ). Therefore, the parameter is very sensitive to the quality of the wave function, as high-order interference contributions between the spin-orbit and electron correlation effects become important.

It follows from Eqs. (16) to (24) that the action of the corresponding operators is heavily concentrated in the atomic core regions. At the same time, the leading contribution to the corresponding ME (mean values) is due to the valence electrons as contributions from the inert (usually closed and spherically

symmetric) inner-core shells compensate each other or are negligible in most cases of practical interest for the operators, in particular, dependent on the total angular momentum and spin. Note, however, that the spin-polarization of core (subvalence or outer-core) shells induced by the valence unpaired electrons can provide a comparable contribution by magnitude to such properties as that from the valence electrons, for example, see Refs. [100,121,133]. We shall call such properties as the "core characteristics" assuming that the main contribution to them comes from the spatially localized core region rather than from core shells.

It was stated in section "The scheme of the GRECP generation" that the wavefunction obtained within the GRECP approach has incorrect behavior in the core region. However, the correct four-component behavior of the wave-function can be restored.<sup>[112,129]</sup> This is based on a proportionality property of valence and virtual (unoccupied in the reference Slater determinant) spinors<sup>[129]</sup> in the inner-core regions of heavy atom. Recently, we have developed an efficient procedure of restoration<sup>[112]</sup> which is interfaced to the well-developed codes on correlation treatment such as DIRAC,<sup>[134]</sup> MRCC,<sup>[135,136]</sup> and CFOUR.<sup>[133,137,138]</sup> The codes were used in the calculations given below in this section.

The computational scheme used to calculate core characteristics in ThO and ThF<sup>+</sup> is as follows.<sup>[91,110,112]</sup> The  $1s-4f$  inner-core electrons of Th were excluded from correlation calculations using the valence version of the GRECP method in all the stages described below.

- i. The leading contributions were obtained within 38-electron, two-component coupled-cluster with single, double, and perturbative triple cluster amplitudes, 38e-2c-CCSD(T). In the calculation, we used MBas basis set: (30,20,10,11,4,6,5)/[30,8,10,4,4,2,1]. For oxygen and fluorine, we used the aug-ccpVQZ basis set<sup>[139]</sup> with two removed g-type basis functions.
- ii. Higher-order correlation effects were considered as correction. For this, we have performed two-component calculations within the coupled-cluster method with single, double, triple, and perturbative quadruple cluster amplitudes, CCSDT(Q), and within the CCSD(T) method. The correction was calculated as a difference between the calculated parameters within the CCSDT(Q) and CCSD(T) methods. In the calculations, we have frozen 20 outer core electrons ( $5s^2 5p^6 5d^{10}$  shells of Th and  $1s^2$  shell of O and F). Besides we used compact atomic natural basis sets CBasSO which were generated using the same procedure that was used and described in.<sup>[75,110,112]</sup>
- iii. Calculation of the corrections on the basis set enlargement to the considered parameters. They were calculated as differences between the values obtained within the scalar-relativistic CCSD(T) calculation using the same basis set as used for the main two-component calculation and scalar-relativistic CCSD(T) calculation utilizing the extended basis set on Th (Lbas basis set (37,29,15,14,10,10,5)/[22,17,15,14,10,10,5] generated in Ref. [110]).

**Table 5.** Calculated values of the molecule-frame dipole moment ( $d$ ), effective electric field ( $E_{\text{eff}}$ ), parameter of the T,P-odd pseudoscalar–scalar electron–nucleus neutral currents interaction ( $W_{\text{T,P}}$ ), parameter of T,P-odd MQM interaction ( $W_M$ ), hyperfine structure constant ( $A_{\parallel}$ ) and  $g$ -factor ( $G_{\parallel}$ ) of the  $^3\Delta_1$  state of  $\text{ThF}^+$  compared with the corresponding values of ThO from Refs. [109,110] using the coupled-cluster methods.

Method	$d^{[a]}$ , Debye	$E_{\text{eff}}$ , GV/cm	$W_{\text{T,P}}$ , kHz	$W_M$ , $\frac{10^{13}\text{Hz}}{e\text{ cm}^2}$	$A_{\parallel}$ , $\frac{\mu_{\text{Th}}}{\mu_{\text{N}}}$ ·MHz	$G_{\parallel}$
38e-2c-CCSD	2.69	35.5	48	0.87	−4214	0.039
38e-2c-CCSD(T)	2.66	38.1	51	0.90	−4164	0.033
Correlation correction	0.07	0.0	0	−0.01	13	0.001
Basis set correction	−0.01	−0.6	−1	−0.02	−14	−
Vibr. contribution	0.03	−0.1	0	—	2	−
<b>Final (ThF<sup>+</sup>)</b>	2.74	37.3	50	0.88	−4163	0.034
<b>Final (ThO)</b>	4.23	81.5	112	1.66	−2949	0.007
(See Refs. [109,110])						
<b>ThO, Experiment</b>	4.098(3) <sup>[165]</sup>	—	—	—	—	0.0083 <sup>[107,166]</sup>

[a] The dipole moment is calculated with respect to the Th nucleus.

iv. Finally, the vibrational contribution to the considered core properties and molecule-frame dipole moment,  $d$ , corresponding to zero vibrational level of the  $^3\Delta_1$  electronic state as a difference between the value averaged over zero vibration wave function and the nonaveraged value at the given equilibrium internuclear distance (3.75 a.u. for  $\text{ThF}^+$ <sup>[140]</sup> and 3.511 a.u. for  $\text{ThO}$ <sup>[141,142]</sup>).

The final value of a considered parameter  $Y$ , where  $Y = d, E_{\text{eff}}, W_{\text{T,P}}, A_{\parallel}$  and  $G_{\parallel}$  of the  $^3\Delta_1$  state of ThO and  $\text{ThF}^+$  was obtained as:

$$\begin{aligned}
 Y(\text{FINAL}) = & Y(38\text{e-}2\text{c-CCSD(T)}, \text{MBas}) + \\
 & Y(38\text{e-}1\text{c-CCSD(T)}, \text{LBas}) - Y(38\text{e-}1\text{c-CCSD(T)}, \text{MBas}) \\
 & + Y(18\text{e-}2\text{c-CCSDT(Q)}, \text{CBasSO}) \\
 & - Y(18\text{e-}2\text{c-CCSD(T)}, \text{CBasSO})
 \end{aligned}
 \quad (26)$$

Table 5<sup>[112]</sup> lists the calculated values of effective electric field along with the parameter of the T,P-odd pseudoscalar–scalar electron–nucleus neutral currents interaction, hyperfine structure constant,  $W_M$  parameter and  $g$ -factor for the  $^3\Delta_1$  state of  $\text{ThF}^+$  and ThO. It follows from Table 5 that the calculated value of  $E_{\text{eff}}$  is stable with respect to the electron correlation improvement and basis set enlargement. Unfortunately, there are no experimental data on  $A_{\parallel}$  for  $^{229}\text{ThO}$  or  $^{229}\text{ThF}^+$  up to now. However, we found quite good agreement between theoretical and experimental data for molecule frame dipole moment and  $g$ -factor of ThO.

Recently Dirac–Coulomb calculations of  $E_{\text{eff}}$  and other parameters of ThO and  $\text{ThF}^+$  molecules have been performed in [111,143] using generalized active space configuration interaction (GAS–CI) approach. The values of  $E_{\text{eff}}$  (75.2 GV/cm for ThO and 35.2 GV/cm for  $\text{ThF}^+$ ) obtained in Refs. [111,143] and the values obtained within coupled cluster calculations in Refs. [109,110,112] (see Table 5) are quite close. However, as was analyzed in details in Ref. [110] for the case of ThO the slight disagreement of the results can be caused by different approximation of used wavefunctions: GAS–CI<sup>[111]</sup> versus CC<sup>[110]</sup> 18 correlated electrons<sup>[111]</sup> versus 38 correlated electrons<sup>[110]</sup> as well as different Hamiltonians, in particular, Dirac–Coulomb<sup>[111]</sup>

versus GRECP (followed by restoration to Dirac–Coulomb–Breit)<sup>[110]</sup> and so forth.

### Relativistic DFT calculations on polyatomic molecules

DFT methods are usually considered as an attractive alternative to *ab initio* wavefunction theory computational approaches in applications to electronic structure modeling of actinide compounds. Provided that the (G)RECPs are built of field-independent one-body terms, the many-electron Hamiltonian (4) formally coincides with that for a nonrelativistic electronic gas in the external “field,” defined by  $U^{\text{GRECP}}$ . Therefore, the exchange–correlation functional (XCF) appearing in DFT for the systems with such Hamiltonians is nonrelativistic. This justifies the use of conventional nonrelativistic XCF approximants and defines a certain advantage of the (G)RECP models over all-electron relativistic approaches, as the latter ones imply the unpleasant choice between the utilization of relativistic XCF expressions<sup>[144]</sup> and at least the irrevocable loss of Breit contributions to the electron–electron repulsion energy. However, it is still not clear whether these contributions are of significant importance for ground electronic state properties. A very good agreement between the results of calculations on closed-shell molecules of actinide compounds (i.e., where the spin-dependent relativistic effects are expected to be small) by one-component (1c) relativistic DFT (RDFT) with averaged small-core energy-adjusted pseudopotentials<sup>[16]</sup> and scalar relativistic 4-component DFT with the same XCF has been stated in Ref. [19]; in contrast, the discrepancy between the molecular characteristics obtained with different (but allegedly reliable) XCF approximations was significant. It seems that the proper choice of these approximations rather than the accuracy of particular small-core RECP model is of crucial importance for successful RDFT applications to actinide chemistry. Nevertheless, the results presented in Refs. [19,145] demonstrate that RDFT with rather simple hybrid XCF approximations, such as the famous B3LYP,<sup>[146]</sup> is competitive with *ab initio* wavefunction methods as a tool of quantitative modeling of ground states even of relatively small molecules of actinide compounds. In our applications of the combination of GRECP model and RDFT to actinide chemistry we mostly used the



hybrid PBE0 XCF<sup>[147]</sup> which, according to our experience, is not inferior to the B3LYP one in accuracy, at the same time having the advantage of its quasionempirical nature.

For open-shell systems playing an extremely important role in actinide chemistry, an appropriate relativistic generalization of the *spin density* (rather than total density) functional theory should be used. For the time being, the most popular approach in heavy element quantum chemistry, known as the noncollinear approximation,<sup>[148–150]</sup> consists in replacing the spin density in the XCF expression by the absolute value of spin magnetization. Offering the possibility to treat effective spin–orbit interactions on the same footing as Coulomb terms, noncollinear 2c RDFT formulations ensure the invariance of the results on the choice of coordinate axes and reasonable spin–orbit-free limit. In all our 2c RDFT calculations on actinide compounds, we used the implementation of this approach described in Ref. [150].

A great advantage of DFT computational techniques (using basis set expansions of the components of molecular spinors) over conventional wavefunction correlation methods (based on the similar strategy) consists in much more rapid convergence of the results with respect to the basis set size, so that one can approach the basis set limit in practical RDFT calculations on rather complex systems. Ensuring the smoothness of Kohn–Sham pseudospinors in the vicinity of atomic nuclei and thus simplifying their fitting by combinations of Gaussian functions, shape-consistent (G)RECP models are particularly suitable for constructing compact weakly contracted Gaussian basis sets. We have built moderate-sized (10s 9p 8d 6f 2g)/[8s 8p 6d 5f 2g] bases for U through Cf using the simultaneous optimization of nonlinear ( $\alpha_i$ , see Eq. (10)) and linear ( $c_j$ ) basis function parameters directly in spin–orbit-coupled calculations.<sup>[151]</sup> The latter circumstance was essential for suppressing the superposition errors in molecular calculation; for instance, the Boys–Bernardi estimates of contributions from actinide atoms to 2c RDFT binding energies of diatomic oxides and fluorides in calculations with light atom bases of “augmented triple zeta” quality never exceeded a few tenths of kilojoule per mole.

The noncollinear 2c RDFT computational scheme within the valence GRECP approximation was applied to electronic structure modeling of higher oxide molecules of plutonium and early transplutonium elements.<sup>[152–155]</sup> These systems are of interest from the point of view of general chemistry and theory of chemical structure (due to the possibility of reaching extremely high oxidation states) and because of the problem of identification of volatile compounds of these actinides presumably formed in oxidative media (see Refs. [156,157] and references therein). Ground-state equilibrium geometries, energies, vibrational frequencies of various isomers of  $AnO_n$  and  $An_2O_n$ , where  $An$ =Pu through Cf, were computed. Magnetization and charge density distributions were analyzed to interpret the results in traditional chemical terms (bond order, oxidation states, etc).

In spite of the lack of experimental or accurate *ab initio* data on higher molecular oxide energetics, the adequacy of our computational scheme is indirectly confirmed by the reproduction of available experimental data on the processes involving lower oxides and changing the oxidation state of

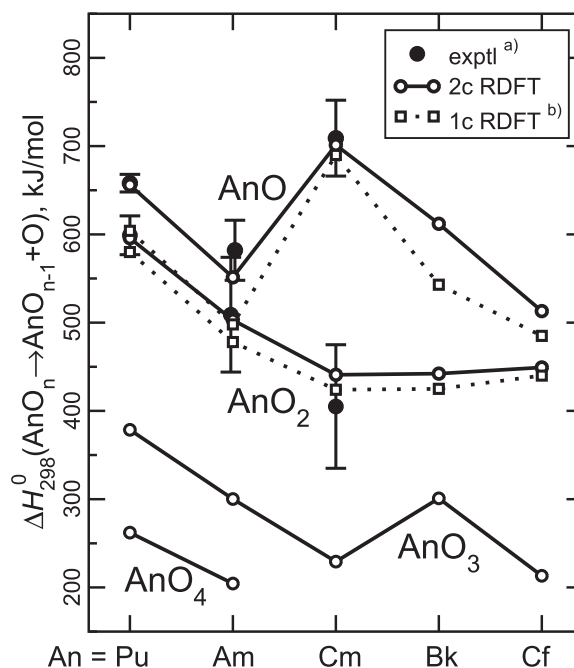


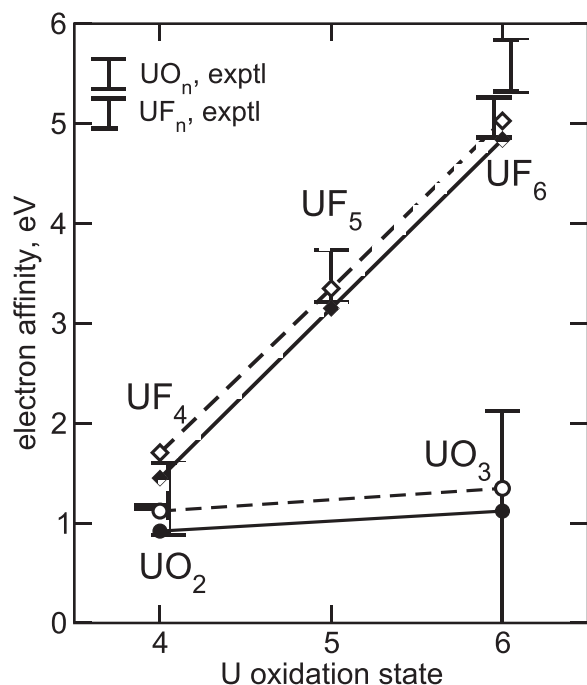
Figure 4. Bond breaking enthalpies for the oxides of Pu and early transplutonium elements from two-component RDFT calculations with valence RECP.<sup>[153,155,159]</sup> a) Experimental-based estimates, Ref. [162], b) one-component RDFT, Ref. [20].

actinide atom (the example can be found in Fig. 4) as well as on higher atomic ionization potentials, corresponding to the elimination of several *f*-electrons.

The main qualitative results of this study can be summarized as follows:

- Simple tetroxide molecules  $Am(VIII)O_4$  and, probably,  $Pu(VIII)O_4$  should be metastable<sup>[153,154]</sup>; they have square equilibrium structures and very high energies of deformation to tetrahedral configurations similar to those of  $OsO_4$  and  $IrO_4$ . From Cm onward, oxidation state (VIII) cannot be reached even in tetroxides.<sup>[154]</sup> Deformed square coordination of oxygen atoms to the actinide one should also be characteristic for  $Pu(VII)$  and  $Am(VII)$  oxides;
- Peroxides and superoxides should play an exceptionally important role in the chemistry of oxygen–transuranium element systems. For instance, dioxo superoxides  $[AnO_2](O_2)$  are the most stable systems with stoichiometry  $An_4O$  for  $An$ =Am, Cm, Bk, and probably Pu.<sup>[154,155]</sup> It might be worth noting that the  $Pu(VIII)O_4 \rightarrow [Pu(V)O_2](O_2)$  conversion energies obtained with valence GRECP in Ref. [154] and the energy-adjusted pseudopotential in Ref. [158] are in a very good agreement (see Ref. [154] for further discussions);
- The stability of higher actinide oxidation states with respect to lower ones in oxygen compounds decrease gradually from Pu to Cf, with the only exception for rather stable higher oxidation states of berkelium<sup>[154,155,159]</sup> (see Fig. 4).

Density functional methods can be a tool of choice for studying negative molecular ions known as particularly difficult objects



**Figure 5.** Electron affinities for uranium fluoride and oxide molecules. Filled symbols: 2c RDFT/PBE0, empty symbols: 2c RDFT/B3LYP, Ref. [152]. Experimental data from Refs. [163,164] ( $\text{UF}_n$ ), Ref. [161] ( $\text{UO}_2$ ), Ref. [160] ( $\text{UO}_3$ ).

for *ab initio* wavefunction-based calculations. Relativistic electronic structure model defined by the valence GRECP component and 2c RDFT correlation treatment has been used to determine the equilibrium structures, energetic harmonic vibrational frequencies, and energetics of molecular ions  $\text{UF}_n^-$ ,  $n=4-6$ ,  $\text{UO}_2^-$ , and  $\text{UO}_3^-$ .<sup>[152]</sup> The results obtained for  $\text{UF}_n^-$  anions were in a good agreement with the available experimental data on electron affinities of the corresponding neutral molecules (Fig. 5). The computed electron affinity value for  $\text{UO}_3^-$  (1.1–1.3 eV) supported the result of mass-spectrometric experiment<sup>[160]</sup> which had established an unexpectedly low upper bound for this property (2.125 eV). Very recently,<sup>[161]</sup> our estimates of  $\text{UO}_2$  electron affinity (0.9–1.1 eV) have been confirmed by photoelectron spectroscopy of  $\text{UO}_2^-$  ( $1.159 \pm 0.020$  eV). It is worth noting that the computational scheme used in our studies is economical enough to be used for modeling of much more complex molecular anions, for instance, heavier  $\text{An}_n\text{O}_m^-$  species generated by laser ablation of solid actinide oxides.

## Conclusions

Actinide compounds are very difficult and challenging objects for quantum chemical simulation. The GRECP model provides a reliable basis for such simulation, offering the possibility to build economical computational schemes both for highly accurate calculations of small molecules of these compounds and intermediate accuracy studies of complex polyatomic molecules. The model can be used not only for the evaluation of “valence-type” properties (for instance, ground- and low-lying excited state potential surfaces, energies of chemical reactions, molecule-frame dipole moment, *g*-factors) but also for estimat-

ing of the molecular characteristics that are sensitive to behavior of valence spinors in the vicinity of heavy atom nucleus. The latter is achieved by combining the GRECP model with the subsequent restoration of these spinors in the vicinity of heavy atomic nuclei. The use of the GRECPs, which were generated for the actinides and accessible from <http://qchem.pnpi.spb.ru/recp>, in two-component DFT ground-state calculations on polyatomic actinide-containing species allows one to ensure the smallness of the errors due to the approximate nature of relativistic Hamiltonian and incompleteness of basis sets in comparison to those arising from the approximation for the XCF.

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**Keywords:** relativistic effective core potential • relativistic pseudopotential • actinide compound calculations • coupled cluster method • density functional theory

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