Generalized RECPs accounting for Breit effects: uranium, plutonium and superheavy elements 112, 113, 114

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The Generalized Relativistic Effective Core Potential (GRECP) method is described which allows one to simulate Breit interaction and finite nuclear models by an economic way and with high accuracy. The corresponding GRECP’s for the uranium, plutonium, eka-mercury (E112), eka-thallium (E113) and eka-lead (E114) atoms are generated. The accuracy of these GRECPs and of the RECPs of other groups is estimated in atomic numerical SCF calculations with Coulomb two-electron interactions and point nucleus as compared to the corresponding all-electron Hartree-Fock-Dirac-Breit calculations with the Fermi nuclear charge distribution. Different nuclear models and contributions of the Breit interaction between different shells are studied employing all-electron four-component methods.

Introduction

Investigation of physical and chemical properties of recently synthesized relatively long-living isotopes of superheavy elements (SHEs) with the nuclear charges $Z=105$ to 116 [1, 2, 3, 4] and their compounds is of fundamental importance for science. Their experimental lifetimes reach several hours now and the nuclei near the top of the “island of stability” are predicted to exist for many years. The experimental study of SHE properties is very difficult because of their extremely small quantities, only single atoms are available for research. Accurate calculations for SHEs and their compounds are needed in order to better understand their physical and chemical properties that often differ from those of the lighter homologs in the chemical groups due to very strong relativistic effects on their electronic shells. Besides, for elements decaying by spontaneous fission, the chemical identification is the only way to prove their $Z$ number.

Experimental investigations of spectroscopic and other physical-chemical properties of actinides are severely hampered by their radioactive decay and radiation which lead to chemical modifications of the systems under study. The diversity of properties of lanthanide and actinide compounds is unique due to the multitude of their valency forms (which can vary over a wide range) and because of particular importance of relativistic effects. They are, therefore, of great interest both for fundamental research and for development of new technologies and materials. The most important practical problems involve storage and processing of radioactive waste and nuclear fuel, as well as pollution of the environment by radioactive waste, where most of the decayed elements are actinides.

From the formal point of view, four-component correlation calculations [5, 6] based on Dirac-Coulomb-Breit (DCB) Hamiltonian (see [7, 8, 9, 10, 11] and references) can provide a very high accuracy of physical and chemical properties for molecules containing heavy atoms. However, such calculations were not widely used for such systems during last decade because of the following theoretical and technical complications [12]:

- too many electrons are treated explicitly in heavy-atom systems and too large number of Gaussians is required for accurate description of the large number of oscillations, which valence spinors have in heavy atoms;
- the necessity to work with four-component Dirac spinors leads to serious complication of calculations as compared to the nonrelativistic case:

(a) the number of kinetically-balanced two-component (“2c”) uncontracted Gaussian basis spinors for the Small components, $N^2c_L$, can be estimated as $2N^2c_L$, where $N^2c_L$ is the number of basis spinors for Large components; so the total number of uncontracted Gaussian basis spinors in the relativistic four-component (“4c”) calculations $N^{4c}_{bas} \sim 3N^{2c}_L$ and the number of two-electron integrals as [12]

$$N^{4c}_{2eInt} \sim (1+2^2+2^4)N^{2c}_{2eInt} \equiv 25\cdot N^{2c}_{2eInt};$$

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Note, however, that the situation is seriously improved here during last years, see [5, 6, 13, 14].

(b) the number of basis 2e-spinors, \( N_{bas}^{2c} \), is twice more than the number of nonrelativistic basis one-component ("1c") orbitals, \( N_{bas}^{1c} \), therefore

\[
N_{2e\text{Int}}^{2c} \sim 2^1 / 2 \cdot N_{2e\text{Int}}^{1c} \equiv 8 \cdot N_{2e\text{Int}}^{1c}
\]

The minimal number of two-electron integrals in the spin-orbit basis set, which are required to be saved coincides, obviously, with \( N_{2e\text{Int}}^{1c} \).

The Relativistic Effective Core Potential (RECP) method is most widely used in calculations on molecules containing heavy atoms [15, 16] because it reduces drastically the computational cost at the integral generation, SCF and integral transformation stages. In our papers [17, 18, 19], the conventional radially-local (semi-local) form of the RECP operator (used by many groups up to now but suggested and first applied about 40 years ago [20, 21, 22]) was shown to be limited by accuracy and some nonlocal corrections to the RECP operator were suggested [17, 19, 23, 24], which have already allowed us to improve significantly the RECP accuracy [18, 19, 25, 26].

It is known that the Breit interaction can give contributions in excess of one thousand wave numbers even to energies of transitions between lowest-lying states of very heavy elements (see, e.g., tables IV and V). It is also clear that the point nuclear model becomes less appropriate when the nuclear charge is increased. Therefore, the RECPs designed for accurate calculations of actinide and SHE compounds should allow one to take into account the Breit interaction and the finite size of nuclei. The most economic way is to incorporate the corresponding contributions into the RECP operator.

I. GENERALIZED RECP METHOD

In a series of papers (see [17, 18, 19, 24, 27] and references), we introduced and developed the Generalized RECP (GRECP) method. Its main features are:

- The inner core (IC), outer core (OC) and valence (V) electrons are first treated employing different approximations for each (including relaxation of the IC shells which are explicitly excluded from GRECP calculations).

- GRECP involves both radially-local, separable and Huzinaga-type potentials as its components and particular cases.

- The GRECP operator includes terms of other types for economical treatment of transition metals, lanthanides and actinides (see sections I A–I B).

- The Outer core pseudospinors (nodeless) together with valence pseudospinors (nodal) are used for constructing the GRECP components [28].

- Quantum electrodynamics effects (see [29] and section I C), arbitrary nuclear models, and correlation with IC shells [30] can be efficiently treated within GRECPs.

The GRECP method is described in detail in the above papers and we only add here that it allows one to avoid the complications of the four-component calculations described in the introduction (see also [30]) and to attain very high accuracy, limited in practice by possibilities of the correlation methods, while requiring moderate computational efforts when the IC, OC and V subspaces are appropriately chosen.

The contributions of different nuclear models which are described by local potentials can be easily taken into account in the framework of the (G)RECP method. The situation is more complicated in the case of the Breit interaction because it is represented by a two-electron operator. General justification of the possibility to simulate the Breit effects by means of an one-electron (G)RECP operator with good accuracy and the scheme of such GRECP generation are presented in [29] (see also section I C). This scheme is applied in the present work to generate GRECPs for the uranium, plutonium, eka-mercury (E112), eka-thallium (E113) and eka-lead (E114) atoms. The 32, 34, 20, 21 and 22 electrons are explicitly treated in calculations with these GRECPs, correspondingly. Moreover, the 52 electron GRECP (52e-GRECP) version for E112 was also generated. The conventional Coulomb operator for two-electron interactions and the point nuclear model should be used in these GRECP calculations. However, they will account for the Fermi nuclear charge model that is close to the experimental distribution. Moreover, the Breit interactions of the electrons from the state used for the GRECP generation with the electrons explicitly treated in the subsequent calculations are simulated by the GRECP (in some sense, the Breit interaction is “frozen” here).
A. Self-consistent GRECP version for $d$- and $f$-elements

The Self-Consistent (SfC) (G)RECP version [19, 23, 24, 27] allows one to minimize errors for energies of transitions with the change of the occupation numbers for the OuterMost Core (OMC) shells without extension of space of explicitly treated electrons. It allows one to take account of relaxation of those core shells, which are explicitly excluded from the GRECP calculations, thus going beyond the frozen core approximation. This method is most optimal for studying compounds of transition metals, lanthanides, and actinides. Features of constructing the self-consistent GRECP are:

1. The all-electron HFDB calculations of two generator states with different occupation numbers $N_1$ and $N_2$ of the OMC $d$ or $f$ shell are carried out for an $d$- or $f$-element.

2. The GRECP versions with separable correction $U^{N_1}$ and $U^{N_2}$ are constructed for these generator states employing the standard scheme [17, 18, 19, 24]. The GRECP operator with the separable correction has the form

$$U^{N_i} = E^{N_i}_{\text{core}} + \sum_{l=0}^{l=1/2} \sum_{j=|l-1/2|}^{l+1/2} \left\{ [U^{N_i}_{n_e \ell J}(r) - U^{N_i}_{n_e LJ}(r)] P_{ij} + \sum_{n_c} [U^{N_i}_{n_c \ell J}(r) - U^{N_i}_{n_c LJ}(r)] P^{N_i}_{n_c \ell J} + \sum_{n_c} \bar{P}^{N_i}_{n_c \ell J} \left[ \frac{U^{N_i}_{n_c \ell J}(r) + U^{N_i}_{n_c LJ}(r)}{2} - U^{N_i}_{n_c LJ}(r) \right] \bar{P}^{N_i}_{n_c \ell J} \right\},$$

(1)

where

$$P_{ij} = \sum_{m=-j}^{j} |ljm\rangle \langle ljm|,$$

$$\bar{P}^{N_i}_{n_c \ell J} = \sum_{m=-j}^{j} \langle n_c \ell jm \rangle^{N_i} \langle n_c \ell jm |^{N_i} |,$$

$|ljm\rangle \langle ljm|$ is the projector on the two-component spin-angular function $X_{ljm}$, $\langle n_c \ell jm \rangle^{N_i} \langle n_c \ell jm |^{N_i}$ is the projector on the outer core pseudospinor $\varphi^{N_i}_{n_c \ell J} X_{ljm}$, $U^{N_i}_{n_c \ell J}$ and $U^{N_i}_{n_c LJ}$ are the radial components of the GRECP derived for valence $\varphi^{N_i}_{n_c \ell J}$ and outer core $\varphi^{N_i}_{n_c LJ}$ pseudospinors for the OMC $d$ or $f$ shell occupation number $N_i$ ($i=1, 2$), $E^{N_i}_{\text{core}}$ is the core energy, $L$ is one more than the highest orbital angular momentum of the inner core spinors and $J = L + 1/2$. The separable terms (the second and third lines in Eq. (1)) are added to the conventional radially-local RECP operator. These terms take into account the difference between the potentials acting on the outer core and valence electrons with the same $l$ and $j$.

3. The self-consistent GRECP, $U^{SfC}$, with the quadratic correction writes as

$$U^{SfC} = \frac{U^{N_1} + U^{N_2}}{2} + \frac{U^{N_1} - U^{N_2}}{N_1 - N_2} \left( N_{\text{OMC}} - \frac{N_1 + N_2}{2} \right) + B \left( N_{\text{OMC}} - \frac{N_1 + N_2}{2} \right)^2,$$

(2)

where $B$ is some adjustable parameter, $N_{\text{OMC}} = \langle \tilde{\Psi} \mid N_{\text{OMC}} \mid \tilde{\Psi} \rangle$, $\tilde{\Psi}$ is the many-electron wavefunction for the calculated state, and $N_{\text{OMC}}$ is the occupation number operator of the considered $d$ ($f$) shell that is written as

$$N_{\text{OMC}} = \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^{j} \tilde{a}_{n_{\text{OMC}} \ell \ell J m} \tilde{a}_{n_{\text{OMC}} \ell \ell J m}^\dagger,$$

(3)
\[ a_{\text{omc}, \text{omc}, jm}^\dagger (a_{\text{omc}, \text{omc}, jm}) \text{ is the creation (annihilation) operator for the electron in the pseudostate } |n_{\text{omc}}l_{\text{omc}}, jm\rangle \text{ corresponding the original one-electron state } |n_{\text{omc}}l_{\text{omc}}, jm\rangle, n_{\text{omc}} \text{ and } l_{\text{omc}} \text{ are the principal and orbital quantum numbers of the OMC shell.} \]

4. The \( \mathbf{P}^N_{n, lj} \) projectors in \( \mathbf{U}^N \) from Eq. (2) are replaced by the projectors

\[
\mathbf{P}^{av}_{n, lj} = \sum_{m=-j}^j \langle n_ljm^{av}\rangle \langle n_ljm^{av} | (n_ljm^{av}) \rangle
\]

for simplicity, where \( \langle n_ljm^{av}\rangle \langle n_ljm^{av} | (n_ljm^{av}) \rangle \) is the projector on the outer core pseudospinor \( \mathbf{\tilde{v}}^{av}_{n, lj} \chi_{ljm} \),

\[
\mathbf{\tilde{v}}^{av}_{n, lj}(r) = C_{\text{norm}} \left[ \mathbf{\tilde{v}}^{N1}_{n, lj}(r) + \mathbf{\tilde{v}}^{N2}_{n, lj}(r) \right],
\]

and \( C_{\text{norm}} \) is the normalizing factor.

The comparison of self-consistent and conventional GRECP versions by accuracy in calculations on the uranium and plutonium atoms can be found in paper [29].

## B. Term-splitting correction for \( d, f \)-elements

The self-consistent (G)RECP correction gives no improvement in description of splittings to terms, e.g., of the configuration 5\( f_2^36d_{3/2}^17s_{1/2}^27p_{1/2} \) of uranium as compared to the parent (G)RECPs [19, 24]. Analysis of the corresponding errors shows that the main contribution (about 90 \%) is due to smoothing the original OMC spinors in the core region. The simplest way to minimize these errors is to use such (G)RECPs, in which the 5\( f \) shell is described by nodal pseudospinors, whereas the 4\( f \) pseudospinors are nodeless. To reduce computational efforts, the 4\( f \) shell can be treated as “frozen” using the level-shift technique [19, 31].

If the small magnitude of the OMC shell (5\( f \) here) relaxation is taken into account, there is another way out that can be optimal for the low-lying states. It was suggested in [19] to add the Term-Splitting (TS) correction (see also [24]) to the (G)RECP operator

\[
\mathbf{U}^{TS} = \sum_{x_1,x_2,x_3,x_4} \lambda_{x_1x_2,x_3x_4} \langle x_1 \rangle \langle x_3 \rangle \langle x_2 \rangle \langle x_4 \rangle
\]

\[
-2 \sum_{w} \sum_{x_1,x_2,x_3} (\lambda_{x_1x_2,x_3x_3} - \lambda_{x_1x_3,x_3x_2}) \delta_{wx_3} \langle x_1 \rangle \langle x_2 \rangle,
\]

where \( \lambda_{x_1x_2,x_3x_4} \) is the difference between the two-electron integrals calculated with original spinors and pseudospinors for the generator state, the indices \( w \equiv (n_{\text{occ}}l_{\text{occ}}l_{\text{occ}}n_{\text{occ}}) \) correspond to the occupied spinors for the calculated state, the indices \( x \equiv (n_{\text{omc}}l_{\text{omc}}jm) \) run over all possible \( j = |m_{\text{omc}}| \pm 1/2 \) and \( m = -j, -j + 1, \ldots, j \) for the given OMC shell. These terms correct the one- and two-electron integrals containing only the 5\( f \) pseudospinors of uranium in the considered case.

## C. Accounting for the Breit interaction between different shells

Let us analyze contributions of the Breit interaction between electrons from different shells to the energy of a heavy atom [27]. We will use the estimate (e.g., see [32])

\[
\langle P, \mathbf{P}' | (\vec{a}_i, \vec{a}_j') | P, \mathbf{P}' \rangle \sim \frac{1}{c} \langle (\vec{v}_P, \vec{v}_P') \rangle;
\]

for an uncoupled one-electron state \( P \): \( \langle P | \hat{\alpha} P \rangle \sim \frac{1}{c} \langle (\vec{v}_P, \vec{v}_P') \rangle \sim \alpha Z_P^* \), where \( \vec{a}_i \) are 4×4 Dirac matrices for the \( i \)-th electron, \( \vec{v} \) are velocities of light and electron, \( \alpha \approx \frac{e}{c} \) is the fine structure constant. In the above expression a “pseudocharge”, \( Z_P^* \), is introduced which can be most naturally defined in our consideration as [29]

\[
Z_P^* = \langle P | \frac{1}{c} | P \rangle,
\]

(6)
that coincides with the nuclear charges only for nonrelativistic electrons occupying the ground states in hydrogen-like ions. Besides, \( \langle \frac{1}{r_{12}} \rangle \) can be estimated as \( \langle \frac{1}{r} \rangle \) for the outermost of the one-electron states \( P, P' \) [27]:

\[
\langle P, P' \rangle \langle \frac{1}{r_{12}} \rangle |P, P'\rangle \sim \min \left[ \langle P \rangle \langle \frac{1}{r} \rangle, \langle P' \rangle \langle \frac{1}{r} \rangle \right] = \min \left[ |Z_p, Z_{p'}^*| \right].
\]

As a result, the Breit interaction between the one-electron states \( P \) and \( P' \) can be estimated as

\[
B_{PP'} \approx \alpha^2 Z_p^* Z_{p'}^* \cdot \min \left[ |Z_p, Z_{p'}^*| \right] \cdot \mathcal{F}
\]

where the correcting factor \( \mathcal{F} \sim [0.1 \sim 1] \) is introduced, which depends on \( \Delta l = |l_p - l_{p'}|, \Delta j = |j_p - j_{p'}|, \) etc.

Applying Eq. (6) for inner core (\( P = f \)), outer core (\( P = c \)) and valence (\( P = v \)) electrons one has \( Z_f^* \sim 100, Z_c^* \sim 3, Z_v^* \sim 1 \) by the order of magnitude (\( Z_p^* \) differs from an “effective charge” of the core with respect to the electron in the \( P \)-th state, \( Z_P^* = Z - N_c^P \), that is usually used in RECP calculations, where \( Z \) is the nuclear charge, \( N_c^P \) is the number of core electrons with respect to the \( P \)-th state). Therefore, \( B_{P P'} \equiv \mathcal{F}^{-1} B_{PP'} \) is as

\[
B_{ff'} \sim 10 000 000 \text{ cm}^{-1}, \quad B_{fc} \sim 9 000 \text{ cm}^{-1}, \quad B_{fv} \sim 1000 \text{ cm}^{-1},
\]

\[
B_{cf} \sim 9 000 \text{ cm}^{-1}, \quad B_{cc'} \sim 270 \text{ cm}^{-1}, \quad B_{cv} \sim 30 \text{ cm}^{-1},
\]

\[
B_{vc} \sim 1000 \text{ cm}^{-1}, \quad B_{cc} \sim 30 \text{ cm}^{-1}, \quad B_{vv'} \sim 10 \text{ cm}^{-1}.
\]

Let us consider approximations in accounting for the Breit interaction, that we made when outer core and valence electrons are included in GRECP calculations with Coulomb two-electron interactions, but inner core electrons are absorbed into the GRECP. When both electrons belong to the inner core shells, the Breit effect is of the same order as the Coulomb interaction between them. Though \( B_{ff'} \) does not contribute to “differential” (valence) properties directly, it can lead to essential relaxation of both core and valence shells. This relaxation is taken into account when the Breit interaction is treated by self-consistent way in the framework of the HFDB method [33, 34]. The inner core electrons occupy closed shells. The only exchange part of the two-electron Breit interaction between the valence, outer core and inner core electrons, \( B_{fv} \) and \( B_{fc} \), gives non-zero contribution. The contributions from \( B_{fv} \) and \( B_{fc} \), are quite essential for calculation at the level of “chemical accuracy” (about 1 kcal/mol or 350 cm\(^{-1}\) for transition energies). This accuracy level is, in general, determined by the possibilities of modern correlation methods and computers already for compounds of light elements. Note, that the contribution from the exchange interaction is not smaller than that from the Coulomb part [29]. The inner core electrons can be considered as “frozen” in most physical-chemical processes of interest. Therefore, the effective operators for \( B_{fv} \) and \( B_{fc} \) acting on the valence and outer core shells, \( B_{fv}^{\text{Eff}} \) and \( B_{fc}^{\text{Eff}} \), are of the same kind as the exchange \( f - v \) and \( f - c \) contributions of the SCF field in the Huzinaga-type potential, i.e. these terms can be well approximated by the spin-dependent potential of the form:

\[
B_{fv}^{\text{Eff}} + B_{fc}^{\text{Eff}} = \sum_{lj} V_{lj}^{Br}(r) \mathbf{P}_{lj} + \sum_{n lj} [V_{nj lj}^{Br}(r) - V_{lj}^{Br}(r)] \mathbf{P}_{nj lj},
\]

which has basically the same spin-angular structure as the GRECP has. Thus, it can be taken into account directly when the HFDB (not HF) calculation [8] is performed to generate outer core and valence bispinors but in the inversion procedure of the HF equations for generating the components of GRECP, the conventional interelectronic Coulomb interaction should be used instead of the Coulomb-Breit one. Then, in the GRECP calculations one should consider only the Coulomb interaction between the explicitly treated electrons.

Due to small relaxation of outer core shells in most processes of interest, these shells can be also considered as “frozen” when analyzing the Breit contributions and the \( B_{cc'} \) and \( B_{cv} \) terms can be taken into account similarly to the \( B_{fc} \) and \( B_{fv} \) ones. The error of this approximation will be additionally suppressed by relative weakness of the Breit interaction with the outer core electrons as compared to the inner core ones. We note here, that the estimates for \( Z_v^*, Z_c^* \) and, therefore, for \( B_{cc'}, B_{cv} \) and \( B_{vv'} \) given above are rather the upper limits. For heavy atoms these Breit contributions are smaller approximately by one–two orders of magnitude. This decrease is due to enlarged radii of the valence and outer core shells and other effects in heavy atoms [29]. For example, for uranium (\( Z = 92 \)) one has \( Z_{1s}^{\text{nonrel, SCF}} \sim 92.4, Z_{1s}^{\text{DHFB}} \sim 122.4 \) (starting from \( Z \sim 30, Z_{1s}^* \) grows faster than \( Z \) due to relativistic effects, whereas \( Z_{1s}^* \) is essentially smaller than the corresponding effective charge \( Z_{1s}^{\text{Eff}} \) for all other \( n l \)), \( Z_{5f}^* \sim 1, Z_{6s}^* \sim 1, Z_{7p}^* \sim 0.7, Z_{6d}^* \sim 0.4, Z_{7s}^* \sim 0.3 \). Thus, \( B_{cc'}, B_{cv} \), and \( B_{vv'} \) contributions are negligible for the “chemical accuracy” of calculation. Therefore, the above made estimates provide a good background for approximating the Breit interaction by a one-electron GRECP operator that should work well both for actinides and for superheavy elements. The numerical tests of the GRECPs accounting for the Breit effects are discussed in the next section.
II. RESULTS AND DISCUSSION

For all-electron calculations, we used the atomic HFDB code [35, 36] which allows one to account for the Breit interactions both in the framework of the first-order perturbation theory (PT-1) and by the self-consistent way as well as to account for different models of nuclear charge distribution. For test calculations with (G)RECPs, the atomic Hartree-Fock code in the jj-coupling scheme (HFJ) [17] was used (that was quite sufficient for studying errors of the one-electron (G)RECP operators). Both the codes are numerical that allows us to exclude the errors due to the incompleteness of basis sets when estimating accuracy of different RECPs and GRECPs.

The transition energies between states averaged over the low-lying configurations of SHEs 112, 113, 114 and actinides U, Pu are presented in tables I, II, III and IV, V, respectively. One can see that the errors due to the point nuclear model reach a few thousand wave numbers for the SHEs and several hundred wave numbers for the actinides. The considered small variations in the nuclear charge distribution (including the nuclear size) in the framework of finite-size nuclei lead to change of the transition energies for the studied SHEs less than on 60 cm$^{-1}$. The differences between the results with the PT-1 and self-consistent ways of accounting for the Breit interaction are within 7 cm$^{-1}$ for SHEs and actinides whereas neglecting the Breit effects leads to the errors up to a few thousand wave numbers for the studied actinides and several hundred wave numbers for the SHEs.

The GRECP errors in reproducing the results of the all-electron HFDB calculations with the Fermi nuclear model are collected into two groups. First, the GRECP errors for transitions without change in the occupation number of the 6$d$ shell for the SHEs (tables I, II and III) and the 5$f$ shell for the actinides (tables IV and V) are relatively small whereas the corresponding errors of the other tested RECPs for the SHEs are significantly higher. The same number of electrons is explicitly treated in calculations with different (G)RECP versions for a given atom. Here and further, we do not discuss the particular case of the 52e-GRECP for E112 if the opposite is not explicitly stated. The RECPs of other groups for uranium were tested in paper [19]. It should be noted that they do not take into account the large contribution from the Breit interaction. The Breit effects were also not considered at the generation stage of the RECP of Nash et al. [37]. However, it cannot explain the large errors for this RECP in tables I, II and III. It is not clear from paper [37] which nuclear model was used there. The Breit interaction was taken into account only in the PT-1 approximation at the generation stage of the PseudoPotential (PP) of Seth et al. However, the corresponding changes in the transition energies are negligible in comparison with the PP errors.

Second, the GRECP errors for transitions with excitation of one 6$d$ electron for the SHEs or one 5$f$ electron for the actinides are about 400 cm$^{-1}$. These errors have a systematic nature (unlike the corresponding errors for the tested RECPs of other groups) and are connected with the fact that the OMC 6$d$ shell for the SHEs and the OMC 5$f$ shell for the actinides in the present GRECP versions are described with the help of nodeless pseudospinors. Obviously, these errors can be reduced significantly if one includes the 5$d$, 5$f$ electrons for the SHEs and the 4$f$ electrons for the actinides explicitly in the GRECP calculations (see the 52e-GRECP results for E112 in table I). The corresponding pseudospinors can be then “frozen” in these GRECP calculations with the help of the level-shift technique [19, 31] to reduce the computational efforts. Alternatively, the self-consistent GRECP method described in section I.A can be used.

The energies of splittings between terms are considered in table VI for E112 and table VII for U. The errors of the RECP and GRECP approximations and the errors caused by neglecting the Breit effects are within 200 cm$^{-1}$. The latter can be reduced drastically by applying the term-splitting correction (see section I.B and table VII). The results show that addition of the term-splitting correction allows one to reduce the most serious errors up to 10 times for the splittings into terms, thus reducing the errors for the energies of transition between terms to the same order of magnitude as the errors for transitions between the states averaged over the configurations (when only the self-consistent GRECP is applied). Obviously, any transition between two different terms having different occupation numbers of the OMC shell, $N_{omc}$ and $N_{omc}^2$, can be presented as a combination of three consequent transitions: transition from the first term to the average over the configuration with the same $N_{omc}$, transition between averages over configurations with $N_{omc}$ and $N_{omc}^2$ and transition from the latter to the second term with $N_{omc}^2$. Therefore, applying of both the self-consistent and term-splitting GRECP corrections to treatment of transitions between any terms allows one to reduce dramatically the (G)RECP approximation errors without increasing the number of explicitly treated core electrons of a considered $d$, $f$-element.

In tables VIII and IX, the matrix elements of $<r^2>$ and radial integrals $2 \int_0^\infty [f_{n,t}(r)] | \tilde{\varphi}_{n,t}(r) - \tilde{\varphi}_{n,t}(r) | dr$ (where $f_{n,t}$ is the large component of the Dirac spinor, $\tilde{\varphi}_{n,t}$ is the radial part of the corresponding pseudospinor and $R_n$ is the radius of the last spinor node) are considered for the cases of spinors from different configurations of E112. The errors in these matrix elements and integrals characterize the quality of reproducing the electronic density in outer core and valence regions of the atom. One can see that the GRECP allows one to reproduce the electronic density in the valence region (the 7$s_{1/2}$ and 7$p_{1/2}$ spinors) with very high accuracy. The one-electron energies for spinors from different configurations of E112 are presented in table X. Similar conclusion can be made in the latter
Conclusions

Different nuclear models and contributions of the Breit interaction between valence, inner and outer core shells of uranium, plutonium and superheavy elements E112, E113, and E114 are considered in the framework of all-electron four-component and (G)RECP methods. It is concluded on the basis of the performed calculations and theoretical analysis that the Breit contributions with inner core shells must be taken into account in calculations of actinide and SHE compounds with “chemical accuracy” whereas those between valence and outer core shells can be omitted.

The differences in the atomic energies between the cases of the PT-1 and self-consistent ways of treating the Breit interaction as well as small variations in the nuclear charge distribution in the framework of finite-size nuclei are not essential for the considered accuracy of calculations. However, the difference between the point and finite nuclear models is important for the valence (transition) energies. The effects of accounting for the Breit interaction and finite nuclear model can be simulated by GRECPs with very good accuracy when only Coulomb interaction between the explicitly treated electrons is taken into account. Thus, the GRECP method allows one to carry out reliable calculations of actinides, SHEs and their compounds at the level of “chemical accuracy”.

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[1] S. Hoffman and G. Münzenberg, Rev. Mod. Phys. 72, 733 (2000).
[2] Y. T. Oganessian et al., Nature 400, 242 (1999).
[3] Y. Oganessian, Nature 413, 122 (2001).
[4] M. Schädel, ed., The Chemistry of Superheavy Elements (Kluwer, Dordrecht, 2003), 318 pp.
[5] K. Hirao and Y. Ishikawa, eds., Recent Advances in Relativistic Molecular Theory (World Scientific, Singapore, 2004), 328 pp.
[6] P. Schwerdtfeger, ed., Relativistic Electronic Structure Theory. Part 2. Applications, vol. 14 of Theoretical and Computational Chemistry (Elsevier, Amsterdam, 2004), xv + 787 pp.
[7] P. J. Mohr, Phys. Rep. 293, 227 (1997).
[8] I. P. Grant and H. M. Quiney, Int. J. Quantum Chem. 80, 283 (2000).
[9] M. Reih and B. A. Hess, in Modern Methods and Algorithms of Quantum Chemistry, edited by J. Grotendorst (Jülich, 2000), vol. 1, pp. 451–477, [http://www.fz-juelich.de/nic-series].
[10] V. M. Shabaev, Phys. Rep. 356, 119 (2002).
[11] L. N. Labzowsky and I. Goidenko, in Relativistic Electronic Structure Theory. Part I. Fundamentals, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2002), pp. 401–467.
[12] L. Visscher, Chem. Phys. Lett. 253, 20 (1996).
[13] K. G. Dyall, J. Comput. Chem. 23, 786 (2002).
[14] L. Visscher, J. Comput. Chem. 23, 759 (2002).
[15] W. C. Ermler, R. B. Ross, and P. A. Christiansen, Adv. Quantum Chem. 19, 139 (1988).
[16] A. V. Titov, N. S. Mosyagin, A. N. Petrov, and T. A. Isaev, Progr. Theor. Chem. Phys. (2005), in press.
[17] I. I. Tupitsyn, N. S. Mosyagin, and A. V. Titov, J. Chem. Phys. 103, 6548 (1995).
[18] N. S. Mosyagin, A. V. Titov, and Z. Latajka, Int. J. Quantum Chem. 63, 1107 (1997).
[19] A. V. Titov and N. S. Mosyagin, Int. J. Quantum Chem. 71, 359 (1999).
[20] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).
[21] I. V. Abarenkov and V. Heine, Philos. Mag. 12, 529 (1965).
[22] V. Heine and I. V. Abarenkov, Philos. Mag. 9, 451 (1964).
[23] A. V. Titov and N. S. Mosyagin, Structural Chem. 6, 317 (1995).
[24] A. V. Titov and N. S. Mosyagin, Russ. J. Phys. Chem. 74, Suppl. 2, S376 (2000), [arXiv: physics/0008160].
[25] N. S. Mosyagin, E. Eliav, A. V. Titov, and U. Kaldor, J. Phys. B 33, 667 (2000).
[26] T. A. Isaev, N. S. Mosyagin, M. G. Koslov, A. V. Titov, E. Eliav, and U. Kaldor, J. Phys. B 33, 5139 (2000).
[27] A. V. Titov, Doctorate Thesis, (Petersburg Nuclear Physics Institute, RAS, Russia, 2002).
[28] A. V. Titov, A. O. Mitrushenkov, and I. I. Tupitsyn, Chem. Phys. Lett. 185, 330 (1991).
[29] A. N. Petrov, N. S. Mosyagin, A. V. Titov, and I. I. Tupitsyn, J. Phys. B 37, 4621 (2004).
TABLE I: Transition energies (TE) between states averaged over the relativistic configurations of E112 derived from HFDB calculations with Fermi nuclear model and the corresponding absolute errors of all-electron and (G)RECP calculations (in cm⁻¹).

| Configuration                  | TE       | Absolute errors |
|-------------------------------|----------|-----------------|
| 6d³/2,6f⁵/2 7s¹/2 7l³/2 →     |          |                 |
| 6d³/2,6f⁵/2 7s¹/2 7p¹/2       | 46406    | -3              |
| 6d³/2,6f⁵/2 7s¹/2 7p³/2       | 64559    | -4              |
| 6d⁴/2,6f⁵/2 7s¹/2 8s¹/2       | 72571    | -3              |
| 6d⁴/2,6f⁵/2 7s¹/2 7d¹/2       | 81845    | -4              |
| 6d³/2,6d⁵/2 7s¹/2 7p¹/2       | 28701    | 1 -8 -644 2 -576 31 305 -422 -3723 380 |
| 6d³/2,6d⁵/2 7s¹/2 7p³/2       | 52595    | 1 -6 -464 0 -267 37 277 -181 -1254 189 |
| 6d³/2,6d⁵/2 7s¹/2 8s¹/2       | 62635    | 2 -10 -776 0 -252 43 314 -315 -1879 326 |
| 6d³/2,6d⁵/2 7s¹/2 7d³/2       | 72443    | 1 -9 -666 0 -234 43 322 -220 -1514 314 |
| 6d³/2,6d⁵/2 7s¹/2 7d¹/2       | 84449    | 1 -9 -672 0 -234 43 322 -224 -1531 308 |
| 6d³/2,6d⁵/2 7s¹/2 7p¹/2       | 53581    | 2 -10 -765 2 -281 45 387 -376 -3903 22 |
| 6d³/2,6d⁵/2 7s¹/2 7p³/2       | 75273    | 1 -8 -600 0 7 52 437 -84 -1515 -126 |
| 6d³/2,6d⁵/2 7s¹/2 8s¹/2       | 85677    | 2 -12 -915 -1 25 60 477 -213 -2126 22 |
| 6d³/2,6d⁵/2 7s¹/2 7d³/2       | 95546    | 2 -10 -805 -1 43 60 484 -119 -1760 7 |

(a,c) All-electron Hartree-Fock-Dirac-Breit (HFDB) calculations with Fermi and point nuclear charge distributions, accordingly.
(b) All-electron HFDB calculation with the uniform nuclear charge distribution within a sphere.
(d) All-electron HFD calculation with accounting for the Breit interaction within PT-1 (HFD+B) and with Fermi nuclear model.
(e) All-electron HFDB calculation without accounting for the Breit interaction (HFD) and with Fermi nuclear model.
(f) GRECP generated in the present work from HFDB calculation with Fermi nuclear model.
(g) Semi-local RECP generated here from HFDB calculation with Fermi nuclear model on the ionic closed-shell generator-state.
(h) RECP from [37] generated from HFDB calculation.
(i) PP from M. Seth et al. to be published (P. Schwerdtfeger, private communication, 2003) generated from HFDB+B calculation.

[30] N. S. Mosyagin and A. V. Titov, arXiv.org/physics/0406143 (2004); J. Chem. Phys., in press (2005).
[31] A. V. Titov, N. S. Mosyagin, A. B. Alekseyev, and R. J. Buenker, Int. J. Quantum Chem. 81, 409 (2001).
[32] L. N. Labzowsky, G. L. Klimchitskaya, and Y. Y. Dmitriev, Relativistic Effects in the Spectra of Atomic Systems (Institute of Physics Publishing, Bristol and Philadelphia, 1993), 340 pp.
[33] H. M. Quiney, I. P. Grant, and S. Wilson, J. Phys. B 20, 1413 (1987).
[34] E. Lindroth, Å. M. Mårtensson-Pendrill, A. Ynnerman, and P. Öster, J. Phys. B 22, 2447 (1989).
[35] V. F. Bratzev, G. B. Deyneka, and I. I. Tupitsyn, Bull. Acad. Sci. USSR, Phys. Ser. 41, 173 (1977).
[36] I. I. Tupitsyn and A. N. Petrov, in 5-th Session of the V.A. Fock School on Quantum and Computational Chemistry (Novgorod the Great, 2002), p. 62.
[37] C. S. Nash, B. E. Bursten, and W. C. Ermler, J. Chem. Phys. 106, 5133 (1997), [Erratum: JCP 111 (1999) 2347].
TABLE II: Transition Energies (TE) between states averaged over the relativistic configurations of E113 (in cm$^{-1}$). See Table I.

| Configuration | TE | Absolute errors |
|---------------|----|-----------------|
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2} 7p_{3/2}$ | 25106 | 3 221 -2 339 -21 233 275 -349 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 34981 | 0 -2 -128 -3 354 5 112 -205 -307 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 8s_{1/2}$ | 45172 | 0 0 -4 -3 374 9 200 140 -275 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7d_{3/2}$ | 50338 | 0 0 -10 -3 374 9 196 127 -276 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 5g_{1/2}$ | 52811 | 0 0 -10 -3 374 9 196 127 -276 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 5p_{1/2}$ | 57201 | 0 0 -10 -3 374 9 196 127 -276 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 61500 | -4 32 2220 2 -60 28 610 4830 148 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 83184 | -5 36 2485 -1 241 -6 833 5170 -172 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 112678 | -6 41 2843 -3 612 -10 1171 5717 -504 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 115758 | -5 34 2344 -1 250 -3 784 5143 -105 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 149550 | -5 40 2739 -3 654 -9 1163 5784 -454 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 234435 | -5 37 2583 -4 747 -2 1221 6102 -336 |

| Configuration | TE | Absolute errors |
|---------------|----|-----------------|
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 47371 | 2 -13 -864 3 -739 404 -597 -2349 322 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 74898 | 1 -9 -606 1 -391 344 -378 -2055 -44 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 110406 | 1 -4 -244 -2 22 310 -47 -1528 -407 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 110120 | 2 -13 -882 0 -388 386 -451 -2298 41 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 150102 | 1 -7 -477 -2 59 344 -82 -1667 -339 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 239523 | 2 -12 -807 -2 144 416 -39 -1617 -188 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 78821 | 2 -15 -983 2 -375 380 -649 -2230 -270 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 104059 | 1 -11 -742 0 -49 412 -364 -1931 -544 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 137048 | 1 -6 -403 -2 341 481 38 -1402 -804 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 139819 | 2 -15 -1021 0 -42 447 -439 -2161 -466 |
| $6d_{3/2}^4 6f_{5/2}^2 7s_{1/2}^2 7p_{3/2}$ | 177137 | 1 -9 -638 -3 381 516 9 -1523 -736 |
TABLE III: Transition Energies (TE) between states averaged over the relativistic configurations of E114 (in cm\(^{-1}\)). See Table I.

| Configuration | HFDB | HFDB | HFDB | HFDB+\(B\) | HFD | Ionic 22e-RECP 22e-PP |
|---------------|------|------|------|-----------|-----|----------------------|
| \(6d_{5/2}^46f_{7/2}^07s_{1/2}^17p_{1/2}^1\) \(\rightarrow\) | 29093 | -1  | 3    | 314       | -2  | 380      | -46 | 211 | 449 | -457 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{3/2}^1\) \(\rightarrow\) | 41211 | 0   | -1  | -135      | -3  | 370      | -51 | 53  | -333 | -348 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{1/2}^18s_{1/2}^1\) \(\rightarrow\) | 48149 | 0   | 0   | -5        | -3  | 360      | -44 | 114 | 11  | -318 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{1/2}^17d_{3/2}^1\) \(\rightarrow\) | 52230 | 0   | 0   | 16        | -3  | 387      | -44 | 149 | 115 | -320 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{1/2}^16f_{3/2}^1\) \(\rightarrow\) | 57618 | 0   | 0   | 7         | -3  | 384      | -43 | 143 | 86  | -318 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{1/2}^15g_{9/2}^1\) \(\rightarrow\) | 60094 | 0   | 0   | 7         | -3  | 384      | -43 | 143 | 86  | -317 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{1/2}^1\) \(\rightarrow\) | 64483 | 0   | 0   | 7         | -3  | 384      | -43 | 143 | 86  | -317 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{3/2}^1\) \(\rightarrow\) | 66669 | -2  | 6   | 755       | -5  | 833      | -52 | 535 | 1209 | -926 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{3/2}^18s_{1/2}^1\) \(\rightarrow\) | 81879 | -1  | 3   | 277       | -5  | 850      | -64 | 377 | 374 | -834 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^27p_{3/2}^1\) \(\rightarrow\) | 106776| -1  | 4   | 497       | -5  | 872      | -53 | 503 | 969 | -808 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^28s_{1/2}^2\) \(\rightarrow\) | 108893| 1   | -3  | -361      | -6  | 883      | -82 | 174 | -725 | -718 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^28s_{1/2}^2\) \(\rightarrow\) | 136567| 0   | -1  | -207      | -6  | 907      | -72 | 285 | -241 | -680 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^2\) \(\rightarrow\) | 197486| 0   | 1   | 128       | -6  | 961      | -45 | 547 | 853 | -584 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^17p_{3/2}^1\) \(\rightarrow\) | 102896| -6  | 24  | 3110      | 0   | 256      | 96  | 929 | 6650 | -327 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^18s_{1/2}^2\) \(\rightarrow\) | 115405| -5  | 21  | 2745      | -1  | 224      | 59  | 754 | 5987 | -243 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^1\) \(\rightarrow\) | 138842| -6  | 23  | 2905      | -1  | 233      | 73  | 848 | 6439 | -206 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^17p_{3/2}^1\) \(\rightarrow\) | 97736 | 2   | -6  | -771      | 1   | -506     | 472 | -631 | -3156 | -28 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^18s_{1/2}^2\) \(\rightarrow\) | 112486| 3   | -10 | -1277     | 1   | -543     | 473 | -830 | -4091 | 83 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^1\) \(\rightarrow\) | 136356| 2   | -9  | -1129     | 1   | -534     | 487 | -732 | -3647 | 122 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^17p_{3/2}^1\) \(\rightarrow\) | 133837| 2   | -7  | -904      | 0   | -91      | 391 | -746 | -2821 | -675 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^18s_{1/2}^2\) \(\rightarrow\) | 149162| 3   | -11 | -1415     | 0   | -126     | 380 | -952 | -3758 | -579 |
| \(6d_{3/2}^06f_{5/2}^07s_{1/2}^17p_{1/2}^1\) \(\rightarrow\) | 173108| 3   | -10 | -1265     | 0   | -117     | 391 | -855 | -3309 | -541 |
TABLE IV: Transition Energies (TE) between states averaged over the nonrelativistic configurations of uranium (in cm$^{-1}$).
See footnotes in Table I.

| Configuration          | HFDB | HFDB | HFD+B | HFD |
|------------------------|------|------|-------|-----|
|                        | (Fermi, (Point) | (Fermi, (Fermi, 32e-GRECP) |
|                        | A=238) | A=238) | A=238) |
| Configuration          | TE   | Absolute errors |
| $5f^37s^26d^1 \rightarrow 5f^27s^27p^1$ | 7516 | -40 | 0 | -93 | 5 |
| $5f^37s^2$              | 36289 | -68 | 0 | -62 | 9 |
| $5f^37s^16d^2$          | 13124 | 97  | 0 | 78  | -7 |
| $5f^37s^16d^17p^1$      | 17200 | 75  | 0 | 14  | -1 |
| $5f^37s^16d^1$          | 42328 | 63  | 0 | 44  | 0 |
| $5f^16d^2$              | 54576 | 177 | 0 | 138 | -6 |
| $5f^37s^16d^1 \rightarrow 5f^47s^2$ | 15780 | 76  | 2 | 627 | -363 |
| $5f^47s^2$              | 15010 | 78  | 0 | 43  | 3 |
| $5f^47s^16d^1$          | 14932 | 62  | 0 | 21  | -3 |
| $5f^47s^1$              | 38813 | 50  | -1 | 50  | -3 |
| $5f^46d^2$              | 33792 | 147 | 1 | 82  | 6 |
| $5f^46d^17p^1$          | 32115 | 146 | 0 | 79  | 2 |
| $5f^46d^1$              | 53379 | 148 | 0 | 108 | 1 |
| $5f^37s^16d^1 \rightarrow 5f^27s^26d^2$ | 4640 | -85 | -1 | -779 | 362 |
| $5f^27s^26d^2 \rightarrow 5f^27s^16d^17p^1$ | 12809 | -44 | 0 | -118 | 11 |
| $5f^27s^16d^1$          | 42793 | -71 | 0 | -83 | 15 |
| $5f^27s^16d^3$          | 10480 | 113 | 0 | 104 | -12 |
| $5f^27s^16d^27p^1$      | 19217 | 87  | 0 | 15  | -1 |
| $5f^27s^16d^2$          | 45352 | 75  | 0 | 50  | 0 |
| $5f^26d^1$              | 54611 | 204 | 0 | 168 | -12 |
| $5f^37s^16d^1 \rightarrow 5f^17s^26d^3$ | 31450 | -176 | -2 | -1673 | 680 |
| $5f^17s^26d^3 \rightarrow 5f^17s^16d^27p^1$ | 18326 | -48 | 0 | -137 | 11 |
| $5f^17s^16d^2$          | 49329 | -75 | 0 | -96 | 16 |
| $5f^17s^16d^4$          | 7331 | 127 | 0 | 124 | -15 |
| $5f^17s^16d^37p^1$      | 21038 | 98  | 0 | 18  | -1 |
| $5f^17s^16d^3$          | 48001 | 87  | 0 | 57  | 0 |
| $5f^16d^4$              | 53806 | 230 | 0 | 196 | -15 |
| $5f^37s^26d^1 \rightarrow 5f^2$ | 99459 | 252 | 4 | 1126 | -671 |
TABLE V: Transition Energies (TE) between states averaged over the nonrelativistic configurations of plutonium (in cm\(^{-1}\)). See footnotes in Table I.

| Configuration | TE  | Absolute errors |
|---------------|-----|-----------------|
| \(5f^57s^2 \rightarrow 5f^67s^16d^1\) | 17164 | 96 | 0 | 53 | -2 |
| \(5f^67s^17p^1 \rightarrow 5f^67s^17p^1\) | 15678 | 76 | 0 | 19 | -1 |
| \(5f^67s^1 \rightarrow 5f^67s^1\) | 39853 | 61 | 0 | 47 | -1 |
| \(5f^67p^1 \rightarrow 5f^67p^1\) | 56794 | 183 | 0 | 114 | -2 |
| \(5f^67s^2 \rightarrow 5f^77s^1\) | 66677 | 172 | -1 | 71 | 1 |
| \(5f^77s^1 \rightarrow 5f^77s^1\) | 43691 | 159 | 4 | 504 | -377 |
| \(5f^77s^1 \rightarrow 5f^77s^1\) | 19877 | 67 | 0 | 54 | -1 |
| \(5f^77p^1 \rightarrow 5f^77p^1\) | 14816 | 68 | -1 | 62 | -6 |
| \(5f^7 \rightarrow 5f^7\) | 34957 | 70 | -1 | 96 | -9 |
| \(5f^67s^2 \rightarrow 5f^77s^26d^1\) | 35910 | -84 | 0 | -61 | 14 |
| \(5f^77s^26d^1 \rightarrow 5f^77s^26d^1\) | -3099 | -103 | -2 | -704 | 414 |
| \(5f^77s^26d^1 \rightarrow 5f^77s^26d^1\) | 6743 | -50 | 0 | -93 | 10 |
| \(5f^77s^26d^2 \rightarrow 5f^77s^26d^2\) | 15044 | 120 | 0 | 82 | -10 |
| \(5f^77s^26d^26p^1 \rightarrow 5f^77s^26d^26p^1\) | 18246 | 94 | 0 | 17 | 0 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 35910 | -84 | 0 | -61 | 14 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 43764 | 80 | 0 | 48 | 1 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 15425 | -213 | -2 | -1545 | 807 |
| \(5f^77s^26d^1 \rightarrow 5f^77s^26d^1\) | 12434 | -55 | 0 | -116 | 16 |
| \(5f^77s^26d^2 \rightarrow 5f^77s^26d^2\) | 12221 | 141 | 0 | 105 | -16 |
| \(5f^77s^26d^26p^1 \rightarrow 5f^77s^26d^26p^1\) | 20405 | 109 | 0 | 18 | -1 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 42841 | -88 | 0 | -77 | 19 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 46949 | 95 | 0 | 55 | 0 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 62648 | -328 | -3 | -2496 | 1136 |
| \(5f^77s^26d^1 \rightarrow 5f^77s^26d^1\) | 8926 | 159 | 0 | 124 | -20 |
| \(5f^77s^26d^2 \rightarrow 5f^77s^26d^2\) | 18247 | -59 | 0 | -133 | 18 |
| \(5f^77s^26d^26p^1 \rightarrow 5f^77s^26d^26p^1\) | 22323 | 123 | 0 | 21 | -1 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 24140 | 295 | 0 | 231 | -36 |
| \(5f^77s^26d^2 \rightarrow 5f^77s^26d^2\) | 49677 | -92 | 0 | -89 | 22 |
| \(5f^77s^2 \rightarrow 5f^77s^2\) | 49694 | 109 | 0 | 63 | 0 |
TABLE VI: Transition Energies (TE) between terms of E112 (in \text{cm}^{-1}). See footnotes in Table I.

\begin{tabular}{lccccccccc}
\hline
Configuration, term & HFDB & HFD+B & HFD & 52e- & 20e- & Ionic & 20e- & 20e-RECP & 20e-PP \\
& & & (Fermi, GRECP) & & & & & & of Nash et al. \\
& & & (Fermi, RECP) & & & & & & et al. \\
& & & (A=296) & & & & & & (A=296) \\
\hline
6d^{4}_{3/2}6d^{6}_{5/2} \pi s_{1/2} \pi p_{1/2} J=0 & & & & & & & & & \\
J=1 & 9468 & 0 & 54 & 9 & 42 & 59 & 288 & 27 & \\
J=3 & 1958 & 0 & 25 & 6 & 16 & 43 & 165 & 11 & \\
6d^{4}_{3/2}6d^{6}_{5/2} \pi s_{1/2} \pi p_{1/2} J=2 & & & & & & & & & \\
J=1 & -8145 & 1 & -92 & 3 & 172 & 40 & -558 & 100 & \\
J=2 & -1919 & 0 & -24 & -5 & 34 & 14 & -42 & 16 & \\
J=3 & 39 & 0 & -17 & 0 & 74 & 56 & 4 & 78 & \\
J=4 & -3166 & 0 & -27 & -6 & 9 & -13 & -69 & -23 & \\
\hline
\end{tabular}
TABLE VII: Transition Energies (TE) between terms of uranium (in cm$^{-1}$). See footnotes in Table I.

| Configuration, term | TE  | Absolute errors |
|---------------------|-----|-----------------|
| $5f_{3/2}^1 6d_{5/2}^1 7s_{1/2}^2$ J=0 $\rightarrow$ J=1 | 18576 | 0 74 137 -15 67 -102 |
| J=2                | 9710 | 0 22 140 -12 117 -53 |
| J=3                | 7749 | 0 66 -57 -9 -103 -49 |
| J=4                | 6691 | 0 69 -77 -5 -121 -40 |
| J=5                | -8005 | 0 83 -439 8 -470 31 |
| J=6                | -10767 | 0 69 -416 31 -431 69 |
| $5f_{3/2}^1 5f_{7/2}^1 7s_{1/2}^2$ J=1 $\rightarrow$ J=2 | 4399 | 0 -5 159 -35 165 -51 |
| J=3                | 2840 | 0 4 109 -23 113 -33 |
| J=4                | 3468 | 0 11 134 -29 139 -42 |
| J=5                | 2785 | 0 22 117 -24 121 -36 |
| J=6                | 4606 | 1 29 181 -42 188 -62 |
| J=7                | -6030 | 1 78 -176 12 -186 26 |
| J=8                | -5542 | 1 90 -149 6 -158 17 |

| Configuration, term | TE  | Absolute errors |
|---------------------|-----|-----------------|
| $5f_{3/2}^1 6d_{5/2}^1 7s_{1/2}^2$ J=0 $\rightarrow$ J=1 | -19109 | 0 23 -432 -61 -426 -8 |
| J=2                | -15310 | 0 1 -304 -45 -288 5 |
| J=3                | -23656 | 0 41 -598 -77 -593 -8 |
| J=4                | -26013 | 0 21 -638 -69 -618 23 |
| J=5                | -32544 | 0 36 -754 -86 -732 21 |
| J=6                | -39562 | 0 -2 -724 -57 -671 82 |

(a) Term-Splitting (TS) correction generated in the present work from HFDB calculation with Fermi nuclear charge distribution.
(b) Self-Consistent Generalized Relativistic Effective Core Potential (SfC GRECP) generated in [29] from HFDB calculation with Fermi nuclear charge distribution.
TABLE VIII: Matrix Elements (ME) of $< r^2 >$ for some spinors from states averaged over the relativistic configurations of E112 (in a.u.). See footnotes in Table I.

| Config., spinor | ME          | Absolute errors |
|----------------|-------------|-----------------|
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}$ | 3.150       | -0.005          |
| $6d_{3/2}$    | 3.781       | 0.002           |
| $7s_{1/2}$    | 7.157       | -0.023          |
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}7p_{1/2}^{1/2}$ | 3.144       | -0.004          |
| $6d_{3/2}$    | 3.648       | 0.002           |
| $7s_{1/2}$    | 6.898       | -0.020          |
| $7p_{1/2}$    | 13.023      | -0.116          |
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}7p_{1/2}^{1/2}$ | 3.057       | -0.004          |
| $6d_{3/2}$    | 3.522       | 0.002           |
| $7s_{1/2}$    | 6.739       | -0.019          |
| $7p_{1/2}$    | 11.259      | -0.087          |

TABLE IX: Radial integrals $2 \int_0^\infty |f_{nvlj}(r)[f_{nvlj}(r) - \tilde{\varphi}_{nvlj}(r)]| dr$ for valence spinors from states averaged over the relativistic configurations of E112 (in a.u.) where $f_{nvlj}$ is the large component of the Dirac spinor from HFDB calculation with the Fermi nuclear charge distribution for $A = 296$, $\tilde{\varphi}_{nvlj}$ is the radial part of the corresponding pseudospinor (or the large component of the Dirac spinor), $R_n$ is the radius of the last node for the spinor. See footnotes in Table I.

| Configuration, spinor | Integrals         |               |
|-----------------------|-------------------|---------------|
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}$ | 0.0037   | 0.0000       |
| $7s_{1/2}$            | 0.0006            | 0.0131        |
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}7p_{1/2}^{1/2}$ | 0.0036   | 0.0001       |
| $7s_{1/2}$            | 0.0002            | 0.0134        |
| $7p_{1/2}$            | 0.0079            | 0.0002        |
| $6d_{3/2}^{3/2}6d_{5/2}^{5/2}7s_{1/2}^{1/2}7p_{1/2}^{1/2}$ | 0.0034   | 0.0001       |
| $7s_{1/2}$            | 0.0003            | 0.0134        |
| $7p_{1/2}$            | 0.0079            | 0.0002        |
TABLE X: One-electron energies, $\varepsilon$, for some spinors from states averaged over the relativistic configurations of E112 (in a.u.). See footnotes in Table I.

| Config., spinor | $\varepsilon$ | Absolute errors |
|----------------|--------------|-----------------|
| $6d_{5/2}^2$ | 0.5624 | 0.0003 | 0.0000 | 0.0001 | -0.0026 | -0.0112 | -0.0037 |
| $6d_{3/2}$ | 0.4432 | -0.0011 | 0.0000 | -0.0001 | -0.0026 | -0.0095 | -0.0009 |
| $7s_{1/2}$ | 0.4497 | 0.0014 | 0.0000 | -0.0003 | 0.0042 | 0.0272 | 0.0001 |
| $6d_{5/2}^2$ | 0.6148 | -0.0001 | 0.0000 | -0.0001 | -0.0025 | -0.0118 | -0.0039 |
| $6d_{3/2}$ | 0.4870 | -0.0017 | 0.0000 | 0.0000 | -0.0024 | -0.0108 | -0.0009 |
| $7s_{1/2}$ | 0.5217 | 0.0011 | 0.0000 | 0.0000 | 0.0048 | 0.0278 | 0.0004 |
| $7p_{1/2}$ | 0.2248 | 0.0015 | 0.0000 | -0.0001 | 0.0012 | 0.0114 | -0.0004 |
| $6d_{5/2}^2$ | 0.6663 | -0.0002 | 0.0000 | -0.0002 | -0.0042 | -0.0173 | -0.0043 |
| $6d_{3/2}$ | 0.5314 | -0.0018 | 0.0000 | -0.0001 | -0.0040 | -0.0159 | -0.0014 |
| $7s_{1/2}$ | 0.5253 | 0.0010 | 0.0000 | 0.0000 | 0.0044 | 0.0258 | 0.0001 |
| $7p_{1/2}$ | 0.2653 | 0.0017 | 0.0000 | 0.0000 | 0.0011 | 0.0110 | -0.0005 |