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Correlation and relativistic effects in actinide ions

U. I. Safronova^{1,2} and M. S. Safronova³

¹*Physics Department, University of Nevada, Reno, Nevada 89557,*

²*Department of Physics, University of Notre Dame, Notre Dame, IN 46556,*

³*Department of Physics and Astronomy, 217 Sharp Lab,
University of Delaware, Newark, Delaware 19716*

Wavelengths, line strengths, and transition rates are calculated for the multipole (E1, M1, E2, M2, E3 and M3) transitions between the excited $6s^2 6p^5 nl$ and $6s 6p^6 nl$ states and the ground $6s^2 6p^6$ state in Ac^{3+} , Th^{4+} , and U^{6+} Rn-like ions. Relativistic many-body perturbation theory (RMBPT), including the Breit interaction, is used to evaluate energies and transition rates for multipole transitions in these hole-particle systems. The RMBPT method agrees with MCDF calculations in lowest-order, includes all second-order correlation corrections, and includes corrections from negative energy states. The calculations start from a $[\text{Xe}]4f^{14}5d^{10}6s^2 6p^6$ Dirac-Fock potential. First-order perturbation theory is used to obtain intermediate-coupling coefficients, and second-order RMBPT is used to determine the matrix elements. Evaluated multipole matrix elements for transitions from excited states into the ground states are used to determine the line strengths, transition rates, and multipole polarizabilities. This work provides a number of yet unmeasured properties of these actinide ions for various applications and benchmark tests of theory and experiment.

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I. INTRODUCTION

Very few studies of actinide atom and ion properties have been carried out to date owing to difficulties in both accurate theoretical description of these systems and experimental methodologies. The atomic properties of the actinides are also needed for the actinide chemistry models. The radonlike Th^{4+} ion is the most common charge state of thorium in chemical compounds [1]. This work is motivated in part by recent experiments [2–5] to investigate the spectroscopy of high- L Rydberg levels of actinide ions and the dipole and quadrupole polarizabilities. These measurements present an excellent opportunity for benchmark tests of a priori theoretical descriptions of such highly relativistic ions.

In 2010, binding energies of high- L Rydberg levels of Th^{3+} were measured using the Resonant Excitation Stark Ionization Spectroscopy (RESIS) technique by Hanni *et al.* [3]. Analysis of the data with the long-range polarization model was used to determine the dipole and quadrupole polarizabilities of the free Th^{4+} ion, $\alpha_d = 7.61(6)$ a.u., $\alpha_Q = 47(11)$ a.u. [3]. To improve the precision of these properties, rf spectroscopy was used to directly measure intervals separating $n = 37$ levels of Th^{3+} with $9 \leq L \leq 15$ in [4]. The resulting measurement improved the precision of the dipole polarizability by an order of magnitude, but indicated that the previous report of the quadrupole polarizability was an overestimate [4]. The dipole polarizability of Th^{4+} was determined to be $\alpha_d = 7.720(7)$ a.u., and the quadrupole polarizability was found to be $\alpha_Q = 21.5(3.9)$ a.u. In 2011, properties of Fr-like Th^{3+} were determined from spectroscopy of high- L Rydberg levels of Th^{2+} ion [5].

The study of the high- L Rydberg levels of U^{5+} using the RESIS technique [2] led to difficulties which were possibly caused by different numbers of metastable states in

Th^{4+} and U^{6+} ions. The theoretical calculations of U^{6+} atomic properties may aid further experimental studies.

The importance of metastable states for determination of polarizability in Yb^{2+} ion was underlined in Ref. [6]. All states up to $E = 53736 \text{ cm}^{-1}$ (counting from the ground state) that belong to either $[\text{Xe}]4f^{13}5d$ or $[\text{Xe}]4f^{13}6s$ odd configurations were considered [6]. Only three of these $[\text{Xe}]4f^{13}5d$ levels have total angular momentum $J = 1$ and, therefore, can decay to the ground state via strong electric-dipole transitions. As a result, all remaining 21 $[\text{Xe}]4f^{13}5d$ and $[\text{Xe}]4f^{13}6s$ levels with $J = 0, 2 - 6$ are metastable.

Very few studies of Rn-like ions has been carried out to date. Only the total binding energies and ionization potentials in Rn-like ions were presented in Refs. [7–12]. Dirac-Fock total energies, ionization energies, and orbital energies for uranium ions were evaluated by Rashid *et al.* [9]. The total and ionization energies in Rn-like U^{6+} were found to be equal to 761540.14 eV and 88.45 eV, respectively. *Ab initio* pseudopotential and density-functional all-electron study of ionization and excitation energies of actinide atoms was performed by Liu *et al.* [10]. Ionization potential of Rn-like Ac^{3+} ion was found to be equal to 43.78 eV. Recently, a systematic study of atomic binding energies, in the Dirac-Fock (DF) approximation was presented by Rodrigues *et al.* [12]. The total binding energy (DF) of the isoelectronic series of radon with $Z = 89, 90$, and 92 was found equal to -699502 eV, -719769 eV, and -761482 eV, respectively.

In the present paper, we determine energies the excited $[\text{Xe}]4f^{14}5d^{10}6s^2 6p^5 nl$ and $[\text{Xe}]4f^{14}5d^{10}6s 6p^6 n'l'$ states in Ac^{3+} , Th^{4+} , and U^{6+} ions with the nuclear charges $Z = 89, 90$, and 92 . We omit $[\text{Xe}]4f^{14}5d^{10}$ from the level designation below for brevity. The calculations are carried out to second order in relativistic many-body perturbation theory (RMBPT). The RMBPT method

TABLE I: Possible hole-particle states in the $6p_jnl_{j'}(J)$ and $6s_{1/2}nl_j(J)$ complexes; jj coupling scheme.

Even-parity states			Odd-parity states		
$6p_{3/2}7p_{3/2}(0)$	$6p_{3/2}5f_{5/2}(2)$	$6p_{3/2}5f_{7/2}(3)$	$6p_{3/2}6d_{3/2}(0)$	$6p_{3/2}6d_{5/2}(2)$	$6p_{3/2}6d_{3/2}(3)$
$6p_{1/2}7p_{1/2}(0)$	$6p_{3/2}5f_{7/2}(2)$	$6p_{3/2}5f_{5/2}(3)$	$6p_{1/2}7s_{1/2}(0)$	$6p_{3/2}6d_{3/2}(2)$	$6p_{3/2}6d_{5/2}(3)$
$6s_{1/2}7s_{1/2}(0)$	$6p_{1/2}5f_{5/2}(2)$	$6p_{1/2}5f_{7/2}(3)$	$6s_{1/2}7p_{1/2}(0)$	$6p_{3/2}7s_{1/2}(2)$	$6p_{1/2}6d_{5/2}(3)$
	$6p_{3/2}7p_{1/2}(2)$	$6p_{1/2}5f_{7/2}(3)$		$6p_{1/2}6d_{3/2}(2)$	$6s_{1/2}5f_{5/2}(3)$
$6p_{3/2}5f_{5/2}(1)$	$6p_{3/2}7p_{3/2}(2)$	$6p_{3/2}7p_{3/2}(3)$	$6p_{3/2}6d_{3/2}(1)$	$6p_{1/2}6d_{5/2}(2)$	$6s_{1/2}5f_{7/2}(3)$
$6p_{3/2}7p_{1/2}(1)$	$6p_{1/2}7p_{3/2}(2)$	$6s_{1/2}6d_{5/2}(3)$	$6p_{3/2}6d_{5/2}(1)$	$6s_{1/2}5f_{5/2}(2)$	
$6p_{3/2}7p_{3/2}(1)$	$6s_{1/2}6d_{3/2}(2)$		$6p_{3/2}7s_{1/2}(1)$	$6s_{1/2}7p_{3/2}(2)$	$6p_{3/2}6d_{5/2}(4)$
$6p_{1/2}7p_{1/2}(1)$	$6s_{1/2}6d_{5/2}(2)$	$6p_{3/2}5f_{5/2}(4)$	$6p_{1/2}6d_{3/2}(1)$		$6s_{1/2}5f_{7/2}(4)$
$6p_{1/2}7p_{3/2}(1)$		$6p_{3/2}5f_{7/2}(4)$	$6p_{1/2}7s_{1/2}(1)$		
$6s_{1/2}6d_{3/2}(1)$		$6p_{1/2}5f_{7/2}(4)$	$6s_{1/2}7p_{1/2}(1)$		
$6s_{1/2}7s_{1/2}(1)$		$6p_{3/2}5f_{7/2}(5)$	$6s_{1/2}7p_{3/2}(1)$		

is also used to determine line strengths and transition rates for all allowed and forbidden electric-multipole and magnetic-multipole (E1, E2, E3, M1, M2) transitions from the $6s^26p^5nl$ and $6s6p^6n'l'$ excited states into the ground state. These data are used to determine the ground state multipole polarizabilities for Rn-like ions with $Z = 89, 90$, and 92 .

The second-order RMBPT calculations for Rn-like ions start from a $[\text{Xe}]4f^{14}5d^{10}6s^26p^6$ Dirac-Fock potential. We consider the $6s$ and $6p$ holes and the $5f$, $6d$, $7s$, and $7p$ particles leading to the 30 even-parity $6s^26p^55f$, $6s^26p^57p$, $6s6p^66d$, and $6s6p^67s$ excited states and the 25 odd-parity $6s^26p^56d$, $6s^26p^57s$, $6s6p^65f$, and $6s6p^67p$ excited states. In the present paper, we evaluate the corresponding energies, wavelengths, line strengths, and transition rates. We would like to underline that the RMBPT method is based on the relativistic many-body perturbation theory that agrees with MCDF calculations in lowest-order, includes all second-order correlation corrections, and includes corrections from negative energy states.

II. METHOD

Details of the RMBPT method for hole-particle states were presented in Ref. [13] for calculation of energies, in Refs. [6, 13–19] for calculation of multipole matrix elements for transitions from excited states into the ground state, and in Refs. [6, 20–22] for calculation of multipole matrix elements for transitions between excited states. The calculations are carried out using sets of basis Dirac-Fock (DF) orbitals. The orbitals used in the present calculation are obtained as linear combinations of B-splines. These B-spline basis orbitals are determined using the method described in Ref. [23]. We use 50 B-splines of order 10 for each single-particle angular momentum state, and we include all orbitals with orbital angular momentum $l \leq 9$ in our basis set.

For atoms with one hole in the closed shells and one electron above the closed shells, the model space is formed from hole-particle states of the type

$a_v^\dagger a_a |0\rangle$ where a_i^\dagger and a_j are creation and annihilation operators, respectively, and $|0\rangle$ is the closed-shell $[\text{Xe}]4f^{14}5d^{10}6s^26p^6$ ground state. The single-particle indices v and a designate the valence and core states, respectively. For our study of low-lying $6p^{-1}nl$ and $6s^{-1}nl$ states of Rn-like ion, the values of a are $6s_{1/2}$, $6p_{1/2}$, and $6p_{3/2}$ while the values of v are $5f_{5/2}$, $5f_{7/2}$, $6d_{3/2}$, $6d_{5/2}$, $7s_{1/2}$, $7p_{1/2}$, and $7p_{3/2}$.

To obtain orthonormal model states, we consider the coupled states $\Phi_{JM}(av)$ defined by

$$\Phi_{JM}(av) = \sqrt{(2J+1)} \times \sum_{m_a m_v} (-1)^{j_v - m_v} \begin{pmatrix} j_v & J & j_a \\ -m_v & M & m_a \end{pmatrix} a_{vm_v}^\dagger a_{am_a} |0\rangle. \quad (1)$$

Combining the $6p_j$ and $6s$ hole orbitals and the $5f_{5/2}$, $5f_{7/2}$, $6d_{3/2}$, $6d_{5/2}$, $7s_{5/2}$, $7p_{1/2}$, and $7p_{3/2}$ particle orbitals, we obtain 28 even-parity states consisting of 3 $J = 0$ states, 7 $J = 1$ states, 8 $J = 2$ states, 6 $J = 3$ states, 3 $J = 4$ states, and one $J = 5$ state. Additionally, there are 24 odd-parity states consisting of 3 $J = 0$ states, 7 $J = 1$ states, 7 $J = 2$ states, 5 $J = 3$ states, and two $J = 4$ states. The distribution of the 72 states in the model space is summarized in Table I. Instead of using the $6p_j^{-1}nl_{j'}$ and $6s^{-1}nl_j$ designations, we use simpler designations $6p_jnl_{j'}$ and $6s_{1/2}nl_j$ in this table and in all following tables and the text below.

III. EXCITATION ENERGIES

In Table II, we illustrate the relative size of various contributions before diagonalization on the example of the even-parity states $6p_{j_1}5f_{j_2}$ with $J=2$ and odd-parity states $6p_{j_1}6d_{j_2}$ with $J=1$ in Rn-like Th^{4+} . The zeroth, first-, and second-order Coulomb contributions, $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$, and the first- and second-order Breit-Coulomb corrections, $B^{(1)}$ and $B^{(2)}$, are given.

The importance of correlation contribution is evident from this table; the ratio of the first and zeroth orders ($E^{(1)}/E^{(0)}$) is about 20–40%, and the ratio of the second and first ($E^{(2)}/E^{(1)}$) orders is even larger, 20–60%.

TABLE II: Contributions to the $E[6p_{j_1}5f_{j_2}, 6p_{j_3}5f_{j_4} \ J = 2]$ and $E[6p_{j_1}6d_{j_2}, 6p_{j_3}6d_{j_4} \ J = 1]$ energy matrixes before diagonalization for Th^{4+} ion. Units: a.u.

$6p_{j_1}nl_{j_2}$	$6p_{j_3}nl_{j_4}$	$E^{(0)}$	$E^{(1)}$	$B^{(1)}$	$E^{(2)}$	$B^{(2)}$
$6p_{j_1}5f_{j_2}(2) - 6p_{j_3}5f_{j_4}(2)$ energy matrix elements						
$6p_{1/2}5f_{5/2}$	$6p_{1/2}5f_{5/2}$	1.52956	-0.49040	-0.00600	-0.07886	-0.00185
$6p_{3/2}5f_{5/2}$	$6p_{3/2}5f_{5/2}$	1.19553	-0.49145	-0.00175	-0.06277	-0.00375
$6p_{3/2}5f_{7/2}$	$6p_{3/2}5f_{7/2}$	1.21113	-0.46358	-0.00258	-0.06599	-0.00332
$6p_{1/2}5f_{5/2}$	$6p_{3/2}5f_{5/2}$	0.00000	0.01756	-0.00001	-0.00176	0.00007
$6p_{3/2}5f_{5/2}$	$6p_{1/2}5f_{5/2}$	0.00000	0.01756	-0.00001	0.00188	0.00003
$6p_{1/2}5f_{5/2}$	$6p_{3/2}5f_{7/2}$	0.00000	0.04916	0.00000	-0.00837	-0.00010
$6p_{3/2}5f_{7/2}$	$6p_{1/2}5f_{5/2}$	0.00000	0.04916	0.00000	-0.00860	-0.00008
$6p_{3/2}5f_{5/2}$	$6p_{3/2}5f_{7/2}$	0.00000	-0.04483	0.00000	-0.00932	-0.00006
$6p_{3/2}5f_{7/2}$	$6p_{3/2}5f_{5/2}$	0.00000	-0.04483	0.00000	-0.00932	-0.00006
$6p_{j_1}6d_{j_2}(1) - 6p_{j_3}6d_{j_4}(1)$ energy matrix elements						
$6p_{1/2}6d_{3/2}$	$6p_{1/2}6d_{3/2}$	1.50590	-0.32435	-0.00725	-0.06537	0.00610
$6p_{3/2}6d_{3/2}$	$6p_{3/2}6d_{3/2}$	1.17187	-0.38239	-0.00297	-0.01996	0.00440
$6p_{3/2}6d_{5/2}$	$6p_{3/2}6d_{5/2}$	1.19112	-0.25398	-0.00351	-0.07385	0.00443
$6p_{1/2}6d_{3/2}$	$6p_{3/2}6d_{3/2}$	0.00000	-0.00576	-0.00002	-0.01868	-0.00006
$6p_{3/2}6d_{3/2}$	$6p_{1/2}6d_{3/2}$	0.00000	-0.00576	-0.00002	-0.01110	-0.00003
$6p_{1/2}6d_{3/2}$	$6p_{3/2}6d_{5/2}$	0.00000	0.09682	-0.00002	-0.03915	-0.00032
$6p_{3/2}6d_{5/2}$	$6p_{1/2}6d_{3/2}$	0.00000	0.09682	-0.00002	-0.03937	-0.00010
$6p_{3/2}6d_{3/2}$	$6p_{3/2}6d_{5/2}$	0.00000	-0.07149	-0.00001	-0.01920	-0.00014
$6p_{3/2}6d_{5/2}$	$6p_{3/2}6d_{3/2}$	0.00000	-0.07149	-0.00001	-0.01785	-0.00015

TABLE III: Energies of the Th^{4+} even-parity states with $J = 2$ and odd-parity states with $J = 1$ relative to the ground state. $E^{(0+1)} \equiv E^{(0)} + E^{(1)} + B^{(1)}$. Units: cm^{-1} .

jj coupl.	$E^{(0+1)}$	$E^{(2)}$	$B^{(2)}$	E_{LS}	E_{tot}
$6p_{1/2}5f_{5/2}(2)$	146877	-15682	-801	-36	130358
$6p_{3/2}5f_{5/2}(2)$	168907	-12053	-738	-34	156082
$6p_{3/2}5f_{7/2}(2)$	228605	-17832	-421	-4	210349
$6p_{1/2}6d_{3/2}(1)$	165691	-8367	951	36	158309
$6p_{3/2}6d_{3/2}(1)$	203897	-7154	1060	32	197834
$6p_{3/2}6d_{5/2}(1)$	265668	-19413	1267	4	247525

It should be noted that corrections for the frequency-dependent Breit interaction [24] are included in the first order only. The difference between the first-order Breit corrections calculated with and without frequency dependence is small, 1–2%. The Breit corrections are almost two orders of magnitude smaller than the corresponding Coulomb corrections of the same order: the ratio of the first-order Breit and Coulomb corrections is 1–2%.

The ratio of non-diagonal and diagonal matrix elements is larger for the second-order contributions than for the first-order contributions. The first-order non-diagonal matrix elements are symmetric, but the second-order non-diagonal matrix elements are not symmetric. The values of $E^{(2)}[a'v'(J), av(J)]$ and $E^{(2)}[av(J), a'v'(J)]$ matrix elements differ in some cases by a factor 2–3 and occasionally have opposite signs. We now discuss how the final energy levels are obtained from

the above contributions. To determine the first-order energies, we diagonalize the symmetric first-order effective Hamiltonian, including both Coulomb and Breit interactions. The first-order expansion coefficient $C^N[av(J)]$ (often called a mixing coefficient) is the N -th eigenvector of the first-order effective Hamiltonian, and $E^{(1)}[N]$ is the corresponding eigenvalue. The resulting eigenvectors are used to determine the second-order Coulomb correction $E^{(2)}[N]$, the second-order Breit-Coulomb correction $B^{(2)}[N]$ and the QED correction $E_{\text{LS}}[N]$.

In Table III, we list the following contributions to the energies of 6 excited states in Th^{4+} : the sum of the zeroth and first-order energies $E^{(0+1)} = E^{(0)} + E^{(1)} + B^{(1)}$, the second-order Coulomb energy $E^{(2)}$, the second-order Breit-Coulomb correction $B^{(2)}$, the QED correction E_{LS} , and the sum of the above contributions E_{tot} . The Lamb shift E_{LS} is approximated as the sum of the one-electron self energy and the first-order vacuum-polarization energy. The vacuum-polarization contribution is calculated from the Uehling potential using the results of Fullerton and Rinker [25]. The self-energy contribution is estimated for s , $p_{1/2}$ and $p_{3/2}$ orbitals by interpolating among the values obtained by Mohr [26, 27, 28] using Coulomb wave functions. For this purpose, an effective nuclear charge Z_{eff} is obtained by finding the value of Z_{eff} required to give a Coulomb orbital with the same average $\langle r \rangle$ as the DHF orbital.

When starting calculations from relativistic DF wave functions, it is natural to use jj designations for uncoupled energy matrix elements; however, neither jj nor LS coupling describes the *physical* states properly. We find

TABLE IV: Energies (in cm^{-1}) of Th^{4+} odd- and even-parity states relative to the ground state calculated in the first-order, second-order RMBPT (columns labelled RMBPT1 and RMBPT2, respectively) and Hartree-Fock relativistic method implemented in COWAN code (column “COWAN”). The RMBPT values are evaluated with different configuration sets: I = $6p5f$, $6p6d$, II = $6p5f + 6p7p$, $6p6d + 6p7s$ and III = $6p5f + 6p7p + 6s6d + 6s7s$, $6p6d + 6p7s + 6s5f + 6s7p$. Values listed in “COWAN” column are obtained including the configuration set that is equivalent to set III. Values listed in “COWAN2” column are obtained including larger set of configurations: IV = $6pn_1f + 6pn_2p + 6sn_3d + 6sn_2s$, $6pn_3d + 6pn_2s + 6sn_1f + 6sn_2p$ with $n_1 = 5-9$, $n_2 = 7-9$, and $n_3 = 6-9$.

Level	I= $6p5f + 6p6d$		II=I+ $6p7s + 6p7p$		III=II+ $6snl$		III	IV	Level
	RMBPT1	RMBPT2	RMBPT1	RMBPT2	RMBPT1	RMBPT2	COWAN1	COWAN2	
$6p_{3/2}5f_{5/2}(1)$	141555	129246	141547	105289	140482	103961	135015	135013	$6s^26p^55f^3D_1$
$6p_{3/2}5f_{5/2}(2)$	146877	130394	146869	105388	145992	103880	140455	140469	$6s^26p^55f^3D_2$
$6p_{3/2}5f_{5/2}(4)$	150413	136694	150413	112300	150413	111611	143711	143819	$6s^26p^55f^3G_4$
$6p_{3/2}5f_{7/2}(5)$	150707	138834	150707	115935	150707	115151	145498	145606	$6s^26p^55f^3G_5$
$6p_{3/2}5f_{7/2}(3)$	154183	138917	154169	114801	153648	114426	147639	147698	$6s^26p^55f^3F_3$
$6p_{3/2}5f_{5/2}(3)$	157390	143301	157387	118076	157314	117597	150675	150759	$6s^26p^55f^1F_3$
$6p_{3/2}6d_{3/2}(0)$	161473	160273	161270	143308	161118	142323	158046	158019	$6s^26p^56d^3P_0$
$6p_{3/2}5f_{7/2}(4)$	162859	148681	162859	122502	162859	123001	156273	156377	$6s^26p^55f^3F_4$
$6p_{3/2}6d_{3/2}(1)$	165690	158274	165329	141809	165218	142612	161938	161937	$6s^26p^56d^3P_1$
$6p_{3/2}5f_{7/2}(2)$	168907	156116	168895	132377	168847	131630	160896	160980	$6s^26p^55f^1D_2$
$6p_{3/2}6d_{3/2}(3)$	172385	170385	172385	152598	171752	151508	167627	167594	$6s^26p^56d^3F_3$
$6p_{3/2}6d_{5/2}(2)$	172998	170417	172477	152808	172385	152205	168668	168716	$6s^26p^56d^3D_2$
$6p_{3/2}6d_{5/2}(4)$	173587	173071	173587	157264	172707	156599	170023	169952	$6s^26p^56d^3F_4$
$6p_{3/2}6d_{3/2}(2)$	177952	175189	177770	158302	177529	157399	173883	173943	$6s^26p^56d^1D_2$
$6p_{3/2}6d_{5/2}(3)$	184028	182885	184028	163728	183988	163203	180423	180490	$6s^26p^56d^3D_3$
$6p_{3/2}7s_{1/2}(2)$			200043	181307	199837	176394	197339	197368	$6s^26p^57s^3P_2$
$6p_{3/2}6d_{5/2}(1)$	203897	197802	200224	193055	200125	181998	196638	196142	$6s^26p^56d^3D_1$
$6p_{3/2}7s_{1/2}(1)$			206648	204574	206336	184100	201455	201094	$6s^26p^57s^1P_1$
$6p_{1/2}5f_{5/2}(3)$	216016	200234	216016	175538	216008	174712	209762	209865	$6s^26p^55f^3G_3$
$6p_{1/2}5f_{7/2}(3)$	221128	205968	221087	181138	220528	179353	215134	215174	$6s^26p^55f^3D_3$
$6p_{1/2}5f_{7/2}(4)$	223552	208384	223552	182604	223552	181736	217423	217527	$6s^26p^55f^3G_4$
$6p_{1/2}5f_{5/2}(2)$	228605	210352	228536	183656	228343	182566	218808	218875	$6s^26p^55f^1D_2$
$6p_{1/2}6d_{3/2}(2)$	240564	234779	240570	218010	239469	214502	234454	234409	$6s^26p^56d^3F_2$
$6p_{3/2}7p_{1/2}(1)$			241862	225806	241203	225123	239426	239426	$6s^26p^57p^3S_1$
$6p_{3/2}7p_{1/2}(2)$			243260	227234	243127	227154	241353	241220	$6s^26p^57p^3D_2$
$6p_{1/2}6d_{5/2}(2)$	247155	243237	247348	225029	247313	224226	242599	242601	$6s^26p^56d^3D_2$
$6p_{1/2}6d_{5/2}(3)$	249440	245446	249440	226857	248809	225564	244843	244774	$6s^26p^56d^3F_3$
$6p_{3/2}7p_{3/2}(3)$			257423	243556	257358	243547	254321	254057	$6s^26p^57p^3D_3$
$6p_{3/2}7p_{3/2}(1)$			257837	244127	257565	243751	254497	254490	$6s^26p^57p^1P_1$
$6p_{3/2}7p_{3/2}(2)$			260638	245352	260604	245298	257628	257660	$6s^26p^57p^3P_2$
$6p_{3/2}7p_{3/2}(0)$			265082	249010	265006	247409	262805	262436	$6s^26p^57p^1S_0$
$6p_{1/2}6d_{3/2}(1)$	265668	247521	265725	238692	265207	236355	260581	257646	$6s^26p^56d^1P_1$
$6p_{1/2}7s_{1/2}(0)$			271083	248586	270620	242959	267274	267242	$6s^26p^57s^3P_0$
$6p_{1/2}7s_{1/2}(1)$			272272	255027	271974	244433	269390	268988	$6s^26p^57s^3P_1$
$6p_{1/2}7p_{1/2}(1)$			314337	294877	314067	294316	311834	308721	$6s^26p^57p^3D_1$
$6p_{1/2}7p_{1/2}(0)$			319975	295120	319824	294038	317680	317230	$6s^26p^57p^3P_0$
$6p_{1/2}7p_{3/2}(1)$			329978	312026	329480	311070	325794	325548	$6s^26p^57p^3P_1$
$6p_{1/2}7p_{3/2}(2)$			330479	312400	330351	312142	326655	327359	$6s^26p^57p^3D_2$
$6s_{1/2}5f_{5/2}(2)$					379141	268796	373775	373234	$6s6p^65f^3F_2$
$6s_{1/2}5f_{5/2}(3)$					380400	280101	375377	375584	$6s6p^65f^3F_3$
$6s_{1/2}5f_{7/2}(4)$					383146	290684	378968	379915	$6s6p^65f^3F_4$
$6s_{1/2}5f_{7/2}(3)$					393319	295245	387668	388226	$6s6p^65f^1F_3$
$6s_{1/2}6d_{3/2}(1)$					408353	348770	404219	406496	$6s6p^66d^3D_1$
$6s_{1/2}6d_{3/2}(2)$					410065	322551	406013	407733	$6s6p^66d^3D_2$
$6s_{1/2}6d_{5/2}(3)$					414519	340751	411416	412197	$6s6p^66d^3D_3$
$6s_{1/2}6d_{5/2}(2)$					420854	345816	418329	421187	$6s6p^66d^1D_2$
$6s_{1/2}7s_{1/2}(1)$					440017	363232	438376	439210	$6s6p^67s^3S_1$
$6s_{1/2}7s_{1/2}(0)$					445694	398690	444503	444525	$6s6p^67s^1S_0$
$6s_{1/2}7p_{1/2}(0)$					482789	434148	481499	482141	$6s6p^67p^3P_0$
$6s_{1/2}7p_{1/2}(1)$					483650	413518	482498	483198	$6s6p^67p^3P_1$
$6s_{1/2}7p_{3/2}(2)$					498021	405747	495728	496608	$6s6p^67p^3P_2$
$6s_{1/2}7p_{3/2}(1)$					500704	415279	498460	498666	$6s6p^67p^1P_1$

TABLE V: Energies (in cm^{-1}) of odd- and even-parity states in Ac^{3+} and U^{6+} calculated in the first-order and second-order RMBPT (RMBPT1 and RMBPT2, respectively). All values are given relative to the ground state energy.

Level	RMBPT1	RMBPT2	Level	RMBPT1	RMBPT2	Level	RMBPT1	RMBPT2
Rn-like Ac^{3+}								
$6p_{3/2}6d_{3/2}(0)$	142038	124368	$6p_{3/2}7p_{1/2}(1)$	196806	181316	$6p_{1/2}7p_{3/2}(1)$	269663	251835
$6p_{3/2}6d_{3/2}(1)$	145180	126163	$6p_{1/2}5f_{5/2}(2)$	198324	182388	$6p_{1/2}7p_{3/2}(2)$	270351	250787
$6p_{3/2}6d_{5/2}(2)$	150536	131374	$6p_{1/2}5f_{5/2}(3)$	208424	195064	$6s_{1/2}6d_{3/2}(1)$	365044	282364
$6p_{3/2}6d_{5/2}(4)$	150919	135347	$6p_{1/2}6d_{3/2}(2)$	208664	184565	$6s_{1/2}6d_{3/2}(2)$	366332	263154
$6p_{3/2}6d_{3/2}(3)$	150969	131709	$6p_{3/2}7p_{3/2}(1)$	208726	195394	$6s_{1/2}6d_{5/2}(3)$	369412	289445
$6p_{3/2}6d_{3/2}(2)$	155359	136135	$6p_{3/2}7p_{1/2}(2)$	210971	194549	$6s_{1/2}6d_{5/2}(2)$	373809	294984
$6p_{3/2}5f_{5/2}(1)$	158406	127266	$6p_{1/2}6d_{5/2}(2)$	214246	191942	$6s_{1/2}5f_{5/2}(2)$	375275	257234
$6p_{3/2}6d_{5/2}(3)$	160333	140529	$6p_{3/2}7p_{3/2}(0)$	214361	200320	$6s_{1/2}5f_{5/2}(3)$	376279	266253
$6p_{3/2}5f_{5/2}(2)$	163021	125988	$6p_{1/2}6d_{5/2}(3)$	215371	192305	$6s_{1/2}5f_{7/2}(4)$	378368	258153
$6p_{3/2}7s_{1/2}(2)$	163262	140653	$6p_{1/2}7s_{1/2}(0)$	222529	195812	$6s_{1/2}7s_{1/2}(1)$	378646	299676
$6p_{3/2}6d_{5/2}(1)$	164608	138801	$6p_{1/2}6d_{3/2}(1)$	223611	195756	$6s_{1/2}7s_{1/2}(0)$	383436	328361
$6p_{3/2}5f_{7/2}(5)$	166952	136050	$6p_{1/2}5f_{7/2}(3)$	223637	186587	$6s_{1/2}5f_{7/2}(3)$	386293	271861
$6p_{3/2}5f_{5/2}(4)$	167323	133173	$6p_{3/2}7p_{3/2}(3)$	226680	190132	$6s_{1/2}7p_{1/2}(0)$	414440	321913
$6p_{3/2}5f_{7/2}(3)$	169386	135646	$6p_{1/2}7s_{1/2}(1)$	228866	204119	$6s_{1/2}7p_{1/2}(1)$	415115	322430
$6p_{3/2}5f_{5/2}(3)$	172871	138259	$6p_{1/2}5f_{7/2}(4)$	229410	192294	$6s_{1/2}7p_{3/2}(2)$	425336	334106
$6p_{3/2}5f_{7/2}(4)$	177118	142705	$6p_{3/2}7p_{3/2}(2)$	234014	193320	$6s_{1/2}7p_{3/2}(1)$	427437	335361
$6p_{3/2}7s_{1/2}(1)$	177403	158475	$6p_{1/2}7p_{1/2}(1)$	258590	239611			
$6p_{3/2}5f_{7/2}(2)$	183095	150944	$6p_{1/2}7p_{1/2}(0)$	262964	244151			
Rn-like U^{6+}								
$6p_{3/2}5f_{5/2}(1)$	94998	55084	$6p_{3/2}6d_{5/2}(3)$	230270	207864	$6s_{1/2}5f_{7/2}(4)$	389533	289901
$6p_{3/2}5f_{5/2}(2)$	101988	57270	$6p_{3/2}6d_{5/2}(1)$	254864	233974	$6s_{1/2}5f_{7/2}(3)$	400241	300071
$6p_{3/2}5f_{5/2}(4)$	105362	64483	$6p_{3/2}7s_{1/2}(2)$	278438	252308	$6p_{1/2}7p_{1/2}(1)$	432078	410751
$6p_{3/2}5f_{7/2}(5)$	108529	70664	$6p_{3/2}7s_{1/2}(1)$	283002	257632	$6p_{1/2}7p_{1/2}(0)$	440258	414253
$6p_{3/2}5f_{7/2}(3)$	111012	68332	$6p_{1/2}6d_{3/2}(2)$	302991	276027	$6p_{1/2}7p_{3/2}(1)$	457683	437407
$6p_{3/2}5f_{5/2}(3)$	114963	73117	$6p_{1/2}6d_{5/2}(2)$	316064	291979	$6p_{1/2}7p_{3/2}(2)$	458964	438152
$6p_{3/2}5f_{7/2}(4)$	122022	79433	$6p_{1/2}6d_{5/2}(3)$	317833	292780	$6s_{1/2}6d_{3/2}(1)$	497589	420550
$6p_{3/2}5f_{7/2}(2)$	125875	86091	$6p_{3/2}7p_{1/2}(1)$	334373	316388	$6s_{1/2}6d_{3/2}(2)$	500122	406883
$6p_{1/2}5f_{5/2}(3)$	194364	151076	$6p_{3/2}7p_{1/2}(2)$	336877	318700	$6s_{1/2}6d_{5/2}(3)$	507805	426632
$6p_{3/2}6d_{3/2}(0)$	199190	179669	$6p_{1/2}6d_{3/2}(1)$	336883	307969	$6s_{1/2}6d_{5/2}(2)$	517101	431761
$6p_{1/2}5f_{7/2}(3)$	202138	158903	$6p_{3/2}7p_{3/2}(3)$	360871	345607	$6s_{1/2}7s_{1/2}(1)$	569975	490373
$6p_{3/2}6d_{3/2}(1)$	204827	180757	$6p_{3/2}7p_{3/2}(1)$	360906	345845	$6s_{1/2}7s_{1/2}(0)$	577075	426676
$6p_{1/2}5f_{7/2}(4)$	205279	161277	$6p_{3/2}7p_{3/2}(2)$	365284	348152	$6s_{1/2}7p_{1/2}(0)$	626479	540259
$6p_{1/2}5f_{5/2}(2)$	206954	159384	$6p_{3/2}7p_{3/2}(0)$	371487	351760	$6s_{1/2}7p_{1/2}(1)$	627635	540631
$6p_{3/2}6d_{3/2}(3)$	212406	189846	$6p_{1/2}7s_{1/2}(0)$	374193	344198	$6s_{1/2}7p_{3/2}(2)$	651916	569289
$6p_{3/2}6d_{5/2}(2)$	214136	191900	$6p_{1/2}7s_{1/2}(1)$	375981	345896	$6s_{1/2}7p_{3/2}(1)$	655499	570646
$6p_{3/2}6d_{5/2}(4)$	216216	198106	$6s_{1/2}5f_{5/2}(2)$	383261	284422			
$6p_{3/2}6d_{3/2}(2)$	221462	200736	$6s_{1/2}5f_{5/2}(3)$	384876	285957			

that the mixing coefficients are equal to 0.5–0.8. Therefore, we still use the jj designations in Table III. As we discussed above, the correlations corrections are large and have to be included in order to obtain accurate energy values for Rn-like Th^{4+} ion. The second-order Coulomb contribution $E^{(2)}$ gives about 7-11% to the total values of the $6p_j5f_{j'}(2)$ energies and about 5-7% in the case of the $6p_j6d_{j'}(1)$ energies. Therefore, we expect energies to be accurate to few a 1000 cm^{-1} for the $6p_j5f_{j'}$ and $6p_j6d_{j'}$ states. Better accuracy is expected for higher states.

In Table IV, we compare our RMBPT results evaluated with different number of even and parity configurations to establish that the configuration space was chosen to be sufficiently large. We start our calculations with $6p5f$ even configurations and $6p6d$ odd configurations. This set of configurations is labelled set I. We note that in the RMBPT, energies are evaluated relative to the ground state $6s^26p^6$ configuration, so all states are of the hole-particle type. In our designations, the first nl indicates the hole state, and the second nl indicates the particle state. In set II, $6p7p$ and $6p7s$ configurations are added, and in set III $6snl$ configurations are added. Therefore, our largest set, III, contains $6p5f+6p7p+6s6d+6s7s$ even and $6p6d+6p7s+6s5f+6s7p$ odd configurations. To show the size of the correlation contribution, we also included the data evaluated in the first-order approximation in columns labelled ‘RMBPT1’ in Table IV. These data are obtained as a sum of the $E^{(0)}$, $E^{(1)}$, and $B^{(1)}$ values (see explanation of Table III).

Our final second-order values are listed in columns ‘RMBPT2’. The ratios of values in the RMBPT1 and RMBPT2 columns range from 1.2 to 1.6. We also include results obtained in relativistic Hartree-Fock approximation (COWAN code) [29] in the same table. Values listed in ‘COWAN’ column are obtained including the following configurations: $6s^26p^6 + 6s^26p^55f + 6s^26p^57p + 6s6p^66d + 6s6p^67s$ and $6s^26p^56d + 6s^26p^57s + 6s6p^65f + 6s6p^67p$. Therefore, the set of configurations is equivalent to out final set III. We also carried out additional calculations energies of Th^{4+} odd- and even-parity states relative to the ground state evaluated by COWAN code using the large set of configurations: $\text{IV} = 6pn_1f + 6pn_2p + 6sn_3d + 6sn_2s$, $6pn_3d + 6pn_2s + 6sn_1f + 6sn_2p$ with $n_1 = 5 - 9$, $n_2 = 7 - 9$, and $n_3 = 6 - 9$. Results of our calculations are incorporated in Table III in additional column ‘COWAN2’. We find very small differences, 0.003% - 0.5%, between results displayed in columns ‘COWAN1’ and ‘COWAN2’. Slightly larger differences, about 1%, are observed for the energies of the $6s^26p^56d\ ^1P_1$ and $6s^26p^57p\ ^3D_1$ levels. The scaling of electrostatic integrals in the Cowan code allows to correct for correlation effects. In many systems, it leads to good agreement with experimental energies. We used the same scaling factor (0.85) for all electrostatic integrals. The 0.85 scaling factor was introduced for the first time by Fawcett et al. [30]. Authors explained that the 0.85 factor was found empirically to obtain results in good

agreement with experiment. Later, the 0.85 factor was used in other publications. We note that this factor may not produce accurate results in all systems.

The differences in the RMBPT1 values with different number of configurations (column 2, 4, and 6 in Table IV) are very small (about 0.1-0.8%). This means that configuration interaction (CI) does not significantly contribute in the first order RMBPT. The differences in the RMBPT2 values with different number of configurations (column 3, 5, and 7 in Table IV) are much larger (about 7-20%), indicating that including CI contribution leads to additional correlation correction.

As expected, the second-order correction (the difference between the RMBPT2 and RMBPT1 values) depends on number of considered configurations. In the first case ($I = 6p5f, 6p6d$) the differences in results given in columns 2 and 3 are about 1-11%, while the differences in results given in columns ‘4’ and ‘5’, ‘6’ and ‘7’ are about 9-28%. The differences between RMBPT2 $6p5f$ and $6p6d$ values calculated with sets I and II are large for most of the states, indicating that set I that includes mixing only within these configurations is insufficient. The differences between sets II and III for $6p5f$ and $6p6d$ configurations are small for most of the states.

The COWAN results are in a better agreement with RMBPT1 values (about 1-5%). The differences of the COWAN results with our final RMBPT2 values is about 5-25%. We note that second-order RMBPT has a general tendency to overestimate the correlation correction. Full all-order treatment, that may be carried out within the framework of the coupled-cluster approach, is needed for the improvement of accuracy. It may be possible in the future to implement hybrid configuration interaction + linearized coupled-cluster method [31] for hole-particle states. This work provides a starting point for further development of theoretical methods for such highly correlated and relativistic system.

Our RMBPT values presented in Table IV are first *ab initio* values for the levels energy in Th^{4+} . To the best of our knowledge, there are no experimental energy values for this ion.

In Table V, we list energies of odd- and even-parity configurations in Rn-like Ac^{3+} and U^{6+} calculated in the first-order and second-order RMBPT (RMBPT1 and RMBPT2, respectively). All values are given relative to the ground state energy. The RMBPT values are evaluated including the following configurations: $6p5f+6p7p+6s6d+6s7s$ and $6p6d+6p7s+6s5f+6s7p$. This set of states was used to evaluate energies in Rn-like Th^{4+} given in columns 6 and 7 of Table IV (set III). The major difference of the level distribution in Rn-like Ac^{3+} and U^{6+} is in the placement of the metastable states relative to the ground state. In Rn-like U^{6+} , the first eleven levels are metastable, while in Rn-like Ac^{3+} , there is only one metastable level before the odd-parity level with $J = 1$. It should be noted that there are eight first metastable states in the case of Rn-like Th^{4+} . Importance of the existence of the low-lying metastable states was discussed

TABLE VI: E1, E2, E3, M1, M2, and M3 uncoupled reduced matrix elements in length L form for transitions from $av(J)$ states with $J=1, 2$, and 3 into the ground state in Th^{4+} .

$av(J)$	$Z^{(1)}$	$Z^{(2)}$	$B^{(2)}$	$P^{(\text{deriv})}$
E1 uncoupled reduced matrix elements				
$6p_{3/2}6d_{3/2}(1)$	-0.9643	0.2442	-0.0011	-0.9643
$6p_{3/2}6d_{5/2}(1)$	-2.8448	0.6978	-0.0040	-2.8444
$6p_{1/2}6d_{3/2}(1)$	-1.8154	0.6314	-0.0040	-1.8152
$6s_{1/2}7p_{1/2}(1)$	-0.0928	0.1739	0.0010	-0.0926
$6s_{1/2}7p_{3/2}(1)$	0.0611	-0.2119	0.0004	0.0612
E2 uncoupled reduced matrix elements				
$6p_{3/2}5f_{5/2}(2)$	-1.9189	0.1946	-0.0089	-3.8378
$6p_{3/2}5f_{7/2}(2)$	4.8084	-0.5097	0.0185	9.6164
$6p_{1/2}5f_{5/2}(2)$	-3.2324	0.3907	-0.0159	-6.4644
E3 uncoupled reduced matrix elements				
$6p_{3/2}6d_{3/2}(3)$	12.1130	-0.4005	0.0542	36.4897
$6p_{3/2}6d_{5/2}(3)$	10.0607	-0.0287	0.0428	30.0992
$6p_{1/2}6d_{5/2}(3)$	-8.5284	-0.5985	-0.0507	-25.4016
M1 uncoupled reduced matrix elements				
$6p_{3/2}7p_{1/2}(1)$	-0.1333	-0.0200	0.0009	-0.1332
$6p_{1/2}7p_{3/2}(1)$	-0.1001	-0.0229	0.0005	-0.1001
M2 uncoupled reduced matrix elements				
$6p_{3/2}6d_{5/2}(2)$	-12.5437	-0.9870	-0.0177	-25.0863
$6p_{3/2}7s_{1/2}(2)$	-4.3993	-0.4262	-0.0061	-8.7979
$6p_{1/2}6d_{3/2}(2)$	-1.4060	0.0526	-0.0031	-2.8122
$6p_{1/2}6d_{5/2}(2)$	-4.4641	-0.8952	-0.0116	-8.9274
M3 uncoupled reduced matrix elements				
$6p_{3/2}5f_{7/2}(3)$	27.9342	-2.6561	0.1081	83.8009
$6p_{1/2}5f_{7/2}(3)$	14.4537	-1.7104	0.0625	43.3598
$6p_{3/2}7p_{3/2}(3)$	-13.6545	-2.6745	-0.0329	-40.9599
$6s_{1/2}6d_{5/2}(3)$	18.0124	-4.3662	0.0450	54.0327

in the recent experimental work by Hanni *et al.* [2].

IV. MULTIPOLE TRANSITIONS FROM EXCITED STATES INTO THE GROUND STATE

The first 52 excited states in Rn-like Ac, Th, and U ions are $6s^26p^5nl$ and $6s6p^6n'l'$ states. There are 45 metastable levels with $J = 0, 2 - 5$, but only seven $J = 1$ levels that can decay to the ground state via the electric-dipole transitions. Below, we consider all possible multipole (E1, E2, E3, M1, M2, and M3) transitions from the $6s^26p^5nl$ and $6s6p^6n'l'$ states to the $6s^26p^6$ ground state in Rn-like Ac, Th, and U ions.

We calculate the electric-dipole (E1) matrix elements for the transitions between the seven odd-parity $6p_j6d_{j'}(1)$, $6p_j7s(1)$, and $6s7p_j(1)$ excited states and the ground state, magnetic-quadrupole (M2) matrix elements between the 7 odd-parity $6p_j6d_{j'}(2)$, $6p_j7s(2)$, $6s5f_j(2)$, and $6s7p_{j'}(2)$ excited states and the ground state, and electric-octupole (E3) matrix elements between the 5 odd-parity $6p_j6d_{j'}(3)$ and $6s5f_j(3)$ excited states and the ground state.

The magnetic-dipole (M1) matrix elements are calculated for the transitions between the seven even-parity $6p_j5f_{j'}(1)$, $6p_j7p_{j'}(1)$, $6s6d_j(1)$, and $6s7s(1)$ excited

states and the ground state, electric-quadrupole (E2) matrix elements between the 8 even-parity $6p_j5f_{j'}(2)$, $6p_j7p_{j'}(2)$, and $6s6d_j(2)$ excited states and the ground state, and magnetic-octupole (M3) matrix elements between the 6 even-parity $6p_j5f_{j'}(3)$, $6p_j7p_{j'}(3)$, and $6s6d_{j'}(3)$ excited states and the ground state.

Analytical expressions in the first and the second order RMBPT are given by Eqs. (2.12)-(2.17) of Ref. [13] for the E1 matrix elements and in Refs. [15, 17, 18] for the M1, M2, M3, E2, and E3 matrix elements.

We refer to the first- and second-order Coulomb corrections and second-order Breit-Coulomb corrections to reduced multipole matrix elements as $Z^{(1)}$, $Z^{(2)}$, and $B^{(2)}$, respectively, throughout the text. In Table VI, we list values of *uncoupled* first- and second-order E1, E2, E3, M1, M2, and M3 matrix elements $Z^{(1)}$, $Z^{(2)}$, $B^{(2)}$, together with derivative terms $P^{(\text{deriv})}$, for Th^{4+} (see Refs. [15, 17, 18] for detail). Importance of correlation contribution is evident from this table; the ratio of the second and first orders $Z^{(2)}/Z^{(1)}$ is very large for E1 transitions (25–35% for the $6p_j6d_{j'}(1)$ states and a factor of 2–3 for the $6s7p_j(1)$ states). However, the ratio of the second and first orders $Z^{(2)}/Z^{(1)}$ is much smaller for the E2 and E3 transitions (10% and 5%, respectively). The $Z^{(2)}/Z^{(1)}$ ratio for the M1 magnetic dipole transitions is about 15–20% for the two $6p_j7p_{j'}(1)$ states. We note that we do not list M1 transitions with almost zero value of the $Z^{(1)}$ matrix elements for the $6p_{3/2}5f_{5/2}(1)$, $6s6d_{3/2}(1)$, $6s7s(1)$ states. The second-order $Z^{(2)}$ contributions for these states are comparable with the $Z^{(2)}$ contributions for the $6p_j7p_{j'}(1)$ states listed in Table VI. The ratio of the second and first orders $Z^{(2)}/Z^{(1)}$ for the M2 and M3 transitions is about 10–20%.

The E1, E2, E3, M2, M3, and M3 transition probabilities A_r (s^{-1}) for the transitions between the ground state and $6p_jnl_{j'}(J)$ and $6snl_j(J)$ states are obtained in terms of line strengths S (a.u.) and energies E (a.u.) as

$$A(Ek) = \frac{C^{(k)} [E]^{2k+1}}{(2J+1)} S(Ek), \quad (2)$$

$$C^{(1)} = 2.14200 \times 10^{10},$$

$$C^{(2)} = 5.70322 \times 10^4,$$

$$C^{(3)} = 7.71311 \times 10^{-2},$$

$$A(Mk) = \frac{D^{(k)} [E]^{2k+1}}{(2J+1)} S(Mk), \quad (3)$$

$$D^{(1)} = 2.85161 \times 10^5,$$

$$D^{(2)} = 7.59260 \times 10^{-1},$$

$$D^{(3)} = 1.02683 \times 10^{-6}.$$

The line strengths $S(E1)$, $S(E2)$, $S(E1)$, $S(E3)$, $S(M1)$, $S(M2)$, and $S(M3)$ are obtained as squares of the corresponding *coupled* E1, E2, E3, M2, M3, and M3 matrix elements. The E1, E2, E3, M2, M3, M2, and M3 *coupled* matrix elements are evaluated using an intermediate-coupling scheme (see Ref. [13] for detail). Results of our calculations are given in Tables VII and

TABLE VII: Wavelengths (λ in Å), line strengths (S in a.u.), and radiative rates (A_r in s^{-1}) for the electric-multipole (E1, E2, and E3) and magnetic-multipole (M1, M2, and M3) transitions from $6pnl$ and $6snl$ states to the ground state in Rn-like Th^{4+} . The wavelengths, line strengths, and radiative rates calculated in the first-order RMBPT are listed in columns labeled ‘(a)’. The second-order RMBPT results are listed in columns labeled ‘(b)’. Numbers in brackets represent powers of ten.

$6ln'l'$		Wavelength		Line strength		Transition rate		$6ln'l'$		Wavelength		Line strength		Transition rate	
		(a)	(b)	(a)	(b)	(a)	(b)			(a)	(b)	(a)	(b)	(a)	(b)
M3	$6p_{3/2}5f_{7/2}$	650.8	873.9	6.1[2]	1.9[3]	7.3[-6]	2.9[-6]	E3	$6p_{1/2}6d_{5/2}$	401.9	443.3	8.7[1]	2.9[2]	2.3[0]	3.8[0]
M3	$6p_{3/2}5f_{5/2}$	635.7	850.4	3.0[2]	8.6[2]	4.3[-6]	1.6[-6]	M3	$6p_{3/2}7p_{3/2}$	388.6	410.6	2.1[2]	3.7[2]	9.5[-5]	1.1[-4]
E1	$6p_{3/2}6d_{3/2}$	605.3	701.2	5.8[-3]	6.7[-3]	1.8[7]	1.3[7]	M1	$6p_{3/2}7p_{3/2}$	388.3	410.3	1.1[-3]	1.9[-3]	1.6[2]	2.4[2]
E3	$6p_{3/2}6d_{5/2}$	543.5	612.7	1.3[2]	1.6[2]	4.3[-1]	2.2[-1]	E2	$6p_{3/2}7p_{3/2}$	383.7	407.7	2.3[0]	1.4[0]	6.2[4]	2.9[4]
M2	$6p_{3/2}7s_{1/2}$	500.4	566.9	5.9[0]	3.6[0]	5.6[-1]	1.8[-1]	E1	$6p_{1/2}6d_{3/2}$	377.1	423.1	7.6[0]	3.2[0]	9.6[10]	2.8[10]
E1	$6p_{3/2}7s_{1/2}$	484.6	543.2	5.5[0]	4.0[0]	3.3[10]	1.7[10]	E1	$6p_{1/2}7s_{1/2}$	367.7	409.1	2.7[-1]	3.4[-1]	3.6[9]	3.4[9]
M3	$6p_{1/2}5f_{5/2}$	462.9	572.4	2.0[1]	3.7[1]	2.6[-6]	1.1[-6]	M1	$6p_{1/2}7p_{3/2}$	303.5	321.5	1.1[-2]	2.0[-2]	3.6[3]	5.4[3]
M2	$6p_{1/2}6d_{3/2}$	417.6	466.2	5.2[0]	2.8[0]	1.2[0]	3.8[-1]	E2	$6p_{1/2}7p_{3/2}$	302.7	320.4	9.3[-1]	6.2[-1]	8.2[4]	4.1[4]
M1	$6p_{3/2}7p_{1/2}$	414.6	444.2	1.6[-2]	1.9[-2]	2.0[3]	1.9[3]	M2	$6s_{1/2}5f_{5/2}$	263.8	372.0	3.5[-3]	9.0[-3]	8.2[-3]	3.8[-3]
E2	$6p_{3/2}7p_{1/2}$	411.3	440.2	5.8[0]	3.1[0]	1.1[5]	4.3[4]	E2	$6s_{1/2}6d_{3/2}$	243.9	310.0	1.0[0]	7.5[-1]	2.6[5]	5.8[4]
M2	$6p_{1/2}6d_{5/2}$	404.3	446.0	8.5[0]	6.6[0]	2.4[0]	1.1[0]	M2	$6s_{1/2}7p_{3/2}$	200.8	246.5	2.3[-1]	1.9[-1]	2.0[0]	6.3[-1]

TABLE VIII: Wavelengths (λ in Å), line strengths (S in a.u.), and radiative rates (A_r in s^{-1}) for the electric-multipole (E1, E2, and E3) and magnetic-multipole (M1, M2, and M3) transitions from $6pnl$ and $6snl$ states to the ground state in Rn-like Ac^{3+} and U^{6+} ions. The wavelengths, line strengths, and radiative rates calculated in the first-order RMBPT are listed in columns labeled ‘(a)’. The second-order RMBPT results are listed in columns labeled ‘(b)’. Numbers in brackets represent powers of ten.

$6ln'l'(J)$		Wav. λ		Line strength		Transition rate		$6ln'l'(J)$		Wav. λ		Line strength		Transition rate	
		(a)	(b)	(a)	(b)	(a)	(b)			(a)	(b)	(a)	(b)	(a)	(b)
Radon-like Actinium								Radon-like Uranium							
E1	$6p_{3/2}6d_{3/2}(1)$	689	793	3.1[-3]	4.3[-2]	6.4[6]	5.8[7]	M1	$6p_{3/2}5f_{5/2}(1)$	1053	815	1.8[-25]	8.2[-15]	3.2[-9]	1.4[-4]
M2	$6p_{3/2}6d_{5/2}(2)$	664	761	1.6[4]	5.1[3]	2.9[0]	8.3[-1]	E2	$6p_{3/2}5f_{5/2}(2)$	981	746	1.6[-1]	3.9[-2]	4.0[1]	5.3[-1]
E3	$6p_{3/2}6d_{3/2}(3)$	662	759	1.8[2]	5.9[3]	1.4[-1]	1.8[0]	M3	$6p_{3/2}5f_{7/2}(3)$	901	464	1.3[4]	4.9[4]	1.4[-7]	9.2[-9]
M2	$6p_{3/2}6d_{3/2}(2)$	644	735	7.2[1]	3.8[1]	1.9[0]	5.3[-1]	E3	$6p_{3/2}6d_{5/2}(3)$	434	481	6.1[1]	5.9[1]	9.4[-1]	4.5[-1]
E1	$6p_{3/2}6d_{5/2}(1)$	608	721	4.1[-1]	6.5[-1]	1.2[9]	1.2[9]	E1	$6p_{3/2}6d_{5/2}(1)$	392	427	3.5[0]	1.8[0]	3.9[10]	1.6[10]
E1	$6p_{3/2}7s_{1/2}(1)$	564	631	6.4[0]	6.6[0]	2.4[10]	1.8[10]	M2	$6p_{3/2}7s_{1/2}(2)$	359	396	1.1[1]	6.3[0]	5.4[0]	1.9[0]
M1	$6p_{3/2}7p_{1/2}(1)$	508	552	1.3[-2]	2.1[-2]	9.0[2]	1.1[3]	E1	$6p_{3/2}7s_{1/2}(1)$	353	388	1.4[0]	1.4[0]	2.1[10]	1.6[10]
E2	$6p_{1/2}5f_{5/2}(2)$	504	548	7.2[0]	3.5[0]	5.0[4]	1.6[4]	M2	$6p_{1/2}6d_{3/2}(2)$	330	362	4.4[0]	3.4[0]	3.4[0]	1.6[0]
M3	$6p_{1/2}5f_{5/2}(3)$	480	513	2.4[2]	4.7[2]	2.4[-5]	3.0[-5]	E3	$6p_{1/2}6d_{5/2}(3)$	315	342	4.2[1]	8.8[1]	6.2[0]	7.3[0]
M2	$6p_{1/2}6d_{3/2}(2)$	480	542	5.4[0]	2.9[0]	6.4[-1]	1.9[-1]	M1	$6p_{3/2}7p_{1/2}(1)$	299	316	2.0[-2]	2.5[-2]	6.8[3]	7.1[3]
M1	$6p_{3/2}7p_{3/2}(1)$	479	512	1.0[-3]	1.6[-3]	8.3[1]	1.0[2]	E2	$6p_{3/2}7p_{1/2}(2)$	297	314	4.0[0]	2.4[0]	3.9[5]	1.8[5]
E2	$6p_{3/2}7p_{1/2}(2)$	474	514	3.4[0]	1.7[0]	3.2[4]	1.1[4]	E1	$6p_{1/2}6d_{3/2}(1)$	297	325	6.6[0]	3.4[0]	1.7[11]	6.7[10]
E1	$6p_{1/2}6d_{3/2}(1)$	447	511	1.4[-1]	9.9[-2]	1.1[9]	5.0[8]	M3	$6p_{3/2}7p_{3/2}(3)$	277	289	1.4[2]	2.4[2]	6.6[-4]	8.5[-4]
M3	$6p_{1/2}5f_{7/2}(3)$	447	536	2.8[1]	6.9[1]	4.7[-6]	3.2[-6]	M1	$6p_{3/2}7p_{3/2}(1)$	277	289	9.8[-4]	1.1[-3]	4.2[2]	4.0[2]
M3	$6p_{3/2}7p_{3/2}(3)$	441	526	2.0[2]	3.7[2]	3.6[-5]	2.0[-5]	E2	$6p_{3/2}7p_{3/2}(2)$	274	287	1.9[0]	1.3[0]	2.8[5]	1.5[5]
M1	$6p_{1/2}7p_{1/2}(1)$	387	417	3.8[-7]	8.1[-7]	5.9[-2]	1.0[-1]	E1	$6p_{1/2}7s_{1/2}(1)$	266	289	1.8[-1]	2.6[-1]	6.6[9]	7.3[9]
M1	$6p_{1/2}7p_{3/2}(1)$	371	397	9.3[-3]	2.3[-2]	1.6[3]	3.4[3]	M1	$6p_{1/2}7p_{1/2}(1)$	231	244	8.9[-7]	1.8[-6]	6.5[-1]	1.1[0]
E2	$6p_{1/2}7p_{3/2}(2)$	370	399	6.4[-1]	4.3[-1]	2.1[4]	9.5[3]	M1	$6p_{1/2}7p_{3/2}(1)$	219	229	1.4[-2]	8.8[-3]	1.2[4]	6.6[3]

VIII, where we present wavelengths (in Å), line strengths (S), and radiative rates (A_r) for the electric-multipole (E1, E2, and E3) and magnetic-multipole (M1, M2, and M3) transitions from $6pnl$ and $6snl$ states to the ground state in Rn-like Th^{4+} , Ac^{3+} , and U^{6+} ions. Wavelengths, line strengths and radiative rates are calculated in the first-order and the second-order RMBPT. As expected, we find substantial differences between first-order and second-order MBPT results, given in columns labelled “a” and “b”. These differences give the value of the second-order correlation correction. We discuss results for Th^{4+} ion first. The ratios of transition rates A_r^{E1}/A_r^{E2}

and A_r^{E2}/A_r^{M1} are equal to 10^3 – 10^6 and 10 – 10^2 , respectively. M3 transitions are the weakest transitions, as expected (10^{-6} – 10^{-3} s^{-1}). The values of the transition rates change inside the of complex states with fixed J by three to four orders of magnitude. As a result, the values of transition rates given in Table VIII vary from 10^{-6} s^{-1} for the M3 transitions up to 10^{10} s^{-1} for the E1 transitions.

The difference between results in Rn-like Ac^{3+} (left columns) and U^{6+} ions (right columns) is not only in the values of wavelengths, line strengths, and radiative rates but in the order of transitions. The study of the order

TABLE IX: Multipole ground state polarizabilities α^{Ek} , and parameters β_D , and γ_D , calculated using DF and RPA approximation (a.u) in Rn-like ions with $Z = 89, 90$, and 92 . Experimental values from [4] are given in line “Expt”.

Z		α^{E1}	α^{E2}	α^{E3}	β_D	γ_D
89	RPA	10.08	42.39	344.1	4.419	1.999
89	DF	11.42	35.70	261.1	4.668	2.056
90	RPA	7.750	28.82	192.5	2.971	1.177
90	Expt.	7.720(7)	21.5(3.9)			
90	DF	8.957	24.54	148.5	3.209	1.240
92	RPA	5.029	15.97	74.06	1.554	0.498
92	DF	5.977	13.44	58.68	1.729	0.541

of first five energy levels given in Table V shows that the order of possible strongest decay channels is E1, M2, E3 for the Ac^{3+} ion and M1, E2, and M3 for the U^{6+} ion (other two levels can not decay to the ground state via any of the 6 transitions up to $k = 3$).

V. GROUND STATE MULTIPOLE POLARIZABILITIES IN RN-LIKE ACTINIUM, THORIUM, AND URANIUM IONS

The ground-state multipole polarizabilities are evaluated here in the DHF and random-phase approximation (RPA) [32] using the sum-over-state approach:

$$\alpha^{Ek} = \frac{2}{2k+1} \sum_{n,a} \frac{|\langle nl_j \| r^k C_{kq} \| al'_{j'} \rangle|^2}{E_{nl_j} - E_{al'_{j'}}}, \quad (4)$$

where $C_{kq}(\hat{r})$ is a normalized spherical harmonic and where $al'_{j'}$ include all core states in Rn-like ions from the $1s_{1/2}$ up to $6p_j$ states, nl_j includes all valence states above the core, and $k = 1, 2$, and 3 , for dipole, quadrupole, and octupole polarizabilities, respectively [33]. The α^{E1} and α^{E2} are dipole and quadrupole polarizabilities labelled α_D and α_Q in [4]. We also calculated parameters β_D and γ_D defined in [4] as

$$\beta_D = \frac{1}{3} \sum_{n,a} \frac{|\langle nl_j \| D \| al'_{j'} \rangle|^2}{(E_{nl_j} - E_{al'_{j'}})^2}, \quad (5)$$

$$\gamma_D = \frac{1}{6} \sum_{n,a} \frac{|\langle nl_j \| D \| al'_{j'} \rangle|^2}{(E_{nl_j} - E_{al'_{j'}})^3}, \quad (6)$$

where D is the dipole operator. All sums are carried out with the finite basis set described above, making the sums finite (with $n_{max} = 50$). The reduced matrix elements in the above sum are evaluated using both DF and RPA approximations.

In Table IX, we give ground state multipole polarizabilities α^{Ek} , and parameters β_D , and γ_D calculated using DF and RPA approximation in Rn-like ions with $Z =$

TABLE X: Comparisons of the RPA and coupled-cluster (CC) calculations for the ground state dipole polarizabilities of closed-shell systems. The coupled-cluster data are from Refs. [35–37]. Last three rows give values from the present work.

Ion	DF	RPA	CC	Dif.% RPA vs. DF	Dif.% RPA vs. CC
Xe	26.87	26.97	27.06 [37]	0.4%	-0.3%
Ba ²⁺	11.70	10.61	10.491 [35]	-10.3%	1.1%
Rn	34.42	34.99	33.18 [37]	1.6%	5.2%
Fr ⁺	21.56	20.40	20.4(2)[36]	-5.7%	consistent
Ra ²⁺	15.19	13.79	13.361 [35]	-10.1%	3.1%
Ac ³⁺	11.42	10.08		-13.3%	
Th ⁴⁺	8.957	7.750		-15.6%	
U ⁶⁺	5.977	5.029		-18.9%	

89, 90, and 92. The correlation contributions (difference between the RPA and DF values) are about 15%. RPA is expected to give results for the dipole ground state polarizability that are accurate to about 5% based on the comparison of the RPA values with more accurate coupled-cluster calculations [34]. We discuss this analysis in the next section. Unfortunately, such analysis could not be carried out for the quadrupole polarizabilities. Our RPA E1 polarizability value for Th^{4+} is in excellent agreement with experimental result of [4]. Our DF value for the quadrupole polarizability is consistent with the experimental results, while RPA value is somewhat larger.

VI. UNCERTAINTY ESTIMATES AND CONCLUSION

Comparison of the RMBPT1 and RMBPT2 energies and transition rates presented in Tables IV, V, VII, and VIII gives us the first rough estimates of the uncertainties of our results as it gives the second-order correlation correction. The differences in the RMBPT1 and RMBPT2 values are about 8% for energies, about 50% for the largest values of transition rates A_r , and a factor of 2 for the smallest values of A_r . The third-order corrections for the energies and transition rates were evaluated for monovalent atomic systems (see, for example, Refs. [38–40]). The differences between the RMBPT3 and RMBPT2 energies were about 2-3% for Ba II, Sr II, and Hg II ions. In addition, we evaluated the energies and wavelengths in Rn-like Ac, Th, and U ions using the COWAN codes. These results are between our RMBPT1 and RMBPT2 values (see Table IV).

To check the accuracy of our RPA results for the electric-dipole polarizability, we compare the RPA values for other relevant heavy systems with theoretical results obtained by more sophisticated coupled-cluster approaches in Table X. The calculated static polarizabilities of the doubly charged Ba and Ra at the nonrelativis-

tic, relativistic Douglas-Kroll and Dirac-Coulomb level of theory were presented by Lim *et al.* in Refs. [35]. Recommended dipole polarizabilities of the positively charged Fr, calculated from relativistic CCSD(T) including spin-orbit contributions were given by Lim *et al.* in Refs. [36]. The relativistic effects for static polarizabilities α of rare gas atoms (Xe and Rn) were investigated theoretically with the third-order Douglas-Kroll method [37]. In columns “RPA” and “CC” of Table X, we present results from Refs. [35–37]. In columns “RPA vs. DF” and “RPA vs. CC”, we give the difference of the corresponding values in percent, relative to the RPA values. From this comparison, we can expect the RPA value for the dipole polarizability to be accurate to about 5%. The difference between DF and RPA for Rn-like Ac^{3+} , Th^{4+} , and U^{6+} increases from 13.3% for Ac^{3+} up to 18.9% for U^{6+} , demonstrating the importance of relativistic effects in the calculation of ground state polarizability.

We have presented a systematic second-order relativistic MBPT study of excitation energies, reduced matrix elements, and transition rates for multipole transitions in Rn-like Ac^{3+} , Th^{4+} , and U^{6+} ions. Our multipole matrix elements include correlation corrections from Coulomb

and Breit interactions. We determine energies of the $6p_j5f_{j'}(J)$, $6p_j6d_{j'}(J)$, $6p_j7s(J)$, $6p_j7p_{j'}(J)$, $6s5f_j(J)$, $6s6d_j(J)$, $6s7s(J)$, and $6s7p_j(J)$ excited states. Wavelengths, line strengths, and transition rates were evaluated for the 40 multipole matrix elements for transitions from excited states into ground state. Ground state multipole polarizabilities in Rn-like actinium, thorium, and uranium ions were calculated in DF and RPA approximation. Our RMBPT results presented in this paper are the first *ab initio* calculations of energies, and transition rates in Ac^{3+} , Th^{4+} , and U^{6+} ions. This work provides a starting point for further development of theoretical methods for such highly correlated and relativistic system.

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