

Nuclear clock based on the Th v ion

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We propose that a nuclear clock based on the Th v ion can surpass the accuracy of clocks built with other thorium ions. The Th⁴⁺ ion has a rigid closed-shell core with zero total electron angular momentum, suppressing frequency shifts from black-body radiation and stray external fields that act mainly on electrons. We calculate the energy shift of the nuclear clock transition frequency in ²²⁹Th due to the Coulomb field of atomic electrons and find a relative frequency difference of 2.8×10^{-7} between Th IV and Th v, 12 orders of magnitude larger than the projected 10^{-19} fractional uncertainty of a nuclear clock. We also perform calculations for Th v energy levels, ionization potential, static polarizability, quadratic Zeeman shift, and the black-body radiation shift of the nuclear line. Additionally, we determine the nuclear transition frequencies in two thorium ions and a neutral atom: $\nu_N = 2, 020, 406.964(70)$ GHz in Th III, $\nu_N = 2, 020, 408.264(100)$ GHz in Th II, and $\nu_N = 2, 020, 408.364(100)$ GHz in Th I.

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I. INTRODUCTION

The nucleus of the ²²⁹Th isotope uniquely possesses a very low-energy excited state with spin and parity $I^P = 3/2^+$, connected to the ground state $I^P = 5/2^+$ by a magnetic dipole (M1) transition (see, e.g. Refs. [1,2] and references therein). In the Nilsson scheme these states correspond to a valence neutron on the orbitals $3/2[6, 3, 1]$ and $5/2[6, 3, 3]$. The half-life of the nuclear excited state in Th IV is measured to be $T_{1/2} = 1400^{+600}_{-300}$ s [3]. It is practically not affected by the electronic bridge mechanism [4] and agrees with the values obtained in the solid-state experiments [5–13] after introducing the correction for the enhanced spontaneous decay in the dielectric medium.

The measurement of the energy of this nuclear clock transition in ²²⁹Th has been an ongoing effort for many years [14–16]. Recently, a very high accuracy was obtained in Refs. [3,5–7,17]. The latest, most precise measurement, gives the value $\nu_N = 2, 020, 407, 384, 335(2)$ kHz ($67\,393\text{ cm}^{-1}$) for ²²⁹Th dopant ions embedded in a calcium fluoride crystal [7]. A still higher accuracy is expected for a nuclear clock with trapped ions [18,19] because of the absence of the crystal electric and magnetic fields and because of the ultralow temperatures that are attainable with laser cooling.

This low-energy nuclear transition attracted many researchers planning to build a nuclear clock of exceptionally high accuracy see, e.g., Refs. [18,20]. The relative uncertainty was expected to reach 10^{-19} [19]. In addition, there

were strong arguments that this nuclear clock would be very sensitive to physics beyond the standard model, including space-time variation of the fundamental constants, violation of the Lorentz invariance and the Einstein equivalence principle, and the search for scalar and axion dark matter fields [21–30]. There are plans to use trapped Th ions [19,31,32] and solid-state Th nuclear clocks [33–35]. It was shown in Ref. [36] that in all these systems the frequency of the nuclear clock will be different. This is due to the Coulomb interaction of atomic electrons with the nucleus, leading to the significant electronic shift of the nuclear transition frequency. Additionally, there is a frequency shift due to magnetic interaction between atomic electrons and the nucleus. Specifically, the electronic shifts in Th IV, Th III, Th II ions, and the neutral Th atom were calculated in Ref. [36] (in the present paper we calculate these shifts with a different method which provides a higher accuracy). Our calculations provide the conversion needed to predict the nuclear transition frequency in one ion charge state when it was measured in another. There may also be a shift due to the interaction with electric and magnetic fields in the solid or with external fields for the ion trap.

In this paper we consider a nuclear clock based on the Th v ion. This ion has zero electron angular momentum in the ground state, effectively eliminating magnetic interaction effects for the electron shell, including the hyperfine structure in the nuclear clock transition. The coupling of electron and nuclear angular momenta into a hyperfine structure component in other ions could produce an entanglement between electron and nuclear variables. There is no such entanglement in the Th v ion. Since electrons interact with black-body radiation and stray fields many orders of magnitude stronger than the nucleus, eliminating the effects of this interaction on the nucleus helps to improve the stability and accuracy of the nuclear clock (see below).

Since Th v does not possess an optical electronic resonance in the wavelength range of readily available lasers, the readout of the nuclear state can be performed via a cotrapped quantum

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logic ion that will also provide sympathetic laser cooling [37]. Either Ca ii or Sr ii can be used as a logic ion. These ions are routinely laser-cooled in many laboratories around the world (see Ref. [38] and references therein). The charge-to-mass ratios q/m are relatively close for these ions: 0.0175 for ^{229}Th v, 0.0208 for ^{48}Ca ii and 0.0114 for ^{88}Sr ii (in units of e/amu).

In the present work, we discuss the benefits of using the Th v ion for a nuclear clock and consider the effect of electrons on the nuclear transition frequency, including the change of the frequency between Th v and other Th ions. Additionally, we calculate the energy levels of Th v. The electronic structure of the Th v ion was studied theoretically in Ref. [39]. This included calculations of energy levels for the low even states and $M1$ and $E2$ transition amplitudes. We perform calculations of energy levels for both even and odd states, the ionization potential, and the effect of electrons on the nuclear clock frequency. Experimentally known energy levels of the La iv ion are used to control the accuracy of the calculations in the present work and in Ref. [39].

II. SYSTEMATIC SHIFTS OF THE NUCLEAR TRANSITION FREQUENCY

Electrons influence the nuclear transition frequency in two distinct ways. The first type of effect introduces uncertainties in frequency measurements, while the second results in a frequency shift between systems with different electron configurations [36].

Previous studies identified two kinds of electronic states that are well suited for interrogating the nuclear resonance: spherically symmetric states with $J = 0$ or $J = 1/2$ [18] and “stretched” states with $F = J + I$ [19]; the latter criterion is generally applicable for all values of J . In the Th iv ion, the first condition is fulfilled by a metastable $7s^2 S_{1/2}$ state.

A detailed analysis of uncertainties in the Th iv ion was presented in our previous work [19]. Later in Ref. [40] Beloy argued that the dominant systematic effect in Th iv is the second-order ac Zeeman shift, which arises from the mixing of hyperfine structure levels due to the ac magnetic field in a Paul trap. However, most of these effects are either absent or significantly suppressed in the Th v ion due to its closed-shell configuration with zero total electron angular momentum. The Th v ion has no hyperfine structure in its ground state, and its nuclear magnetic moment, nuclear electric quadrupole moment, and nuclear polarizability are very small on the atomic scale.

Additional suppression of some systematic frequency shifts in Th v ion is due to the shielding of the nucleus from external electric fields by atomic electrons, see, e.g., Ref. [41]. For a static electric field or a low frequency field (when the frequency is smaller than electron excitation energies), the shielding factor is $Z_i/Z = 4/90$, where $Z_i = 4$ is the ion charge, and $Z = 90$ is the nuclear charge.

This shielding factor also applies to the electric component of black-body radiation (BBR) acting on the nucleus. Even more importantly, the intrinsic BBR shift for a nuclear transition is suppressed by the extremely small nuclear polarizability, $\alpha_N = (0.57 \pm 0.03)A^{2/3} \text{ fm}^3 \approx \langle r^2 \rangle \text{ fm}$, which is dominated by the giant dipole resonance contribution

(see Ref. [42] for references). The BBR shift is proportional to the polarizability difference between the excited and ground nuclear states, $\delta\alpha_N \approx \delta\langle r^2 \rangle \text{ fm}$. Because the external electric field at the Th v nucleus is screened by the factor $Z_i/Z = 4/90$, we introduce an effective polarizability difference $\delta\alpha_{\text{eff}} \approx (4/90)^2 \delta\langle r^2 \rangle \text{ fm} \approx 2 \times 10^{-5} \text{ fm}^3 \approx 1.3 \times 10^{-19} a_B^3$, where a_B is the Bohr radius and we use $\delta\langle r^2 \rangle \approx 0.010 \text{ fm}^2$ for the mean square radius change between the two clock states in ThV (see discussion of data for $\delta\langle r^2 \rangle$ in ^{229}Th below). Thus the nuclear polarizability difference is 19 orders of magnitude smaller than the typical electronic polarizability differences in atomic transitions. The direct nuclear contribution to the BBR shift can therefore be safely neglected.

A further contribution to the BBR shift arises from nuclear-induced changes in the electronic polarizability. Indeed, the nuclear spin, magnetic moment, and electric quadrupole moment are different in the ground and excited nuclear states [7,20]. Their effect appears due to the mixing of electron states by the hyperfine interaction (hfi) with the nucleus which affects the electron polarizability. The energy denominators in the formula for the polarizability are also affected by hfi. These effects are suppressed by the ratio of the hfi matrix element to the electron excitation energy, which is $\sim 10^{-5}$. Moreover, in Th v, the first-order hfi effect vanishes since electron angular momentum is zero.

However, there is an effect of the nuclear radius change $\delta\langle r^2 \rangle \approx 0.010 \text{ fm}^2$. According to our calculation, the static polarizability of Th v is $\alpha_0 = 7.78 a_B^3$, where a_B is the Bohr radius. The calculated difference between polarizabilities due to the change in the nuclear radius is $\delta\alpha_0 = -0.95 \times 10^{-4} a_B^3 \delta\langle r^2 \rangle / \text{fm}^2 = -1.0 \times 10^{-6} a_B^3$. This gives a BBR shift of the nuclear transition at the temperature $T = 300 \text{ K}$ equal to $\delta\nu = 8.6 \times 10^{-9} \text{ Hz}$, i.e., $\delta\nu/\nu = 4.3 \times 10^{-24}$.

Because the nuclear spin of ^{229}Th is a half-integer ($I = 5/2$ in the nuclear ground state and $I' = 3/2$ for the isomer) a small first-order frequency shift with the magnetic-field strength is present for all Zeeman components of the nuclear transition in the Th v electronic ground state. The effect can be corrected for by averaging the frequency under constant magnetic-field strength over two symmetric components of the Zeeman multiplet, for example, the pair of resonances originating from the $m_F = \pm 1/2$ levels under excitation with circularly polarized light with a sensitivity of $\pm 0.04 \text{ Hz}/\mu\text{T}$. The small sensitivity results from the near equal absolute values of the g factors of ground state and isomer with opposite sign [20,43]. A similar method is routinely applied in optical clocks, for example with ^{87}Sr and $^{87}\text{Sr}^+$ [38] (see also Ref. [44] and references therein).

The quadratic Zeeman shift of the nuclear transition is given by

$$\delta E = 2 \frac{(M_z B)^2}{\hbar \omega_N}, \quad (1)$$

where M_z is the matrix element of the nuclear magnetic moment between the upper and lower nuclear clock states, and $\hbar \omega_N = 8.4 \text{ eV}$ is the energy interval between these states. The reduced matrix element $\|M\| = 0.47(11)\mu_N$ is found from the lifetime of the upper state, where μ_N is the nuclear magneton. For $m_F = \pm 1/2$ levels this gives

$$\delta E = 1.2(6) \times 10^{-15} \text{ Hz} \left(\frac{B}{\mu\text{T}} \right)^2. \quad (2)$$

The most notable remaining systematic frequency shift in the ^{229}Th nuclear clock is the relativistic second-order Doppler shift due to micromotion in the ion trap. It was demonstrated in Refs. [19,44,45] that this shift was small and can be controlled on the level ($\Delta\nu/\nu \sim 10^{-20}$) in a well-designed ion trap.

Collisional shifts and broadenings depend on the specific collision partner, yet for Th v any such effects on the nuclear transition are expected to be highly suppressed. When the ion interacts with neutral molecules, the process is well described by the Langevin model (see, e.g., Refs. [44,46]). In the Th v nuclear transition, both nuclear clock states share the same electronic configuration, so the differential polarizability and a resulting collisional phase shift between the two nuclear states is significantly smaller than in any atomic clock transition. For collisions with charged particles, the electric field from a neighboring ion is attenuated at the nucleus by the 4/90 screening factor discussed earlier, reducing any shift. The same arguments apply to the nuclear frequency shifts induced by laser light or stray electric fields. The nucleus itself is many orders of magnitude less responsive to external fields than the electronic cloud, as illustrated by the tiny nuclear polarizability, BBR shift and nuclear Zeeman effects.

III. FREQUENCY SHIFTS OF THE NUCLEAR TRANSITIONS DUE TO ELECTRONS

We now consider the frequency shift between Th iv and Th v ions. It was demonstrated in our previous work [36] that the Coulomb interaction of atomic electrons with the nucleus leads to a significant shift of the nuclear transition frequency. This shift for electronic state a is given by

$$\Delta E_a = F_a \delta \langle r^2 \rangle, \quad (3)$$

where F_a is the field-shift constant of state a which can be obtained from atomic calculations; $\delta \langle r^2 \rangle$ is the change of the nuclear root-mean square radius between the excited and ground nuclear states. We use the value for $\delta \langle r^2 \rangle$ derived in Ref. [32], $^{229m,229}\delta \langle r^2 \rangle = 0.0105(13) \text{ fm}^2$. Thus, the difference of the nuclear frequencies between Th iv and Th v is given by

$$\Delta \nu_N = [F_a(\text{Th iv}) - F_a(\text{Th v})] \delta \langle r^2 \rangle. \quad (4)$$

State a is the ground electronic state of the ion.

In our previous work [36], we calculated the field-shift constant F_a for Th i, Th ii, Th iii, and Th iv. The closed-shell core of all these ions is the same, corresponding to the Th v ion. In this approximation, the valence electron contribution to Th v is effectively $F_a(\text{Th v}) \equiv 0$, allowing the result for Th iv from Ref. [36] to be used in calculating the frequency shift via Eq. (4).

Note that the modification of the electronic core contribution due to the additional valence $5f$ electron in Th iv was included as a core relaxation effect in Ref. [36]. To improve reliability and estimate the accuracy of our results, we employ two additional methods to calculate the energy shift in Eq. (4). In these approaches, the $6p$ electrons are treated as part of the valence space (see the Appendix), meaning that the field-shift constant for Th v is no longer zero.

TABLE I. Field-shift constants F and their differences ΔF (GHz/fm²) for the ground states of Th i, Th iii, Th iv, and Th v ions found in different approaches: first, by changing nuclear radius (ΔR_N) and second in RPA calculations. Two more approaches were used for Th iv: it was treated as a system with one external electron and as a system with seven valence electrons (N_v).

N_v	Ions	ΔR_N	RPA
3	$F(\text{Th ii})$	51.7	49.6 ^a
2	$F(\text{Th iii})$	-68.2	-68.0 ^a
1	$F(\text{Th iv})$	-54.2	-55.0 ^a
7	$F(\text{Th iv})$	-269	-281
6	$F(\text{Th v})$	-222	-230
3-2	$\Delta F(\text{Th ii-Th iii})$	119.9	117.6
2-1	$\Delta F(\text{Th iii-Th iv})$	-14.0	-13.0
1-0	$\Delta F(\text{Th iv-Th v})$	-54.2	-55.0 ^a
7-6	$\Delta F(\text{Th iv-Th v})$	-47	-51

^aReference [36].

First, we perform calculations using two different values of the nuclear radius and apply Eq. (3) to determine the field-shift constant F_a .

Second, we treat the nuclear radius change as a perturbation and employ the random-phase approximation (RPA), which incorporates core relaxation effects, to compute the field-shift constant F (see the Appendix for details).

The results are presented in Table I. We also add the results for other Th ions obtained via the change of the nuclear radius since this method includes corrections missing in the RPA method used in Ref. [36], and is expected to be significantly more accurate (see the Appendix).

The agreement between the values of F for Th iv and Th v obtained using two different methods demonstrates a correlation between the complexity of the system and the accuracy of the results. The greater the number of valence electrons, the larger the observed difference. The values of ΔF are further affected by cancellations in the case when the values of F for two ions are close. Assuming that the values obtained with the ΔR_N method are more accurate, we use the value $\Delta F = -54.2 \text{ GHz/fm}^2$ for the Th iv-Th v pair.

Taking this value and the change of nuclear radius between the ground and isomeric nuclear states $\delta \langle r^2 \rangle = 0.0105(13) \text{ fm}^2$, we obtain the nuclear frequency shift between the Th iv and Th v ions to be $-570 \text{ MHz} = -2.4 \times 10^{-6} \text{ eV}$. The relative shift $|\Delta \nu_N/\nu_N| = 2.8 \times 10^{-7}$ is larger than the projected uncertainty of the frequency measurement by 12 orders of magnitude. See Table II for a comparison with other ions.

After a preprint of the present paper [47] appeared in arxiv, another preprint [13] appeared with extended calculations of the electron-induced energy shifts of the nuclear transition frequency to Th ions in the solid state environment. Combined with the measurements [7] and calculations of the frequency difference between the free ion and Th ion in solid, this allowed them to find the absolute values of the nuclear transition frequencies $\nu_N = 2, 020, 407.114(70) \text{ GHz}$ in Th iv and $\nu_N = 2, 020, 407.648(70) \text{ GHz}$ in Th v ions. The difference of these frequencies -0.534 GHz agrees with our result -0.570 GHz . An apparent deviation 0.036 GHz (which

TABLE II. Shift in the nuclear transition frequency ν_N between different ions of ^{229}Th . Results for Th I to Th IV and the bare ^{229}Th nucleus are taken from Ref. [36], while the frequency difference between Th IV and Th V is calculated in the present work.

Ions			$\Delta\nu_N$		$\Delta\nu_N/\nu_N$
			(GHz)	(eV)	
Th I	—	Th II	0.10	4.1×10^{-7}	5.0×10^{-8}
Th II	—	Th III	1.3	5.4×10^{-6}	6.4×10^{-7}
Th III	—	Th IV	−0.15	$−6.2 \times 10^{-7}$	$−7.4 \times 10^{-8}$
Th IV	—	Th v	−0.57	$−2.4 \times 10^{-6}$	$−2.8 \times 10^{-7}$
Th v	—	Th XCr ^a	2.1×10^4	8.7×10^{-2}	1.0×10^{-2}

^aBare ^{229}Th nucleus.

is much smaller than the estimated uncertainty of 0.1 GHz is due to the slightly different value of $\delta\langle r^2 \rangle = 0.0097(26)\text{fm}^2$ [3] used in Ref. [13] (we use $^{229m,229}\delta\langle r^2 \rangle = 0.0105(13)\text{fm}^2$ [32]). The experimental uncertainty in $\delta\langle r^2 \rangle$ at the moment is the main source of errors in the calculated values of ν_N . Improved values of $\delta\langle r^2 \rangle$ and the calculated values of the field-shift constants F in Table I will allow one to improve predictions of ν_N .

Using our calculations of the frequency differences between Th ions from Table II and the frequencies in Th IV and Th V from Ref. [13], we obtain $\nu_N = 2,020,406.964(70)$ GHz in Th III, $\nu_N = 2,020,408.264(100)$ GHz in Th II, $\nu_N = 2,020,408.364(100)$ GHz in Th I, and $\nu_N = 1,999,700(3000)$ GHz = $8.270(12)$ eV for the bare nucleus $^{229}\text{Th}^{+90}$. The result for the latter is $\nu_N = 8.272(22)$ eV in Ref. [13].

IV. ENERGY LEVELS OF TH V AND LA IV

To provide theoretical support for further experiments with Th ions, it may be useful to calculate the unknown electronic energy levels of the Th V ion. The Th V and La IV ions have similar electronic structures, both featuring closed shells with an outermost subshell configuration of ns^2np^6 in the core ($n = 5$ for La IV and $n = 6$ for Th V). The experimental data for the La IV spectrum is available in the NIST database [48], whereas no experimental data exist for Th V. Therefore, we estimate the accuracy of our method by comparing our calculated energy levels for La IV with the available experimental data.

Calculations of several low-energy even-parity levels in La IV and Th V were performed in Ref. [39] using an advanced method that combined the configuration interaction (CI) with a linearized coupled-cluster approach [49]. A sophisticated procedure was employed to select the most important configurations, resulting in agreement with measured La IV levels within 1%.

In the present work, we calculate a significantly larger number of levels. We use a less computationally demanding but highly efficient method that combines CI with perturbation theory, known as the CIPT method [50] (see the Appendix for details). The efficiency is gained by reducing the size of the effective CI matrix, which is generated using many-body perturbation theory.

TABLE III. Experimental [48] and calculated excitation energies (in cm^{-1}) and g factors of the La IV ion. Ground-state configuration is $[\text{Pd}]5s^25p^6$, symbols F and D indicate leading configurations for outermost electrons: symbol F indicates the $5p^54f$ configuration, symbol D indicates the $6p^55d$ configuration. The symbol J^P stands for the total angular momentum and parity.

State			J^P	This work		NIST [48]	Ref. [39]
1	GS	1S	0^+	0	0.0000	0.0	0
2	F	$2[3/2]$	1^+	151 189	0.5000	143 354.7	142 168
3	F		2^+	153 213	1.1373	145 949.0	144 910
4	F	$2[5/2]$	3^+	157 704	1.2750	149 927.1	149 153
5	F		2^+	169 914	0.8320	160 486.4	160 592
6	F	$2[7/2]$	4^+	158 020	1.0408		157 252
7	F		3^+	162 326	0.8803	153 339.1	153 130
8	D	$2[1/2]$	0^-	156 068	0.0000	156 100.3	
9	D		1^-	157 993	1.4444	158 412.6	
10	D	$2[3/2]$	2^-	162 794	1.4185	162 867.6	
11	D		1^-	182 319	0.5782	181 155.0	
12	D	$2[7/2]$	4^-	163 680	1.2500	163 693.3	
13	D		3^-	165 503	1.0933	165 070.7	
14	D	$2[5/2]$	2^-	168 593	0.8897	167 921.7	
15	D		3^-	173 718	1.2041	173 335.5	

The results for the 15 lowest-excited states of La IV are presented in Table III. Comparison with experiment shows satisfactory agreement for even states ($\sim 6\%$) and very good agreement for odd states ($\sim 1\%$).

Calculated energy levels of Th V are presented in Table IV. The electronic energy levels of Th V lie far above the 8.4-eV nuclear transition ($\omega_N = 67\,353\text{cm}^{-1}$), so even a two-step, tunable laser scheme cannot match the energy spacing between electronic levels to the nuclear transition. Without such near-degeneracy, an electronic-bridge process (see, e.g., Refs. [4,51,52]) is intrinsically inefficient: lasers can drive electronic transitions, but the subsequent hyperfine-mediated transfer of energy to the nucleus remains strongly off-resonant. Hence, using an electronic bridge to excite the ^{229}Th nucleus in Th V is impractical.

Although a few pairs of excited electronic states differ in energy by nearly $\omega_N = 67\,353\text{cm}^{-1}$, accessing these very high-lying states with current laser technology is extremely challenging, further limiting any realistic electronic-bridge excitation scheme in Th V.

The ionization potential of Th V is calculated as the energy difference between ground states of Th V and Th VI. It is in good agreement with the previous results found in Refs. [48,53].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX: METHOD OF CALCULATION

In the present work we use an efficient method which combines CI with perturbation theory (the CIPT method [50]).

We perform the calculations in the V^{N-1} approximation which means that the initial Hartree-Fock (HF) procedure is done for an ion with one hole in the outermost subshell ($5p^5$ for La iv and $6p^5$ for Th v). The single-electron basis states are calculated in the field of frozen core using the B-spline technique [54].

It was demonstrated in Ref. [39] that the $5s$ electrons in La iv and $6s$ electrons in Th v should be attributed to valence

TABLE IV. Calculated excitation energies (in cm^{-1}) and g factors of the Th v ion. Ground-state configuration of outermost electrons is $6s^2 6p^6$, symbols F , D , P , and S indicate leading configurations for outermost electrons: symbol F indicates the $6s^2 6p^5 5f$ configuration, symbol D indicates the $6s^2 6p^5 6d$ configuration, symbol P indicates the $6s^2 6p^5 7p$ configuration, symbol S indicates the $6s^2 6p^5 7s$ configuration. The symbol J^P stands for the total angular momentum and parity. IP stands for ionization potential.

State	J^P	This work	Ref. [39]
1	GS	0^+	0
2	F	1^+	138 922
3	F	2^+	143 129
4	F	4^+	146 618
5	F	5^+	147 335
6	F	3^+	149 812
7	F	3^+	151 891
8	F	4^+	157 311
9	D	0^-	159 866
10	F	2^+	161 992
11	D	1^-	163 431
12	D	3^-	169 790
13	D	2^-	170 331
14	D	4^-	171 779
15	D	2^-	174 617
16	D	3^-	181 285
17	D	1^-	195 273
18	D	2^-	196 523
19	D	1^-	201 481
20	F	3^+	208 580
21	F	3^+	212 757
22	F	4^+	215 662
23	F	2^+	219 266
24	D	2^-	233 093
25	P	1^+	238 044
26	P	2^+	239 200
27	D	3^-	243 125
28	P	1^+	254 730
29	D	1^-	254 896
30	S	0^-	263 152
IP	$3/2^-$	472 331 ^a	

^aOther theory, IP = 468 000(15 000) [48,53].

space for better results. Any excited states of the ions involve at least one excitation of an electron from either the ns^2 or np^6 subshell, making the ion an open-shell system with eight electrons in the open shells. Full-scale CI calculations are challenging for eight valence electrons. Therefore, we use a simplified but very efficient approach especially developed for open-shell systems. It is called the CI with perturbation theory (CIPT) method [50]. The CIPT equations have the form

$$\langle i|H^{\text{eff}}|j\rangle = \langle i|H^{\text{CI}}|j\rangle + \sum_k \frac{\langle i|H^{\text{CI}}|k\rangle \langle k|H^{\text{CI}}|j\rangle}{E - E_k}. \quad (\text{A1})$$

Here H^{CI} is the CI Hamiltonian for eight external electrons

$$H^{\text{CI}} = \sum_n \hat{H}_n^{\text{HF}} + \sum_{n<m} \frac{e^2}{r_{nm}}, \quad (\text{A2})$$

$\hat{H}_n^{\text{HF}}$ is the relativistic HF operator for the valence electron number n . The indices i, j, k in Eq. (A1) numerate eight-electron basis states which are constructed by exciting one or two electrons from the reference $ns^2 np^6$ configuration. All basis states are divided on the energy scale into two groups, low-energy states (i, j), and high-energy states (k). Low-energy states are included directly into the CI matrix while high-energy states are included perturbatively. E in Eq. (A1) refers to the energy of the state of interest, and E_k is the diagonal matrix element for high-energy states, $E_k = \langle k|H^{\text{CI}}|k\rangle$. The ummation in Eq. (A1) goes over all high-energy states. The energies E and wave functions X are found by solving the matrix eigenvalue problem

$$(H^{\text{eff}} - EI)X = 0, \quad (\text{A3})$$

with H^{eff} matrix given by Eq. (A1), while I is the unit matrix. Note that the H^{eff} matrix depends on unknown energy E . Therefore, iterations over energy are needed. Usually five to ten iterations are enough for full convergence.

The results for the 15 lowest-excited states of La iv are presented in Table IV. A comparison with the experiment shows satisfactory agreement for even states ($\sim 6\%$) and very good agreement for odd states ($\sim 1\%$).

Calculations of the field-shift constant on the first stage are very similar to the calculation of energy levels. One significant difference is that the $6s$ electrons are moved to the core and the CI equations are solved for six ($6p^6$) or seven ($6p^6 5f$) valence electrons. This is because the $6s$ electrons give a large contribution to the field-shift constants of both ions, Th iv and Th v, enhancing the numerical error in the difference ΔF . Moving them to the core leads to more stable results.

We perform the calculations in two different ways. First, we perform the calculations with two values of nuclear radius, then apply Eq. (3) to find the values of F_a . This way is simpler but it may be sensitive to numerical noise. After changing the nuclear radius one needs to perform extra HF iterations to account for the core relaxation effect. These iterations themselves produce some shift in energy, which might be comparable to the isotope shift. For this reason the method does not work for light atoms since the shift of energy is very small there. However, this method is sufficiently accurate for heavy ions like Th iv and Th v. It is important to make an appropriate choice for the value of the change of nuclear radius. It should

TABLE V. Calculation of the field-shift constant F for the ground state of Th IV by changing the nuclear radius.

R_N fm	RMS fm	$\delta\langle r^2 \rangle$ fm ²	$E(5f_{5/2})$ cm ⁻¹	ΔE cm ⁻¹	F GHz/fm ²
6.9000	5.68780	0	-238 643.210	0	0
7.0000	5.76065	0.834	-238 644.719	-1.509	-54.24
7.1000	5.83362	1.680	-238 646.248	-3.038	-54.21
7.2000	5.90670	2.538	-238 647.789	-4.578	-54.08

be large enough to suppress numerical noise in the energy difference. However, it should not be too large to avoid contributions from higher-order terms, ($\sim\delta\langle r^4 \rangle$, $\delta\langle r^2 \rangle^2$, etc.). We find that $\delta\langle r^2 \rangle \approx 1$ fm² is sufficiently good for these purposes (see Table V).

In a second approach we use the RPA method to perform the calculations. The RPA equations have a form (see, e.g., Refs. [55])

$$(\hat{H}^{\text{HF}} - \epsilon_c)\delta\psi_c = -(\hat{F} + \delta V_{\text{core}}), \quad (\text{A4})$$

where H^{HF} is the relativistic Hartree-Fock operator for the atomic core, index c numerates single-electron states in the core, ψ_c and $\delta\psi_c$ are corresponding single-electron functions and corrections due to the field-shift operator $\hat{F}$, and δV_{core} is the change of the self-consistent Hartree-Fock potential due to the change in all core functions. Solving Eqs. (A4) self-consistently allows to determine δV_{core} . The field-shift constant is given by

$$F_a = \langle a | \hat{F} + \delta V_{\text{core}} | a \rangle. \quad (\text{A5})$$

We use the hat to distinguish between the field-shift constant F and the field-shift operator $\hat{F} = \delta V_{\text{nuc}}/\delta\langle r^2 \rangle$. The wave function $|a\rangle$ in Eq. (A5) is the many-electron wave function for valence electrons found in the CIPT calculations. The RPA equations are linear in $\delta\langle r^2 \rangle$ by definition; they are also free from the numerical noise caused by extra Hartree-Fock iterations. Note, however, that Eq. (A5) does not take into account some minor contributions like the change of the correlation operator $\hat{\Sigma}$, renormalization of the wave function, and so on. In the end, the RPA method is simpler if minor contributions are ignored. However, with the proper choice of the value for the change of nuclear radius (see, e.g., Table V) the alternative approach is likely to be significantly more accurate since it includes the corrections missing in the RPA method.

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