Effects of Electrons on Nuclear Clock Transition Frequency in ^{229}Th Ions

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We perform calculations of the energy shift of the nuclear clock transition frequency ^{229}Th as a function of the number of electrons in Th ion. We demonstrate that the dependence of the nuclear frequency on electron configuration is significant, for example, removing one electron from the atom leads to relative shift of the nuclear frequency $\sim 10^{-7}$, which is 12 orders of magnitude larger than the expected relative uncertainty of the nuclear clock transition frequency ($\sim 10^{-19}$). This leads to the difference of the nuclear clock frequencies in Th IV, Th III, Th II, and Th I. The relative change of the nuclear frequency between neutral Th and its bare nucleus is 1%. We also calculate the field shift constants for isotopic and isomeric shifts of atomic electron transitions in Th ions.

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The nucleus of the ^{229}Th isotope has a unique feature of having very low-energy excitation connected to the ground state by the magnetic dipole (M1) transition (see, e.g., Refs. [1,2] and references therein). The latest, most precise measurements, give the value of 8.338(24) eV [3] (see also [4–8]) for the energy of this excitation, which is very small on a nuclear scale. This feature attracted many researches for plans to build a nuclear clock of exceptionally high accuracy—see, e.g., [9,10]. The relative uncertainty is expected to reach 10^{-19} [11]. In addition, there are 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 Einstein equivalence principle, and the search for scalar and axion dark matter fields [12–20]. There are plans to use Th ions of a different ionization degree [11,21,22] and even a solid-state Th nuclear clock [23–25]. In this work we show 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. There is also a smaller shift due to the magnetic interaction.

This electronic shift depends on electron configuration and it is different in different systems, like Th IV, Th III, Th II, and Th I, leading to different nuclear frequencies. This shift for electronic state a is given by

$$\Delta E_a = F_a \delta\langle r^2\rangle, \qquad (1)$$

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 ($\delta\langle r^2\rangle = \langle r^2\rangle^{229m} - \langle r^2\rangle^{229}$). The most accurate value for $\delta\langle r^2\rangle$ was recently derived in Ref. [22], $^{229m,229}\delta\langle r^2\rangle = 0.0105(13)$ fm^2. This enables us to determine the electronic shift of nuclear transition frequency for different thorium systems by calculating the field shift constants F_a and using (1). For example, the difference between the nuclear frequencies of Th III and Th IV is given by

$$\Delta\omega_N = [F_a(\mathrm{Th}^{2+}) - F_a(\mathrm{Th}^{3+})]\delta\langle r^2\rangle^{229m,229}.$$

State a in this case is the ground electronic state of the ion.

Note that these field shift constants F appear also in the calculations of the isotopic and isomeric field shifts of electronic transition frequencies. The difference is that in the isotopic and isomeric shifts we need the difference of F for final state b and initial state a of the electronic transition. The nuclear state does not change in this electronic transition. For the isotope shift it is usually the ground nuclear state. For the isomeric shift it is the isomeric (excited) state or ground state of the same nucleus. The isotopic and isomeric field shifts of the electronic transition frequency are given by

$$\Delta\omega_{ab} = (F_b - F_a)\delta\langle r^2\rangle. \qquad (2)$$

Numerical values of $\Delta\omega_N$ and $\Delta\omega_{ab}$ can be calculated using values of the constants F for different electron states in Th IV, Th III, Th II, and Th I presented in Table I. For the isomeric shifts one may use $^{229m,229}\delta\langle r^2\rangle = 0.0105(13)$ fm^2 measured in Ref. [22].

We use the combination of the single-double coupled cluster and the configuration interaction methods (SD + CI [27]) and random-phase approximation (RPA) method to perform the calculations. The SD + CI method gives us the wave functions, while the RPA method gives an effective operator of the field shift. The details of the calculations are

TABLE I. Field shift constant F for the ground and some excited states of Th IV, Th III, Th II, and Th I.

Atom or ion	State		Experimental energy (cm^{-1}) [26]	F (GHz/fm^2) Present	F (GHz/fm^2) Ref. [22]
Th IV	$5f$	$^2F^o_{5/2}$	0	−55.0	
	$5f$	$^2F^o_{7/2}$	4325	−53.0	
	$6d$	$^2D_{3/2}$	9193	−23.3	
	$6d$	$^2D_{5/2}$	14 586	−20.5	
	$7s$	$^2S_{1/2}$	23 130	92.1	
	$7p$	$^2P^o_{1/2}$	60 239	2.7	
	$7p$	$^2P^o_{3/2}$	73 055	−5.3	
Th III	$5f6d$	$^3H^o_4$	0	−68.0	−68.7
	$6d^2$	$^3F_2$	63	−39.9	−36.6
	$5f^2$	$^3H_4$	15 148	−83.3	−89.5
	$5f6d$	$^1P^o_1$	20 711	−62.2	−63.6
	$5f^2$	$^3F_4$	21 784	−86.5	−85.5
	$5f^2$	$^3P_0$	29 300	−82.2	−84.1
Th II	$6d^27s$	$^2D_{3/2}$	0	49.6	54.6
	$5f6d^2$	$*_{3/2}$		−65.0	
	$5f6d7s$	$*_{3/2}$	15 145	−45.8	
	$5f6d7s$	$*_{3/2}$	15 711	−36.9	
	$5f6d^2$	$*_{3/2}$	17 122	−29.1	−31.6
	$5f6d7s$	$^2F^o_{5/2}$	12 472	−18.3	
	$5f6d7s$	$*_{5/2}$		−36.3	
	$5f6d7s$	$^4D^o_{5/2}$	14 545	−63.9	
	$5f6d7s$	$*_{5/2}$	16 033	−46.8	
Th I	$6d^27s^2$	$^3F_2$	0	58.6	

presented in the Appendix. Note that we do not include a contribution of the core electrons which cancels out in the difference of the values of F presented in the Table I (this contribution appears in the difference of the nuclear frequencies between the neutral atom and the bare nucleus—see below). However, we include the core polarization (RPA) corrections and dominating correlation corrections due to the valence electron–core electron interaction (CD + CI) which contribute to the difference of the field shift constants F (see Appendix).

The results of the calculations are presented in Table I. We present energy levels and field shift constants for the ground and some excited states of Th IV, Th III, Th II, and Th I. We have chosen low-energy excited states and also some other states of Th III and Th I for which other calculations and experimental data on isotope shift are available [22]. The values of the field shift constants are compared with earlier calculations in Ref. [22].

The difference of the field shift constants between our calculations and calculations in Ref. [22] is a few percent. This difference may be used as an accuracy estimate since the calculations have been done by different methods. The largest difference is for the ground state of Th II, which is 10%. However, our number leads to more consistent results for values of $\delta\langle r^2\rangle$ extracted from the isotope shift measurements in ions Th II and Th III. Indeed, using our numbers, $F = 49.6$ GHz/fm^2 for the ground state and $F = 29.1$ GHz/fm^2 for the state at $E = 17122$ cm^{-1}, for extracting the difference in root-mean-square radii $\delta\langle r^2\rangle^{232,229}$ from the isotope shift data [22] leads to the value $\delta\langle r^2\rangle^{232,229} = 0.321(32)$ fm^2 (we assume 10% uncertainty for the values of F), which is closer to the data extracted from four transitions in Th III [0.315(32), 0.312(42), 0.338(44), 0.322(53), see Table I in [22]]. When all five numbers are taken into account, four numbers for Th III from Ref. [22] and our number for Th II, 0.321(32), the final result is $\delta\langle r^2\rangle^{232,229} = 0.320(15)$ fm^2 [the final value of [22] is $\delta\langle r^2\rangle^{232,229} = 0.299(15)$ fm^2]. Our result is in better agreement with the latest most accurate literature value $\delta\langle r^2\rangle^{232,229} = 0.334(8)$ fm^2 presented in Ref. [28]. The new value of $\delta\langle r^2\rangle^{232,229}$ leads to a slightly different value of $\delta\langle r^2\rangle^{229m,229}$. Using the ratio of the isomeric and isotopic shifts from Ref. [10] we find $\delta\langle r^2\rangle^{229m,229} = 0.0112(13)$ fm^2. It is 7% larger but agrees within error bars with the value $\delta\langle r^2\rangle^{229m,229} = 0.0105(13)$ fm^2 presented in [22]. We adopt this new evaluation in the following analysis.

It is instructive to explain why the field shift constants F have different signs for different electron states. Orbitals $s_{1/2}$ and $p_{1/2}$ penetrate nucleus and are highly sensitive to the nuclear radius (the lower component of the Dirac spinor of the relativistic $p_{1/2}$ orbital has angular quantum numbers of $s_{1/2}$ orbital). An increase of the nuclear radius leads to a decrease of the attraction to the nucleus, therefore energies $s_{1/2}$ and $p_{1/2}$ move up and constant F is positive. Higher orbitals $p_{3/2}$, d, and f do not penetrate the nucleus, so the direct term $\hat{F}$ in Eq. (A5) is negligible. The effect comes from the correction to the electron core potential δV_{core} which is dominated by the Coulomb field of $s_{1/2}$ electrons. An increase of the nuclear radius makes the attraction to the nucleus weaker, increases the radii of the $s_{1/2}$ orbitals, and makes negative correction δV_{core} to the core electron Coulomb potential. This is why F for $p_{3/2}$, d, and f electrons is negative. The sign may also be explained as the addition of valence $p_{3/2}$, d, or f electron acting to increase the positive Coulomb energy of the electron repulsion. As a result, the $s_{1/2}$ electron energies and distances from the nucleus increase and their sensitivity to the change of the nuclear radius decreases. Thus, the effect of the higher wave valence electron is negative.

Using the field shift constants for the ground states of each ion from Table I (we use our numbers for consistency), the value $\delta\langle r^2\rangle^{229m,229} = 0.0112(13)$ fm^2 (see above) and a formula similar to Eq. (2) we obtain the differences between nuclear frequencies in different thorium ions. The results are presented in Table II. We see that the difference is significant. It exceeds the projected relative

TABLE II. Change of nuclear frequency ω_N between ions of ^{229}Th.

Ions			$\Delta\omega_N$ (GHz)	$\Delta\omega_N$ (eV)	$\Delta\omega_N/\omega_N$
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	-6.2×10^{-7}	-7.4×10^{-8}
Th II	⋯	Th IV	1.2	5.0×10^{-6}	6.0×10^{-7}

uncertainty of the nuclear clocks by many orders of magnitude. It is worth noting that the shift does not contribute to the uncertainty budget. It only means that the frequency of the nuclear transition is different in different thorium systems.

It is interesting to determine the nuclear frequency difference between neutral (or nearly neutral) ^{229}Th and the bare ^{229}Th nucleus. This difference is strongly dominated by contributions from $1s$ electrons. Using the RPA calculation (A4) we get $F(1s) = 8.23\times10^{8}$ MHz/fm^2. The total energy shift caused be two $1s$ electrons is 1.73×10^{7} MHz; the total shift from all core electrons is 2.07×10^{7} MHz $= 8.57\times10^{-2}$ eV, which is ~1% of the nuclear frequency.

Electronic correction to the nuclear frequency comes also from magnetic interaction between electrons and nucleus. The first order gives ordinary magnetic hyperfine splitting of the transition frequencies. The magnetic shift is given by the second-order magnetic dipole hyperfine correction to the energy

$$\delta E_g^{\rm hfs} = \sum_n \frac{\langle g|\hat{H}^{\rm hfs}|n\rangle^2}{E_g - E_n}. \qquad (3)$$

Here, index g stands for the ground electronic state, $\hat{H}^{\rm hfs}$ is the magnetic dipole hyperfine structure operator. Values of $\delta E_g^{\rm hfs}$ are different for the ground and isomeric nuclear states since their magnetic moments and spins are different. In addition, there is the second order contribution from the mixing of the ground and isomeric nuclear states by the magnetic filed of electrons. Magnetic moment values can be found in Ref. [10]. Calculations show that the frequency shift due to the second-order hyperfine interaction is significantly smaller than the electronic shift considered in the present work. This relative magnetic shift ranges from $\sim10^{-14}$ to $\sim10^{-11}$ depending on the Th ion.

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Appendix: Method of the calcualtions.—We start the calculations from the relativistic Hartree-Fock (RHF) procedure for the closed-shell Th V ion. The RHF Hamiltonian has the form

$$\hat{H}^{\rm RHF} = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta - 1)mc^2 + V_{\rm nuc} + V_{\rm Breit} + V_e, \qquad (A1)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β are the Dirac matrixes, $\mathbf{p}$ is the electron momentum, $V_{\rm nuc}$ is the nuclear potential obtained by integrating the Fermi distribution of the nuclear charge density, $V_{\rm Breit}$ is the operator of the Breit interaction which includes magnetic interaction and retardation [29]. The single-electron basis states for valence electrons are calculated in the field of the frozen core using the B-spline technique [30]. These basis states are used in all calculations. This corresponds to the so-called V^{N-M} approximation [31], where N is the total number of electrons, M is the number of valence electrons ($M = 1$, 2, 3 or 4 in our case), and $N - M$ is the number of core electrons.

We use the single-double coupled-cluster method [27] to include the correlations between valence and core electrons. Solving the SD equations involves iterations for the core and for the valence states until full convergence is achieved. As a result, the all-order correlation operators $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ are produced. The $\hat{\Sigma}_1$ operator is the single-electron operator which describes the correlation interaction of a particular valence electron with the core. The $\hat{\Sigma}_2$ operator is the two-electron operator which describes the screening of the Coulomb interaction between valence electrons by core electrons. The resulting effective CI Hamiltonian has the form

$$\hat{H}^{\rm CI} = \sum_{i=1}^{M}(\hat{H}^{\rm RHF} + \hat{\Sigma}_1)_i + \sum_{i<j}^{M}\left(\frac{e^2}{r_{ij}} + \hat{\Sigma}_{2ij}\right). \qquad (A2)$$

The energy and wave function of the many-electron state a is found by solving the CI equation

$$(\hat{H}^{\rm CI} - E_a)X_a = 0, \qquad (A3)$$

where X_a contains the coefficients of the expansion of the valence wave function over single-determinant basis states.

To calculate the field shift constants we need an effective operator of the field shift $\hat{F}$. Its initial form can be written as $\hat{F} = \delta V_{\rm nuc}/\delta\langle r^2\rangle$, where $\delta V_{\rm nuc}$ is the change of nuclear potential due to the change of nuclear radius. Then the RPA method [32] is used to include the effect of core polarization, i.e., to take into account the effect of changing nuclear radius on all atomic electrons.

The RPA equations have a form (see, e.g., [32,33])

$$(\hat{H}^{\rm RHF} - \epsilon_c)\delta\psi_c = -(\hat{F} + \delta V_{\rm core})\psi_c, \qquad (A4)$$

where $\hat{H}^{\rm RHF}$ is given by (A1), 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 us to determine δV_{core}. Note that the core is the same for Th IV, Th III, Th II, and Th I. Therefore the SD and RPA equations have to be solved only once. Then the field shift constant is given by

$$F_a = \langle X_a | \sum_{i=1}^{M} (\hat{F} + \delta V_{\text{core}})_i | X_a \rangle, \qquad \text{(A5)}$$

where the wave function for state a comes from solving the CI Eq. (A3).

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