²²⁹Th³⁺ as an ionic optical clock for fine-structure-constant variations

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In this paper, we propose the $5f_{5/2} \rightarrow 5f_{7/2}$ transition in ²²⁹Th³⁺ as an ionic clock with accuracy of 10^{-18} level, which can be also used together with the nuclear clock transition for measuring variations of fine-structure constant with common-mode rejection of certain systematic effects. The many-body perturbation theory and Dirac-Fock plus core polarizability method are used to perform theoretical calculations. Calculation results show that several systematic frequency shifts can be suppressed to 10^{-18} level or even below. Assuming the accuracy of ionic clock frequency can be achieved in 10^{-18} level, ²²⁹Th³⁺ potentially offers a precision of drift of fine-structure constant of $\dot{\alpha}/\alpha$ in 10^{-21} -yr⁻¹ level by measuring the frequency ratio of nuclear clock frequency and ionic clock frequency.

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I. INTRODUCTION

In the realm of modern science and technology, atomic clocks stand as remarkable instruments, serving pivotal roles in various critical applications. These precision devices meticulously count the quantum oscillations of atoms, underpinning fundamental aspects of our daily lives [1]. They enable the accurate synchronization of global navigation systems (GPS), ensuring the reliability of GPS technology, and play a crucial role in synchronizing communication networks, making real-time data transmission and international communication possible [2].

Beyond their practical utility, atomic clocks are also at the forefront of the search of new physics [3]. By detecting the shift of the atomic clock frequency over time, it is possible to check whether the fine-structure constant changes over time. Even the smallest variations in this constant hold the potential to reveal profound insights into uncharted realms of the universe. These insights encompass the search for elusive dark matter [4] and the exploration of dark energy [5]. Amidst the potential optical clock candidates, ²²⁹Th emerges as an exceptional luminary [6-14] due to its unique characteristics, including a nuclear transition energy of a few electron volts (eV), narrow linewidth, and insensitivity to external fields [15-17]. The development of a nuclear clock utilizing the ²²⁹Th nucleus holds the potential to achieve accuracy levels on the order of 10^{-19} [18,19]. The nuclear transition frequency of ²²⁹Th has undergone continuous refinement through nuclear physical measurements. Initial measurements indicated a transition energy of 7.6(5) eV [20], evolving into the present measurements of 8.28(17) eV [8], 8.30(92) eV [9], 8.338(24) eV [11], and a somewhat inconsistent measurement 8.10(17) eV [10]. Recently, two new results of 8.355770(29) eV [12] and $8.355733(2)_{\text{stat}}(10)_{\text{sys}} \text{ eV } [13]$ were reported, and these measurements represent the most accurate to date. In addition to nuclear physical measurements, the unique electronic bridge process and internal conversion channel provide the alternative avenue to measure the nuclear transition frequency through atomic spectrum methods [8,21-24]. These endeavors pave the way for the development of narrow linewidth lasers corresponding to the nuclear transition frequency.

Meanwhile, recent studies have indicated high sensitivity to variations of the fine-structure constant of nuclear transition frequency in ²²⁹Th [26-28]. To probe the variations of fine-structure constant, the measurement of frequency ratio between two clocks presents a valuable approach, circumventing the limitations associated with Cs primary standards and offering reduced statistical and systematic uncertainties compared to absolute frequency shift measurements [5]. Furthermore, as demonstrated in the ¹⁷¹Yb⁺ ion clock, measuring the frequency ratio of two distinct clock transitions within the same ion brings about common-mode rejection of various systematic effects, such as gravitational redshift and relativistic time dilation [25]. Hence, the possibility of using atomic transitions in ²²⁹Th³⁺ for fine-structure-constant variation experiments was previously considered [29]. This simplifies the experimental setup of the measurement, making it a simpler approach.

In our paper, we show the potential of 229 Th³⁺ as an ionic clock with accuracy of 10^{-18} level based on $5f_{5/2} \rightarrow 5f_{7/2}$ transition. Through calculations by the many-body perturbation theory (MBPT) and the Dirac-Fock plus core polarizability (DFCP) method, we estimate the blackbody radiation (BBR) shift to be just -3.6 mHz at room temperature, which is below that of most ionic optical clocks such as Ca⁺

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and Sr⁺ [30,31]. Both the superheavy nucleus of ²²⁹Th³⁺ and low cooling limit temperature $T_{min} = 13 \,\mu\text{K}$ also give a great advantage in the suppression of motion-induced frequency shifts. Therefore, ²²⁹Th³⁺ not only provides good clock performance but also exhibits a significantly great sensitivity to variations of fine-structure constant, potentially offering a limit of variations of fine-structure constant of $\dot{\alpha}/\alpha$ in 10^{-21} -yr⁻¹ level by measuring the frequency ratio of nuclear clock frequency and ionic clock frequency.

II. COMPUTATIONAL METHODS

We use two methods for the relativistic atomic structure calculations on 229 Th³⁺. Both MBPT method and DFCP method initiate with the V^{N-1} Dirac-Fock potential.

A. Many-body perturbation theory

In this subsection, we provide a brief introduction to the MBPT method. We use the AMBIT package for the MBPT calculation [32]. In the MBPT method, we approximate corevalence correlation effects using the second-order self-energy operator $\Sigma^{(2)}(E)$ within the Brillouin-Wigner perturbation formalism, delivering high-accuracy *ab initio* results. The valence-electron equation in this framework is represented as

$$[\hat{H} + \Sigma^{(2)}(E)]|\psi\rangle = E|\psi\rangle, \qquad (1)$$

where

$$\hat{H} = c\alpha \cdot \mathbf{p} + (\beta - 1)mc^2 + V_{\text{nuc}}(r) + V^{N-1}, \qquad (2)$$

where $V_{\text{nuc}}(r)$ is the nuclear potential and the nuclear model is the Fermi model. V^{N-1} describes the direct and exchange interaction between core electrons and valence electron. The single-electron orbital is generated by Dirac-Fock procedure.

All the Slater determinants $|I\rangle$ with frozen-core configuration form the space *P*. The projection of the true eigenstate in *P* space can be approximated as

$$|\psi\rangle = \sum_{I \in P} C_I |I\rangle.$$
(3)

The nonlocal self-energy operator $\Sigma^{(2)}(E)$, found in matrix form, can be expressed as

$$\Sigma_{IJ}^{(2)} = \sum_{M \in Q} \frac{\langle I|H|M \rangle \langle M|H|J \rangle}{E - E_M},\tag{4}$$

where the Slater determinants $|M\rangle$ belong to the space Q which contains all configurations with core excitations. Subsequently, P and Q form two complementary subspaces within the many-electron Hilbert space. Diagrammatic techniques are used in the $\Sigma^{(2)}(E)$ calculation [32]. Importantly, only one-valence-electron diagrams contribute to $\Sigma^{(2)}(E)$ in the single-valence system calculation.

Substituting $\Sigma^{(2)}(E)$ into the valence-electron equation, we arrive at

$$\sum_{J \in P} \left(H_{IJ} + \sum_{M \in Q} \frac{\langle I|H|M \rangle \langle M|H|J \rangle}{E - E_M} \right) C_J = EC_I.$$
(5)

The reduced matrix elements (RMEs) of electric dipole (E1), electric quadrupole (E2), and magnetic dipole (M1)

transition operators are evaluated by the frequency-dependent form which can be found in the standard relativistic atomic physics textbook [33]. The relativistic random-phase approximation is taken into account [34].

In our MBPT calculation, we use 50 B splines of order k = 11 and set $R_{\text{max}} = 50 a_0$. We expand the true eigenstate by using 20 *spdf* orbitals, and 35 *spdf ghikl* orbitals are used for the calculation of the self-energy operator $\Sigma^{(2)}(E)$. The Breit interaction is taken into account.

B. Dirac-Fock plus core polarizability

In this subsection, we provide a brief introduction to the DFCP method. Further details can be found in Refs. [35,36]. Similar to MBPT method, the DFCP method also initiates with the solution of the Dirac-Fock equation within the V^{N-1} potential. It uses a local core polarizability potential $V_{\text{pol}}(r)$ characterized by an angular ℓj -dependent form to replace the $\Sigma^{(2)}(E)$ operator in the valence-electron equation. The $V_{\text{pol}}(r)$ potential is defined as

$$V_{\rm pol}(r) = -\frac{\alpha^{\rm core}}{2r^4} [1 - \exp(-r^6/\rho_{\ell j}^6)], \tag{6}$$

where α^{core} is the static electric dipole polarizability of the core and the cutoff parameter $\rho_{\ell j}$ is optimized to reproduce the experimental energy levels using the Newton method.

The RMEs of E1, E2, and M1 transition operators are evaluated by the following formulas, which are the long-wavelength limitation of the corresponding RME calculation formulas in MBPT calculations. In atoms and ions with low-ionization calculations, the validity of this approximation has been demonstrated [37]:

$$\langle a||D||b\rangle = \langle \kappa_a ||\mathbf{C}^{(1)}||\kappa_b\rangle \\ \times \int_0^\infty (P_a P_b + Q_a Q_b) R_{\text{mod}}(r, 1) dr, \quad (7)$$

$$a||Q||b\rangle = \langle \kappa_a ||\mathbf{C}^{(2)}||\kappa_b\rangle \\ \times \int_0^\infty (P_a P_b + Q_a Q_b) R_{\text{mod}}(r, 2) dr, \qquad (8)$$

$$\langle a||M||b\rangle = -(\kappa_a + \kappa_b)\langle -\kappa_a||\mathbf{C}^{(1)}||\kappa_b\rangle \\ \times \int_0^\infty (P_a Q_b + Q_a P_b) r dr,$$
(9)

where D, Q, and M represent the E1, E2, and M1 transition operators, respectively. The modified function $R_{\text{mod}}(r, \ell)$ is used to approximate the correlation effect and is defined as follows:

$$R_{\rm mod}(r,\ell) = r^{\ell} \left(1 - \frac{\alpha^{\rm core}}{r^{2\ell+1}} [1 - \exp(-r^6/\rho^6)]^{1/2} \right), \quad (10)$$

where $\rho = \frac{\rho_a + \rho_b}{2}$.

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The RME of the spherical harmonic $\mathbf{C}^{(\ell)}$ can be calculated analytically:

$$\langle \kappa_a || \mathbf{C}^{(\ell)} || \kappa_b \rangle = (-1)^{J_a + 1/2} \sqrt{(2J_a + 1)(2J_b + 1)} \\ \times \begin{pmatrix} J_a & J_b & \ell \\ 1/2 & -1/2 & 0 \end{pmatrix} \pi (l_a + l_b + \ell),$$
(11)

TABLE I. Energy levels, lifetimes τ , and Landé *g* factors in the ²²⁹Th³⁺ ion. Numbers in brackets represent powers of 10. The energy level of the ground state *g* is the ionization energy which is listed in the last row labeled " E_{ion} " and the energy levels of excited states *i* are $E_i - E_g$. The subscripts "expt," "RCC," and "AO" correspond to experimental energy levels [39] and calculation results of relativistic coupled-cluster method [40] and all-order method [41], respectively.

Level	$E_{\rm DFCP}~({\rm cm}^{-1})$	$E_{\rm MBPT}~({\rm cm}^{-1})$	$E_{\rm expt}~({\rm cm}^{-1})$	$g_{ m DFCP}$	$g_{ m MBPT}$	8 _{RCC}	$\tau_{\mathrm{DFCP}} (\mathrm{ns})$	τ_{MBPT} (ns)	$ au_{\rm AO}~({\rm ns})$
$5f_{5/2}$				0.85663	0.85659	0.85635			
$6f_{5/2}$	127824	128767	127269.2	0.85701	0.85699	0.85674	0.306	0.333	0.300
$5f_{7/2}$	4325	4324	4325.33	1.14239	1.14244	1.14275	1.070[9]	1.068[9]	1.069[9]
$6f_{7/2}$	128333	129176	127815.3	1.14275	1.14278	1.14309	0.308	0.319	0.297
$6d_{3/2}$	9193	9140	9193.245	0.79966	0.79908	0.79909	1507	1149	1090
$7d_{3/2}$	120272	120148	119684.60	0.79979	0.79977	0.79949	0.642	0.663	0.667
$6d_{5/2}$	14486	14440	14486.34	1.19976	1.20008	1.20047	900.0	662.6	676.0
$7d_{5/2}$	122065	121861	121427.10	1.19988	1.19990	1.20039	0.820	0.837	0.854
$7s_{1/2}$	23131	23051	23130.75	1.99905	2.00249	2.00414	6.227[8]	6.095[8]	5.70[8]
$8s_{1/2}$	119497	119151	119621.60	1.99915	1.99971	2.00245	0.686	0.709	0.707
$7p_{1/2}$	60239	60129	60239.10	0.66578	0.66580	0.66577	1.188	1.164	1.099
$8p_{1/2}$	134421	134137	134516.50	0.66584	0.66585	0.66586	3.124	3.253	3.194
$7p_{3/2}$	73056	72976	73055.90	1.33310	1.33323	1.33401	0.656	0.666	0.632
$8p_{3/2}$	139796	139517	139870.90	1.33314	1.33318	1.33400	1.920	1.884	1.871
$E_{\rm ion}$	231065	231054	231065						

where

$$\pi(x) = \begin{cases} 1, & \text{if } x \text{ is even} \\ 0, & \text{if } x \text{ is odd} \end{cases}.$$
(12)

By directly diagonalizing the Hamiltonian, we obtain the complete set of pseudostates, which can be used in sumover-states calculations to consider the contributions from high-excited states and continuum states.

In DFCP calculation, we use 100 B splines of order k = 9 and set $R_{\text{max}} = 100 a_0$ to make sure we can get enough bound states. The static E1 polarizability of the core is fixed as 7.7 a.u. [38] and the experimental energy levels from Blaise and Wyart are used [39]. We use the experimental energy levels of 7*s*, 7*p*, 6*d*, and 5*f* in the optimization procedure of the cutoff parameters.

Table I presents a comprehensive comparison of energy levels, lifetimes, and Landé *g* factors in the 229 Th³⁺ ion. We use the MBPT method and DFCP method in our calculations and benchmark the results against other high-accuracy calculation methods [40,41] and experimental values [39].

Remarkably, the DFCP method exhibits exceptional accuracy, with an average relative error of just 0.17% when compared to experimental energy levels. Even in the most challenging cases, the largest relative error observed is a mere 0.59% for the $7d_{5/2}$ state. These results underscore the superior performance of the DFCP calculations for energy levels.

For the calculations of lifetimes and Landé *g* factors, the results from the MBPT method are closely aligned with those from other high-accuracy methods, confirming the reliability of MBPT calculations in transition RMEs. This reliability is further underscored by the data in Table II. As shown in Table II, compared with the transition RMEs calculated by the DFCP method and other high-accuracy relativistic methods, there are some transition RMEs with large deviation, which significantly increase the deviation of lifetimes for certain states, such as $6d_{3/2}$ and $6d_{5/2}$ states. Despite the inclusion of these RMEs with large deviations, the mean deviation of

E1 RMEs remains at 6%, indicating a reasonable level of accuracy in the DFCP calculation of transition RMEs.

III. RESULTS AND DISCUSSION

Here we present our findings on the potential of the finestructure transition of $5f_{5/2} \rightarrow 5f_{7/2}$ as a new ionic clock with accuracy of 10^{-18} level. The energy-level diagram is shown in Fig. 1. The narrow clock transition linewidth of $\Gamma = 0.15$ Hz

TABLE II. The transition RMEs between low-lying states in atomic units. The "RCC" represents calculation results of relativistic coupled-cluster method [40].

Lower	Upper	Туре	DFCP	MBPT	RCC
$5f_{5/2}$	$5f_{7/2}$	M1	1.8506	1.8524	1.8514
$5f_{5/2}$	$5f_{7/2}$	E2	0.0894	1.0674	1.1046
$5f_{5/2}$	$6d_{3/2}$	E1	1.2985	1.4871	1.5616
$5f_{5/2}$	$6d_{5/2}$	E1	0.3559	0.4105	0.4198
$5f_{5/2}$	$7p_{1/2}$	E2	3.5468	2.8550	3.0570
$5f_{5/2}$	$7p_{3/2}$	M1	0.0000	0.0004	
$5f_{5/2}$	$7p_{3/2}$	E2	1.7043	1.3058	1.4220
$5f_{7/2}$	$6d_{5/2}$	E1	1.6642	1.8995	1.9530
$5f_{7/2}$	$7p_{3/2}$	E2	4.4486	3.5244	3.7658
$6d_{3/2}$	$6d_{5/2}$	M1	1.5466	1.5533	1.5500
$6d_{3/2}$	$6d_{5/2}$	E2	3.6819	4.0556	4.0577
$6d_{3/2}$	$7s_{1/2}$	M1	0.0000	0.0022	0.0012
$6d_{3/2}$	$7s_{1/2}$	E2	6.8769	6.9381	7.0929
$6d_{3/2}$	$7p_{1/2}$	E1	2.0394	2.0553	2.1360
$6d_{3/2}$	$7p_{3/2}$	E1	0.8415	0.8142	0.8539
$6d_{5/2}$	$7s_{1/2}$	E2	8.8826	9.0786	9.1844
$6d_{5/2}$	$7p_{3/2}$	E1	2.7048	2.6847	2.7665
$7s_{1/2}$	$7p_{1/2}$	E1	2.3297	2.3657	2.4375
$7s_{1/2}$	$7p_{3/2}$	E1	3.3011	3.2881	3.3919
$7p_{1/2}$	$7p_{3/2}$	M1	1.1298	1.1289	1.1289
$7p_{1/2}$	$7p_{3/2}$	E2	14.9453	14.9390	15.0456



FIG. 1. Schematic energy-level diagram of the 229 Th³⁺ ion excluding hyperfine structure. Energy levels are not scaled.

corresponds to a long lifetime of $\tau = 1.07$ s. These characteristics result in a high quality factor of $Q = 8.71 \times 10^{14}$ and an instability limit of $\sigma_y(t) \approx 3.07 \times 10^{-15} / \sqrt{t/s}$ which is closed to the ¹⁷¹Yb⁺ E2 clock transition [5,25].

For the cooling of the ²²⁹Th³⁺ ion, we could utilize the E1 transition $5f_{5/2} \rightarrow 6d_{3/2}$, aiming to reach the ground state of oscillation in the trap. The linewidth of cooling transition is $\Gamma = 153$ kHz, which is well below the typical frequency $\nu = 1$ MHz of the ²²⁹Th³⁺ ion in the trap. In the strong binding regime $\Gamma < \nu$, the cooling temperature limit can be estimated by

$$T_{\min} = h\nu/k_B \ln(1 + \langle n \rangle^{-1}), \qquad (13)$$

where $\langle n \rangle = \Gamma^2 / \nu^2 \approx 0.02$ represents the mean occupation number [42]. This estimation yields a cooling temperature limit of $T_{\rm min} = 13 \ \mu$ K. Although reaching this temperature limit is challenging due to cooling efficiency and laserinduced heating of ions, we can reasonably expect to achieve a temperature of several tens of μ K. In addition, sympathetic cooling with ⁸⁶Sr⁺ is also a feasible option. Because of the close charge-to-mass ratios of two ions and the mature laser cooling technology of the Sr⁺ ion, sympathetic cooling can be very efficient. The E1 transition wavelengths calculated by experimental energy levels, transition rates, and branching ratios calculated by MBPT method are given in Table III,

TABLE III. Transition wavelengths λ and rates *A* for E1 transition between low-lying states. Branching ratios for each transition are also shown.

Upper	Lower	λ (nm)	$A(s^{-1})$	Branching ratios
$6d_{3/2}$	$5f_{5/2}$	1087.76	8.70×10^{5}	1
$6d_{5/2}$	$5f_{5/2}$	690.31	1.73×10^{5}	0.12
- /	$5f_{7/2}$	984.15	1.28×10^{6}	0.88
$7p_{1/2}$	$6d_{3/2}$	195.90	5.69×10^{8}	0.66
- /	$7s_{1/2}$	269.48	2.90×10^{8}	0.34
$7p_{3/2}$	$6d_{3/2}$	156.59	8.75×10^{7}	0.06
/	$6d_{5/2}$	170.74	7.34×10^{8}	0.49
	$7s_{1/2}$	200.30	6.81×10^8	0.45

TABLE IV. Hyperfine-structure constants *A* and *B* for ground state $5f_{5/2}$ and clock state $5f_{7/2}$ in ²²⁹Th³⁺. The experiment values come from Ref. [45].

State	$A_{\rm MBPT}$ (MHz)	A _{expt} (MHz)	$B_{\rm MBPT}~({ m MHz})$	B _{expt} (MHz)
$5f_{5/2}$	80.77	82.2(6)	2247	2269(9)
$5f_{7/2}$	26.31	31.4(7)	2622	2550(12)

for enhancing the comprehension of the cooling mechanism and the potential existence of a dark state. In transition rate calculations, experimental energy levels are used [39].

The presence of an external magnetic field results in Zeeman shift in the energy levels, which can be expanded into linear and quadratic terms:

$$\Delta E_M = C_{M1}B + C_{M2}B^2, \qquad (14)$$

where $C_{M1} = \mu_B g_J M$ represents the linear dependence on the magnetic quantum number M. This linear Zeeman shift can be suppressed in cases where M = 0 or when the linear Zeeman shifts in the $5f_{5/2}$ and $5f_{7/2}$ states have a closed value. The second-order Zeeman shift arises from the interaction between hyperfine-structure states and can be calculated using second-order perturbation theory [43]:

$$C_{M2}(F,M) = -(\mu_B g_J)^2 \sum_{F'} \frac{\langle F'M | J_z | FM \rangle^2}{E_{F'} - E_F},$$
 (15)

where only terms with $F' = F \pm 1$ contribute to the nonzero value of the second-order Zeeman coefficient. Therefore, selecting adjacent hyperfine-structure states with a large energy splitting can effectively suppress second-order Zeeman shift.

To estimate second-order Zeeman shift, we calculate the hyperfine-structure constants A and B for ground state $5f_{5/2}$ and clock state $5f_{7/2}$ in ²²⁹Th³⁺. In hyperfine-structure cal-culation, we adopt the nuclear magnetic dipole moment $\mu = 0.360 \mu_N$ and nuclear electric quadrupole moment Q =3.11 eb [44]. Table IV presents the calculation results and experimental values of hyperfine-structure constants. Here, we exclusively use the MBPT method in the calculation of hyperfine-structure constants. This choice is based on the fact that the DFCP method, although excellent in many respects, is not suitable for this calculation due to its limited reliability in characterizing wave-function properties in the vicinity of the nucleus, particularly for states featuring high angular momentum. The reason for this limitation stems from the DFCP method's utilization of the local core polarizability potential as a substitute for the second-order self-energy operator $\Sigma^{(2)}(E)$ with strong nonlocal properties at the near nucleus.

Table V presents the calculation results of hyperfinestructure energy levels and second-order Zeeman coefficients of the $5f_{5/2}$ and $5f_{7/2}$ states with M = 0 in ²²⁹Th³⁺. For the transition $5f_{5/2}$, F = 5, $M = 0 \rightarrow 5f_{7/2}$, F = 6, M = 0, the differential second-order Zeeman coefficient is $\Delta C_{M2} =$ -309.0 Hz/mT^2 . Considering a typical value of $B = 1 \mu$ T, this results in a fractional shift of $\Delta f_M/f_{clock} = -2.383 \times 10^{-18}$. For comparison, we do the same calculation using experimental values of hyperfine-structure constants, and the differential second-order Zeeman coefficient changes to $\Delta C_{M2} = -304.7 \text{ Hz/mT}^2$; this shows that even though our

TABLE V. Hyperfine-structure and second-order Zeeman coefficients of $5f_{5/2}$ and $5f_{7/2}$ states with M = 0.

$5f_{5/2}$				5 <i>f</i>	7/2
F	$\frac{E_F}{h}$ (MHz)	C_{M2} (Hz/mT ²)	F	$\frac{E_F}{h}$ (MHz)	C_{M2} (Hz/mT ²)
0	866.2	5745.0	1	1108.7	2162.2
1	407.7	-3049.5	2	412.1	936.1
2	-307.1	71.1	3	-351.7	5260.1
3	-873.7	-8858.3	4	-845.8	-18531.7
4	-685.5	5733.8	5	-620.6	-2168.0
5	1066.6	358.0	6	885.7	48.9

hyperfine-structure-constant calculations are not within the range of experimental uncertainty, the impact of this difference on our conclusion could be negligible.

Since the magnetic field in the ion trap can be finely controlled with an uncertainty on the order of nT, the fractional frequency shift uncertainty can be reduced by two or three orders of magnitude, reaching the level of 10^{-20} or even lower.

The presence of an external electric-field gradient interacts with atom states possessing a nonzero quadrupole moment, resulting in electric quadrupole shift. This shift can be evaluated by

$$\Delta f_Q = -\frac{\Delta \langle Q_0 \rangle}{2h} \frac{\partial E_z}{\partial z},\tag{16}$$

where $\langle Q_0 \rangle \equiv \langle \gamma IJFM | Q_0 | \gamma IJFM \rangle$ represents the expectation value of the quadrupole operator Q_0 , which can be calculated as follows:

$$\langle \gamma JIFM|Q_0|\gamma JIFM \rangle = (-1)^{J+I+F} [3M^2 - F(F+1)] \\ \times \sqrt{\frac{2F+1}{(2F+3)(F+1)(2F-1)}} \\ \times \begin{cases} J & 2 & J \\ F & I & F \end{cases} \langle \gamma J||Q||\gamma J \rangle.$$
(17)

The electric quadrupole moment $\Theta(\gamma J)$ also is related to the diagonal elements of the E2 operator:

$$\Theta(\gamma J) = \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix} \langle \gamma J || Q || \gamma J \rangle.$$
 (18)

To estimate the electric quadrupole shift, we calculate the E2 RME $\langle \gamma J || Q || \gamma J \rangle$ and electric quadrupole moment $\Theta(\gamma J)$ of the ground state and clock state. Table VI displays the calculation results obtained by the MBPT method and the DFCP method, and compares to the calculation results of all-order

TABLE VI. Electric quadrupole moment of ground state and clock state. The subscript "bare" means the modified function is not used in DFCP calculation. The subscript "mod" means the modified function is used in DFCP calculation. The subscript "AO" corresponds to the calculation result of all-order method [46].

State	Θ_{DF}	Θ_{MBPT}	Θ_{bare}	Θ_{mod}	Θ_{AO}
$5f_{5/2}$	0.9162	0.6046	0.0875	0.6237	0.624(14)
$J_{7/2}$	1.11/3	0.7327	0.0197	0.7815	

method [46]. Specifically, we compare the difference between the MBPT and DF calculations, and whether the modified function of Eq. (10) is used in the DFCP calculation; the results show that the modification function greatly improves the DFCP results, and even changes the order of magnitude. After using the modified function, the results of DFCP are in perfect agreement with those of the all-order method.

Using the calculation results of MBPT method and considering a typical value of $\frac{\partial E_c}{\partial z} = 500 \text{ V/cm}^2$, we estimate the electric quadrupole shift $\Delta f_Q = 0.470 \text{ Hz}$ for the transition $5f_{5/2}$, F = 5, $M = 0 \rightarrow 5f_{7/2}$, F = 6, M = 0, corresponding to a fractional shift of $\Delta f_Q/f_{\text{clock}} = 3.549 \times 10^{-15}$. By changing the total angular momentum quantum number F for the clock state and ground state while keeping the magnetic quantum number M = 0, we can find the worst-case and best-case fractional shifts, corresponding to $\Delta f_Q/f_{\text{clock}} = 7.400 \times 10^{-15}$ and 1.782×10^{-15} , respectively. For all F states, the fractional frequency shift consistently remains on the order of 10^{-15} . Using the calculation results of DFCP method, the electric quadrupole shift changes to $\Delta f_Q = 0.460 \text{ Hz}$ for the transition $5f_{5/2}$, F = 5, $M = 0 \rightarrow 5f_{7/2}$, F = 6, M = 0, and the fractional frequency shift remains on the order of 10^{-15} .

The electric quadrupole fractional shift can reach the order of 10^{-19} by suppressing it for three to four orders of magnitude, which is experimentally achievable through rotating the electric-field direction to a magic angle and averaging the m_F sublevels [30,47].

The BBR shift caused by environmental temperature can be evaluated by

$$\Delta f_{\rm BBR} = -\frac{\Delta \alpha^{S}}{2h} (8.319\,430\,\mathrm{V/cm})^{2} (T/300\,\mathrm{K})^{4}.$$
 (19)

Here $\Delta \alpha^{S} = \alpha_{5f7/2}^{S} - \alpha_{5f5/2}^{S}$ and α^{S} is the scalar static E1 polarizabilities, which can be calculated by summing over the contributions from bound and continuum states:

$$\alpha_g^S = \frac{2}{3(2J_g+1)} \sum_i \frac{|\langle i||D||g\rangle|^2}{\epsilon_{ig}},\tag{20}$$

where ϵ_{ig} denotes the energy difference between state *i* and *g*.

For the state with total angular momentum J > 1/2, there is a tensor component of polarizability:

$$\alpha_{J_g}^T = 4 \left[\frac{5J_g(2J_g - 1)}{6(J_g + 1)(2J_g + 1)(2J_g + 3)} \right]^{1/2} \\ \times \sum_i (-1)^{J_g + J_i} \left\{ \begin{array}{cc} 1 & 1 & 2\\ J_g & J_g & J_i \end{array} \right\} \frac{|\langle i||D||g\rangle|^2}{\epsilon_{ig}}.$$
(21)

The coupling of angular momentum J of atomic states and nuclear spin I changes the tensor polarizability. For the state with total angular momentum F > 1/2, the tensor component

			5f _{7/2}			
Contrib. (a.u.)	α_g^S (a.u.)	$\alpha_{J_g}^T$ (a.u.)	Contrib. (a.u.)	α_g^S (a.u.)	$\alpha_{J_g}^T$ (a.u.)	
$\overline{6d_{3/2}}$	5.866	-5.866	$6d_{5/2}$	6.494	-6.494	
$5g_{7/2}$	0.048	-0.017	$5g_{9/2}$	0.097	-0.045	
6g _{7/2}	0.035	-0.013	$6g_{9/2}$	0.044	-0.020	
$7g_{7/2}$	0.027	-0.010	$7g_{9/2}$	0.030	-0.014	
Tail	0.487	-0.243	Tail	0.239	-0.109	
Core	7.70		Core	7.70		
Total	14.16	-6.15	Total	14.60	-6.68	
AO	14.67(60)	-6.07(53)	AO	14.84(59)	-6.95(52)	

TABLE VII. Contributions to the scalar and tensor polarizabilities of $5f_{5/2}$ and $5f_{7/2}$ states in the ²²⁹Th³⁺ ion. The "AO" represents calculation results of all-order method [46].

of polarizability changes to

$$\alpha_{F_g}^{T} = (-1)^{J_g + F_g + I} \begin{cases} F_g & J_g & I \\ J_g & F_g & 2 \end{cases}$$

$$\times \sqrt{\frac{F_g(2F_g - 1)(2F_g + 1)}{(2F_g + 3)(F_g + 1)}}$$

$$\times \sqrt{\frac{(2J_g + 3)(2J_g + 1)(J_g + 1)}{J_g(2J_g - 1)}} \alpha_{J_g}^{T}.$$
(22)

The tensor polarizability has no effect on BBR shifts, but it affects ac Stark shifts caused by the probe beam. Assuming that averaging the m_F sublevels is used to eliminate the electric quadrupole shifts, the contribution of tensor polarizability to ac Stark shifts is also eliminated. The ac Stark shifts can be suppressed by adopting the hyper-Ramsey interrogation scheme [30].

The calculation results of static E1 polarizabilities are shown in Table VII. In this calculation, for RMEs with dominant contribution to polarizabilities, we use the calculation results of MBPT method and itemize their contributions, and for the rest of the RMEs we use the calculation results of DFCP method and treat it as a tail of total polarizabilities, and the energy levels measured by experiment are used [39]. The combination of MBPT method with DFCP method enables us to complete the state summation with both computational accuracy and efficiency, and determines the polarizabilities with high precision. The differential scalar static E1 polarizability was calculated as $\Delta \alpha^{S} = 0.44$ a.u., which is consistent with 0.17 ± 1.05 a.u. calculated by allorder method [46]. For temperatures T = 77 and 297 K, corresponding to liquid nitrogen temperature and room temperature, respectively, we obtain BBR shifts of $\Delta f_{BBR} =$ -16 and -3.6 mHz, resulting in fractional frequency shifts of $\Delta f_{\text{BBR}}/f_{\text{clock}} = -1.3 \times 10^{-19}$ and -2.8×10^{-17} , respectively. For comparison, we do the same calculation using the differential scalar static E1 polarizability $\Delta \alpha^{S} = 0.17$ a.u. calculated by all-order method [46], and the BBR shifts change to $\Delta f_{BBR} = -6.0$ and -1.4 mHz for liquid nitrogen temperature and room temperature, respectively. Both results are still within the same order of magnitude, and the fact that BBR shifts of ²²⁹Th³⁺ at low temperature are negligible remains unchanged.

The micromotion effect induces a Stark shift from the trapping field, which can be estimated by [49]

$$\frac{\Delta f_{MM, \, \text{Stark}}}{f_{\text{clock}}} = -\frac{3k_B T}{2} \frac{\Delta \alpha^S}{h f_{\text{clock}}} \left(\frac{m\Omega^2}{e^2}\right)^2.$$
 (23)

The micromotion effect also induces a second-order Doppler shift, which can be estimated by [49]

$$\frac{\Delta f_{MM,D2}}{f_{\text{clock}}} = -\frac{3k_BT}{2mc^2}.$$
(24)

Since the ²²⁹Th³⁺ ion can be sympathetically cooled by the ⁸⁶Sr⁺ ion, we assume that the ²²⁹Th³⁺ ion at least can reach the temperature T = 1 mK of the Sr⁺ ionic clock [31]. In the case of ²²⁹Th³⁺, secular frequency $\Omega \approx 2$ MHz. Hence the fractional shift is $\Delta f_{MM, \text{Stark}}/f_{\text{clock}} = -1 \times 10^{-22}$ and $\Delta f_{MM,D2}/f_{\text{clock}} = -6 \times 10^{-19}$. Therefore, we can expect the large mass and small differential scalar polarizabilities of the ²²⁹Th³⁺ ion to suppress the micromotion shift to the level of 10^{-19} . Extremely low-temperature limits can further suppress this frequency shift by one or two orders of magnitude.

Table VIII lists the fractional shifts caused by different systematic effects in 229 Th³⁺. From the above estimations, we conclude that the 229 Th³⁺ ion has the potential to achieve an accuracy level of 10^{-18} .

For probing the variations of fine-structure constant, measuring time variations of the frequency ratio between two clock transitions has become a common approach [48]. This method offers lower statistical uncertainty compared to absolute frequency shift measurements. Moreover, when dealing with two clock transitions within the same ion, both clock transitions are measured in precisely the same physical system; many causes of common-mode noise can be rejected during the comparison, facilitating the experimental process

TABLE VIII. Evaluation of fractional shifts caused by different systematic effects.

Effect	Fractional shift
BBR shift (77 K)	-1.3×10^{-19}
BBR shift (297 K)	$-2.8 imes 10^{-17}$
Micromotion shift	-6×10^{-19}
Second-order Zeeman shift	-2.383×10^{-18}
Electric quadrupole shift	-3.549×10^{-15}

[25]. Although the frequency ratio between the ¹⁷¹Yb⁺ E3 clock and strontium optical lattice clock can achieve better stability, the efficiency of the experimental process enables a long-term measurement of the frequency ratio between two clock transitions on the same ¹⁷¹Yb⁺ ion, given the state-of-the-art result of $\dot{\alpha}/\alpha = 1.8(2.5) \times 10^{-19}/\text{yr}$ [5].

The same frequency ratio measurement method used for 171 Yb⁺ can also be used for 229 Th³⁺. In the case of 229 Th³⁺, fractional shift of the frequency ratio can be estimated as follows:

$$\Delta R/R = \frac{1 + \Delta f_{\rm n}/f_{\rm n}}{1 + \Delta f_{\rm e}/f_{\rm e}} - 1 \approx \frac{\Delta f_{\rm n}}{f_{\rm n}} - \frac{\Delta f_{\rm e}}{f_{\rm e}}, \qquad (25)$$

where f_n and f_e correspond to the nuclear transition frequency and electron transition frequency, respectively. Δf_n and Δf_e correspond to the nuclear transition frequency shift and electron transition frequency shift, respectively. Hence some frequency shifts which have the same fraction frequency shifts for two transitions can cancel each other in this ratio, such as those caused by secular motion and gravitational effect.

Time variation of the fine-structure constant is linearly reflected in time variations of the frequency ratio:

$$\dot{R}/R = (K_{\rm n} - K_{\rm e})\dot{\alpha}/\alpha,$$
 (26)

where *K* is the sensitive factor. It has been reported that the nuclear transition frequency in ²²⁹Th³⁺ is incredibly sensitive to variations of the fine-structure constant with the sensitive factor $K_n = -(8.2 \pm 2.5) \times 10^3$, which is greater than that of most highly charged ions [28]. Calculations by using the MBPT and DFCP methods have yielded a sensitive factor $K_e = 1.2(4)$ for the electronic transition, and the uncertainty was set as the difference between the results of MBPT and DFCP methods. This result is in agreement with the early calculation $K_e = 1.3$ [29].

²²⁹Th³⁺ not only provides good clock performance but also exhibits a great sensitivity factor difference. This allows for a precise measurement of the time variations of the fine-structure constant. Given the result $K_n - K_e \approx 10^3$ and assuming that $5f_{5/2} \rightarrow 5f_{7/2}$ clock transition can achieve the accuracy level of 10^{-18} , we anticipate that achieving a measurement precision for the time variations of the frequency ratio \dot{R}/R at the $10^{-18}/\text{yr}$ level will allow us to measure the time variations of the fine-structure constant $\dot{\alpha}/\alpha$ at the $10^{-21}/\text{yr}$ level.

IV. CONCLUSION

In conclusion, we delved into the $5f_{5/2} \rightarrow 5f_{7/2}$ transition of ²²⁹Th³⁺, showcasing its potential as an ion clock with accuracy of 10^{-18} . The ²²⁹Th³⁺ clock exhibits a notable advantage over other ionic optical clocks-it demonstrates lower BBR shifts $\Delta f_{BBR} = -16 \,\mu\text{Hz}$ in the liquid nitrogen temperature, and both the superheavy mass of the ²²⁹Th³⁺ nucleus and cooling limit temperature of approximately 13 µK provide a significant advantage in suppressing motion-induced frequency shifts, which is a benefit to improve the accuracy of the ²²⁹Th nuclear clock. As a result, ²²⁹Th³⁺ not only performs well on clock accuracy but also, owing to the distinct sensitivity factor difference, allows for an accurate measurement of the time variations of the fine-structure constant. Actually, there are other atomic optical clocks with better accuracy and stability available for frequency comparison with ²²⁹Th³⁺ nuclear transition to test the variation of the fine-structure constant. Comparing the $5f_{5/2} \rightarrow 5f_{7/2}$ transition and nuclear transition in ²²⁹Th³⁺ offers an alternative choice to perform the measurement on the temporal variation of fine-structure constant within a single experimental apparatus.

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