

## Clock-related properties of Lu<sup>+</sup>

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Singly ionized lutetium has a number of fortuitous properties well suited for a design of an optical clock and corresponding applications. In this work, we study Lu<sup>+</sup> properties relevant to a development of the clock using the relativistic high-precision method combining configuration interaction and the linearized coupled-cluster approaches. The systematic effects due to interaction of an external electric-field gradient with the quadrupole moment and the dynamic correction to the blackbody radiation shift are studied and uncertainties are estimated. The value of the  $5d6s\ ^1D_2$  polarizability is predicted. We also demonstrate that Lu<sup>+</sup> is a good candidate to search for variation of the fine-structure constant.

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### I. INTRODUCTION

Further development of frequency standards is important for many applications requiring an improved precision and high stability, such as searches for the variation of the fundamental constants [1], tests of the Lorentz invariance [2,3], dark matter searches [4–6], study of many-body physics and quantum simulations [7,8], relativistic geodesy [9], very long baseline interferometry [10], gravitational wave detection [11], and others. The systematic uncertainties at the  $10^{-18}$  level, two orders of magnitude better than for the Cs clock currently defining the SI second [12], were recently demonstrated with both neutral atom lattice clock based on the  $^1S_0 - ^3P_0^o$  transition in Sr [13] and a single trapped ion clock based on the electric octupole  $^2S_{1/2} - ^2F_{7/2}^o$  transition in  $^{171}\text{Yb}^+$  [14].

A bottleneck to an improvement of the trapped ion clocks is the relatively low stability achieved with a single ion. Proposed solutions of this problem include a development of clocks with ion chains [15] and large ion crystals [16,17]. In the recent paper [15] the authors have demonstrated a possibility to control systematic frequency uncertainties at the  $10^{-19}$  level in linear Coulomb crystals for In<sup>+</sup> clock sympathetically cooled with Yb<sup>+</sup> ions.

An important problem affecting both the neutral atom and trapped ion clocks is the blackbody radiation (BBR) shift [18]. Small BBR shift at room temperature is a highly desirable feature that simplifies the clock design removing the requirement to maintain either precise temperature control [13] or cryogenic cooling [19].

A singly ionized lutetium was suggested as a promising novel clock candidate, having a number of favorable properties leading to low systematic shifts [16,17,20]. There are two clock transitions with favorable systematics: the highly forbidden  $6s^2\ ^1S_0 - 5d6s\ ^3D_1\ M1$  transition at 848 nm and the  $6s^2\ ^1S_0 - 5d6s\ ^3D_2\ E2$  transition at 804 nm. A joint experimental and theoretical investigation of the  $6s^2\ ^1S_0 - 5d6s\ ^3D_{1,2}$  clock

transitions in the Lu<sup>+</sup> was carried out in Ref. [21]. The dc and ac polarizabilities of the clock states, lifetimes of the low-lying states, hyperfine quenching rate of the  $6s6p\ ^3P_0^o$  state, and other properties were reported. The BBR frequency shift of the  $^1S_0 - ^3D_1$  clock transition was also calculated in Ref. [22].

In 2018 the differential scalar polarizabilities of these clock transitions were measured at the wavelength  $\lambda = 10.6\ \mu\text{m}$  in Ref. [23] to be  $\Delta\alpha_0(^3D_1 - ^1S_0) = 0.059(4)$  a.u. and  $\Delta\alpha_0(^3D_2 - ^1S_0) = -1.17(9)$  a.u.. From this, Arnold *et al.* [23] extracted the fractional BBR frequency shift for the  $^1S_0 - ^3D_1$  transition to be  $-1.36(9) \times 10^{-18}$  at 300 K. This shift is the lowest of any established atomic optical clocks. In particular, it is a factor of six smaller than the fractional BBR shift for the  $^1S_0 - ^3P_0^o$  transition in Al<sup>+</sup> [24].

Another important systematic issue, crucial to an operation of ion clocks, is the micromotion-induced shift. It is driven by the rf-trapping field and leads to an ac Stark shift and a second-order Doppler shift. If the differential scalar polarizability of the clock transition is negative, there is a trap drive frequency at which the ac Stark and second-order Doppler shifts cancel each other and the micromotion shift vanishes [25,26]. A suppression of this effect in a case of ion clock operating with large ion crystals was discussed in Ref. [16]. Thus, the negative sign of the  $^1S_0 - ^3D_2$  differential polarizability makes this transition a good candidate for an implementation of the micromotion cancellation scheme.

In a discussion of the experimental scheme in Ref. [21] it was noted that an optical pumping via the  $^3P_1^o$  level leads to an undesired population of the  $^1D_2$  state. A decay of this state during optical pumping may be significant systematic effect. The  $^1S_0 - ^1D_2$  transition can be used for diagnostic measurements and potentially a clock transition [27]. As a result, it is important to calculate its properties, in particular the polarizability and the quadrupole shift.

Thus, further investigations of the clock-related properties of Lu<sup>+</sup> and corresponding systematic shifts are urgently

needed, which is the subject of this work. In Sec. II we study relevant properties of the  $5d6s\ ^1D_2$  state, including  $E1$  transition amplitudes and the static polarizability. In Sec. III we discuss the systematic effect caused by the interaction of external electric-field gradient with the quadrupole moment of an atomic state. In Sec. IV we calculate dynamic corrections to the BBR shifts of the  $6s^2\ ^1S_0$ ,  $5d6s\ ^3D_{1,2}$ , and  $5d6s\ ^1D_2$  energy levels. Section V is devoted to study of sensitivity of  $\text{Lu}^+$  to variation of the fine-structure constant, and Sec. VI contains concluding remarks. If not specified otherwise, we use atomic units.

## II. METHOD OF CALCULATION AND THE $5d6s\ ^1D_2$ POLARIZABILITY

A detailed description of the  $^1S_0$  and  $^3D_{1,2}$  polarizability calculations is given in Ref. [21]. Here we use the same approach to calculate the static polarizability of the  $5d6s\ ^1D_2$  state of  $\text{Lu}^+$ . We use the high-precision relativistic methods, combining configuration interaction (CI) with the many-body perturbation theory (MBPT) or with the linearized coupled-cluster (all-order) method [28,29]. The energies and wave functions are determined from the time-independent multiparticle Schrödinger equation

$$H_{\text{eff}}(E_n)|n\rangle = E_n|n\rangle, \quad (1)$$

with the effective Hamiltonian defined as

$$H_{\text{eff}}(E) = H_{\text{FC}} + \Sigma(E). \quad (2)$$

Here  $H_{\text{FC}}$  and  $\Sigma$  are the Hamiltonian in the frozen core approximation and the energy-dependent correction, respectively. The latter takes into account virtual core excitations in the second order of the perturbation theory (the CI+MBPT method) or in all orders (the CI+all-order method).

The static electric dipole polarizability of the  $|0\rangle$  state is given by

$$\alpha(0) = 2 \sum_k \frac{|\langle k|D_0|0\rangle|^2}{E_k - E_0}, \quad (3)$$

where  $D_0$  is the  $z$ -component of the effective electric dipole operator, including the random-phase approximation (RPA), core-Brueckner ( $\sigma$ ), two-particle (2P), structural radiation (SR), and normalization corrections described in Ref. [30].

The scalar static polarizability  $\alpha_0$  can be conventionally separated into three parts:

$$\alpha_0 = \alpha_0^v + \alpha^c + \alpha^{vc}. \quad (4)$$

Here  $\alpha_0^v$  is the valence polarizability,  $\alpha^c$  is the ionic core polarizability, and a small term  $\alpha^{vc}$  accounts for possible excitations to the occupied valence shells. The valence part of the scalar polarizability,  $\alpha_0^v$ , as well as the tensor polarizability,  $\alpha_2$ , are calculated by solving inhomogeneous equation in the valence space. We use the Sternheimer [31] or Dalgarno-Lewis [32] method implemented in the CI+all-order approach [21,33]. The  $\alpha^c$  and  $\alpha^{vc}$  terms are evaluated using the RPA. The  $\alpha^{vc}$  term is calculated as a sum of contributions from the individual electrons, i.e.,  $\alpha^{vc}(5d6s) = \alpha^{vc}(5d) + \alpha^{vc}(6s)$ .

To establish the dominant contributions of the intermediate states to the scalar polarizability, we substitute the electric-dipole matrix elements (MEs) and energies according to the

TABLE I. Contributions to  $\alpha_0(0)$  of the  $5d6s\ ^1D_2$  state (in a.u.). The contributions of several lowest-lying intermediate states are listed separately with the corresponding absolute values of  $E1$  reduced MEs given (in a.u.) in column labeled “ $D$ .” The theoretical and experimental [34] transition energies are (c- )

TABLE II. The static scalar ( $\alpha_0$ ) and tensor ( $\alpha_2$ ) polarizabilities, obtained in the CI+MBPT+RPA, CI+all-order+RPA, and CI+all-order+AC approximations, are presented (in a.u.) in columns (1), (2), and (3), respectively. The recommended values are listed in the last column. The uncertainties are given in parentheses.

Polarizability	(1)	(2)	(3)	Recommend.
$\alpha_0(6s^2\ ^1S_0)^a$	62.5	63.3	63.0	63.0(0.8)
$\alpha_0(5d6s\ ^1D_2)$	54.3	56.0	55.3	55.3(1.7)
$\alpha_2(5d6s\ ^1D_2)$	14.5	15.2	15.7	15.7(1.2)
$\alpha_0(^1D_2) - \alpha_0(^1S_0)$	-8.2	-7.3	-7.7	-7.7(0.9)

<sup>a</sup>These results were obtained in Ref. [21].

In rows labeled “Total ( $J_n = 1, 2, 3$ )” we give the total contribution of *all* intermediate states with the fixed total angular momentum  $J_n$ . The final value of  $\alpha_0^v$  is found as the sum of the values given in these rows.

The contributions from  $\alpha^c$  and  $\alpha^{vc}$  terms are listed together in the respective row. Taking into account that the main contribution to the  $^1D_2$  level comes from the  $5d_{5/2}6s$  configuration (73%), we determined  $\alpha^{vc}$  terms for the  $^1D_2$  polarizability as  $\alpha^{vc}(5d_{5/2}) + \alpha^{vc}(6s)$ . In the row labeled “Total” we present the total value of the scalar static  $^1D_2$  polarizability. The result obtained with use of theoretical energies, considered as recommended, is given in the row labeled “Recommended.”

To determine uncertainty of the polarizability we have also calculated its value using two other approximations: the CI+MBPT+RPA and CI+all-order+RPA. In both cases only RPA corrections were included. The results obtained in the CI+MBPT+RPA, CI+all-order+RPA, and CI+all-order+AC approximations (where abbreviation “AC” means *all corrections*, including RPA,  $\sigma$ , 2P, SR, and normalization) are presented in Table II in columns (1), (2), and (3), correspondingly. All calculations are performed with theoretical energies. The uncertainties were estimated as the spread of the values in columns (1)–(3).

We consider the values obtained in the CI+all-order+AC approximation as the final ones. A comparison of columns (2) and (3) in Table II shows that the corrections beyond RPA only slightly change the value of the  $^1D_2$  polarizability. Our final result for the  $^1D_2$  scalar static polarizability is  $\alpha_0(5d6s\ ^1D_2) = 55.3(1.7)$  a.u.

### III. ELECTRIC QUADRUPOLE SHIFT

The Hamiltonian  $H_Q$  describing the interaction of an external electric-field gradient with the quadrupole moment of an atomic state  $|\gamma JIFM\rangle$  (where  $J$  is the total electronic angular momentum,  $I$  is the nuclear spin,  $\mathbf{F} = \mathbf{J} + \mathbf{I}$  is the total angular momentum,  $M$  is the projection of  $\mathbf{F}$ , and  $\gamma$  encapsulates all other electronic quantum numbers) is given by [35]

$$H_Q = \sum_{q=-2}^2 (-1)^q \nabla \mathcal{E}_q^{(2)} Q_q. \quad (5)$$

The  $q = 0$  component of  $\nabla \mathcal{E}^{(2)}$  can be written as [35,36]

$$\nabla \mathcal{E}_0^{(2)} = -\frac{1}{2} \frac{\partial \mathcal{E}_z}{\partial z}, \quad (6)$$

TABLE III. The energy levels (in  $\text{cm}^{-1}$ ), reduced diagonal MEs of the  $M1$  (in  $\mu_0$ ) and  $Q$  (in a.u.) operators, and electric quadrupole moments  $\Theta$  (in a.u.) for the  $^3D_J$  and  $^1D_2$  states.

Level	Energy	Operator	ME	$\Theta$
$6s5d\ ^3D_1$	11 796	$M1$	-1.22	
		$E2$	-3.58	-1.31
$6s5d\ ^3D_2$	12 435	$M1$	-6.33	
		$E2$	-3.70	-1.77
$6s5d\ ^3D_3$	14 199	$M1$	-12.2	
		$E2$	-8.16	-3.98
$6s5d\ ^1D_2$	17 333	$M1$	-5.53	
		$E2$	0.047	0.022

and we can estimate the energy shift of the atomic state  $|\gamma JIFM\rangle$  as

$$\Delta E \simeq -\frac{1}{2} \langle Q_0 \rangle \frac{\partial \mathcal{E}_z}{\partial z}, \quad (7)$$

where  $\langle Q_0 \rangle \equiv \langle \gamma JIFM | Q_0 | \gamma JIFM \rangle$ .

Then, the fractional electric quadrupole shift of the clock transition  $^3D_J - ^1S_0$  ( $J = 1, 2$ ) is

$$\frac{\Delta \omega}{\omega} \approx -\frac{1}{2\omega} \Delta \langle Q_0 \rangle \frac{\partial \mathcal{E}_z}{\partial z}, \quad (8)$$

where  $\omega$  is the  $^3D_J - ^1S_0$  transition frequency, and  $\Delta \langle Q_0 \rangle$  is the difference of the expectation values of  $Q_0$  for the upper and lower clock states. Taking into account that the quadrupole moment of the  $^1S_0$  state is equal to 0, we have  $\Delta \langle Q_0 \rangle = \langle Q_0(^3D_J FM) \rangle$ .

The expectation value  $\langle Q_0 \rangle$  is given by

$$\begin{aligned} \langle \gamma JIFM | Q_0 | \gamma JIFM \rangle &= (-1)^{I+J+F} [3M^2 - F(F+1)] \\ &\times \sqrt{\frac{2F+1}{(2F+3)(F+1)F(2F-1)}} \\ &\times \begin{Bmatrix} J & J & 2 \\ F & F & I \end{Bmatrix} \langle \gamma J || Q || \gamma J \rangle, \end{aligned} \quad (9)$$

where  $\langle \gamma J || Q || \gamma J \rangle$  is the reduced ME of the electric quadrupole operator.

In Table III we list the diagonal MEs of the magnetic dipole ( $M1$ ) and electric-quadrupole operators and the electric quadrupole moments  $\Theta$ , defined as

$$\Theta = 2 \sqrt{\frac{J(2J-1)}{(2J+3)(2J+1)(J+1)}} \langle \gamma J || Q || \gamma J \rangle \quad (10)$$

for the  $^3D_J$  and  $^1D_2$  states. The MEs of the  $M1$  operator are given in the Bohr magnetons,  $\mu_0 = |e|\hbar/(2mc)$  (where  $e$  and  $m$  are the electron charge and mass,  $\hbar$  is the Planck constant, and  $c$  is the speed of light).

As an example, we estimate the magnitude of the quadrupole shift for the  $^3D_1 - ^1S_0$  clock transition, for the bosonic 176 isotope of Lu<sup>+</sup> with  $I = 7$ . Since  $J = 1$  for the  $^3D_1$  state, the possible values of  $F = 6-8$ .

Putting  $F = 7$ ,  $M = 0$ , using for an estimate  $\partial \mathcal{E}_z / \partial z = 1 \text{ kV/cm}^2 \approx 1.029 \times 10^{-15} \text{ a.u.}$  [27] and

$\langle {}^3D_1 || Q || {}^3D_1 \rangle \approx -3.58$  a.u., we arrive at

$$\frac{\Delta v}{v} \approx 6.3 \times 10^{-15}. \quad (11)$$

Thus, at typical electric field gradients of  $\sim \text{kV/cm}^2$ , the quadrupole shifts for the  ${}^3D_J$  states are on the order of a few Hz and should be accounted for. However, it can be suppressed using various schemes [17,20,37]. Taking into account that

$$\sum_{M=-F}^F [3M^2 - F(F+1)] = 0, \quad (12)$$

we obtain from Eq. (9)

$$\sum_M \langle \gamma JIFM | Q_0 | \gamma JIFM \rangle = 0. \quad (13)$$

This is also true for the  $H_Q$  operator, Eq. (5), as was shown in Ref. [35]. So the quadrupole shift vanishes when averaged over all  $M$  states of a given hyperfine state [37].

In the specific case of the  $\text{Lu}^+$  ion, for which  $I > J$ , averaging over all  $F$  states of a fixed  $|M| \leq I + J$  also cancels the quadrupole shift [20]. An advantage of this approach is that it allows to reduce significantly the number of transitions involved and use magnetically insensitive  $M = 0$  states.

It is worth noting that the  ${}^1D_2$  level has an extremely small quadrupole moment. It is a factor of 2 smaller than the quadrupole moment for the  $\text{Yb}^+$  upper,  ${}^2F_{7/2}^o$ , clock state [38]. In particular, the  $F = 8$ ,  $M = 0$  state would have a quadrupole shift of just a few mHz for typical experimental conditions, and averaging schemes for the quadrupole shift cancellation may not even be necessary [27].

#### IV. BLACKBODY RADIATION SHIFT

The leading contribution to the multipolar BBR shift of the energy level  $|0\rangle$  can be expressed in terms of the electric dipole transition matrix elements [39]

$$\Delta E = -\frac{(\alpha T)^3}{2J_0 + 1} \sum_n | \langle 0 || D || n \rangle |^2 F(y_n). \quad (14)$$

Here  $\alpha \approx 1/137$  is the fine-structure constant,  $y_n \equiv (E_n - E_0)/T$ ,  $T$  is the temperature,  $J_0$  is the total angular momentum of the  $|0\rangle$  state,  $E_i$  is the energy of the  $|i\rangle$  state, and  $F(y)$  is the function introduced by Farley and Wing [39]; its asymptotic expansion is given by

$$F(y) \approx \frac{4\pi^3}{45y} + \frac{32\pi^5}{189y^3} + \frac{32\pi^7}{45y^5} + \frac{512\pi^9}{99y^7}. \quad (15)$$

Equation (14) can be expressed in terms of the dc polarizability  $\alpha_0$  of the  $|0\rangle$  state as [18]

$$\Delta E \equiv \Delta E^{\text{st}} + \Delta E^{\text{dyn}}, \quad (16)$$

where  $\Delta E^{\text{st}}$  and  $\Delta E^{\text{dyn}}$  are the static and dynamic parts, determined as

$$\Delta E = -\frac{2}{15} (\alpha\pi)^3 T^4 \alpha_0 [1 + \eta]. \quad (17)$$

Here  $\eta$  represents a dynamic fractional correction to the total shift that reflects the averaging of the frequency dependence of the polarizability over the frequency of the blackbody radiation spectrum.

The advantage of such a representation is a possibility to accurately measure the static part  $\Delta E^{\text{st}}$  and generally small contribution of the dynamic part. However, the recent measurement [23] of the differential scalar dynamic polarizability of the  ${}^3D_1 - {}^1S_0$  transition at  $\lambda = 10.6 \mu\text{m}$  yielded a very small value,  $\Delta\alpha_0(\lambda) = 0.059(4)$  a.u. An extrapolation to dc [23] leads to even smaller value of the static scalar differential polarizability,  $\Delta\alpha_0(0) = 0.018(6)$  a.u. Therefore it is essential to evaluate the dynamic correction and its uncertainty.

The quantity  $\eta$  can be approximated by [18]

$$\eta \approx \eta_1 + \eta_2 \equiv \frac{80}{63(2J_0 + 1)} \frac{\pi^2}{\alpha_0 T} \times \sum_n \frac{|\langle n || D || 0 \rangle|^2}{y_n^3} \left( 1 + \frac{21\pi^2}{5y_n^2} \right). \quad (18)$$

Contributions of the intermediate odd-parity states to the dynamic fractional corrections  $\eta_1$ ,  $\eta_2$ , and  $\eta = \eta_1 + \eta_2$  of the  $6s^2 {}^1S_0$ ,  $5d6s {}^3D_{1,2}$ , and  $5d6s {}^1D_2$  states are presented in Table IV. Since the energy denominators in the first term of Eq. (18) are proportional to  $(E_n - E_0)^3$ , the sum over  $n$  converges much more rapidly than for the polarizability [where the denominators are  $\sim (E_n - E_0)$ ], and the contribution of the states not listed in Table IV is expected to be negligible. Because the same matrix elements are involved in the calculation of  $\eta$  and the scalar polarizability  $\alpha_0$  for a given state, we estimate that  $\eta$  has the same relative uncertainty as  $\alpha_0$ .

The corresponding static (dynamic) contributions to the BBR shift of a transition frequency are determined by the differences of  $\Delta E^{\text{st(dyn)}}$  of the upper and lower states, and in total

$$\Delta v = \Delta v^{\text{st}} + \Delta v^{\text{dyn}}. \quad (19)$$

The static and dynamic BBR shifts for the  $6s5d {}^1,3D_J - 6s^2 {}^1S_0$  transitions at  $T = 300$  K are given in Table V.

The theoretical values of the  ${}^3D_{1,2}$  and  ${}^1S_0$  polarizabilities are very close to each other. Taking into account the theoretical uncertainties, we are unable to predict reliably the differential polarizabilities and  $\Delta v^{\text{st}}$  for these transitions. For this reason the values of  $\Delta v^{\text{st}}$  for the  ${}^3D_{1,2} - {}^1S_0$  transitions, presented in Table V, are found using the experimental results for  $\Delta\alpha_0({}^3D_{1,2} - {}^1S_0)$  [23]. The polarizabilities of the  ${}^1S_0$  and  ${}^1D_2$  states differ more significantly, and we obtain  $\Delta v^{\text{st}} = 66(17)$  mHz for the  ${}^1D_2 - {}^1S_0$  transition.

In contrast with the scalar static polarizabilities, the  $\eta$  corrections for the ground and  ${}^3D_J$  states differ by a factor of two, and we estimate the uncertainties of our values of  $\Delta v^{\text{dyn}}$  for the  ${}^3,1D_J - {}^1S_0$  transitions to be 12%–18%.

We would like to emphasise that the  ${}^3D_1 - {}^1S_0$  transition is unique in the sense that the static BBR frequency shift is two times (in absolute value) smaller than the dynamic BBR shift. The total BBR frequency shift for this transition is very small,  $\Delta v = -0.48$  mHz. This value is in excellent agreement with the result obtained in Ref. [23].

Since the differential scalar static polarizability of the  ${}^3D_1 - {}^1S_0$  transition is close to zero, we have also considered the third-order contribution to this quantity, involving two interactions of the electric-dipole operator  $\mathbf{D}$  with the external electric field and one hyperfine interaction [40] (see also Ref. [41] for further details). We estimated this contribution to be  $10^{-4}$ – $10^{-5}$  a.u.,

TABLE IV. Contributions of the intermediate odd-parity states to the dynamic fractional corrections  $\eta_1$ ,  $\eta_2$ , and  $\eta = \eta_1 + \eta_2$  of the  $6s^2\ ^1S_0$ ,  $5d6s\ ^3D_{1,2}$ , and  $5d6s\ ^1D_2$  states. The sums of individual contributions are given in the rows labeled “Total.” The numbers in brackets represent powers of 10.

State	Contrib.	$\eta_1$	$\eta_2$	$\eta$	
$6s^2\ ^1S_0$	$6s6p\ ^3P_0^o$	0.000055	1.22[−7]	0.000055	
	$6s6p\ ^1P_1^o$	0.000421	5.19[−7]	0.000421	
	$5d6p\ ^3D_1^o$	0.000013	1.15[−8]	0.000013	
	$5d6p\ ^3P_1^o$	0.000003	2.18[−9]	0.000003	
	$5d6p\ ^1P_1^o$	0.000017	8.68[−9]	0.000017	
	Total	0.000509	0.000001	0.000510	
$5d6s\ ^3D_1$	$6s6p\ ^3P_0^o$	0.000372	2.80[−6]	0.000374	
	$5d6p\ ^3P_0^o$	0.000040	5.00[−8]	0.000040	
	$6s6p\ ^3P_1^o$	0.000223	1.44[−6]	0.000224	
	$5d6p\ ^3D_1^o$	0.000093	1.48[−7]	0.000094	
	$5d6p\ ^3P_1^o$	0.000049	6.03[−8]	0.000049	
	$6s6p\ ^3P_2^o$	0.000009	3.71[−8]	0.000009	
	$5d6p\ ^3F_2^o$	0.000185	3.85[−7]	0.000185	
	$5d6p\ ^1D_2^o$	0.000048	7.71[−8]	0.000049	
	$5d6p\ ^3D_2^o$	0.000074	1.08[−7]	0.000074	
	$5d6p\ ^3P_2^o$	0.000003	3.67[−9]	0.000003	
	Total	0.001097	0.000005	0.001102	
	$5d6s\ ^3D_2$	$6s6p\ ^3P_1^o$	0.000403	2.81[−6]	0.000406
		$6s6p\ ^1P_1^o$	0.000015	4.03[−8]	0.000015
		$5d6p\ ^3D_1^o$	0.000042	6.89[−8]	0.000042
$6s6p\ ^3P_2^o$		0.000071	3.21[−7]	0.000072	
$5d6p\ ^3F_2^o$		0.000105	2.29[−7]	0.000105	
$5d6p\ ^1D_2^o$		0.000000	1.70[−0]	0.000000	
$5d6p\ ^3D_2^o$		0.000066	1.00[−7]	0.000066	
$5d6p\ ^3F_3^o$		0.000156	2.67[−7]	0.000156	
$5d6p\ ^3D_3^o$		0.000061	8.32[−8]	0.000061	
Total		0.000920	0.000004	0.000924	
$5d6s\ ^1D_2$		$6s6p\ ^3P_1^o$	0.000033	4.76[−7]	0.000033
		$6s6p\ ^1P_1^o$	0.000047	1.94[−7]	0.000047
		$5d6p\ ^1P_1^o$	0.000046	4.76[−8]	0.000046
		$6s6p\ ^3P_2^o$	0.000025	1.95[−7]	0.000025
	$5d6p\ ^3F_2^o$	0.000166	5.24[−7]	0.000167	
	$5d6p\ ^1D_2^o$	0.000314	7.14[−7]	0.000314	
	$5d6p\ ^3P_2^o$	0.000044	6.85[−8]	0.000044	
	$5d6p\ ^3F_3^o$	0.000029	6.88[−8]	0.000029	
	$5d6p\ ^3D_3^o$	0.000002	3.17[−9]	0.000002	
	$5d6p\ ^1F_3^o$	0.000106	1.49[−7]	0.000106	
	Total	0.000810	0.000002	0.000813	

resulting in the BBR frequency shift below 1  $\mu$ Hz, negligible at the present level of accuracy.

## V. FINE-STRUCTURE CONSTANT VARIATION

Since frequencies of atomic clocks have different dependencies on the fine-structure constant  $\alpha$ , one can search for the  $\alpha$ -variation by precisely measuring ratios of two clocks frequencies over time [1]. This subject recently became of even higher interest, since the variation of the fundamental constants was directly linked to the dark matter searches [4–6].

To evaluate the sensitivity of the particular clock to the variation of  $\alpha$ , one calculates the relativistic frequencies shifts,

TABLE V. The dynamic corrections  $\Delta E^{\text{dyn}}/h$  ( $h$  is the Planck constant) and  $\Delta\nu^{\text{st(dyn)}}$  to the BBR shifts for the  $5d6s\ ^3D_J$  and  $6s^2\ ^1S_0$  states and the  $^3D_J - ^1S_0$  transitions, respectively, at  $T = 300$  K. Static scalar polarizabilities  $\alpha_0$  are listed. The uncertainties are given in parentheses.

	$\alpha_0$ (a.u.)	$\eta$	$\Delta E^{\text{dyn}}/h$ (mHz)
$6s^2\ ^1S_0$	63.0(0.8) <sup>a</sup>	0.00051(1)	−0.277(5)
$5d6s\ ^3D_1$	63.5(2.8) <sup>a</sup>	0.00110(5)	−0.603(38)
$5d6s\ ^3D_2$	62.1(2.6) <sup>a</sup>	0.00092(4)	−0.494(29)
$5d6s\ ^1D_2$	55.3(1.7)	0.00081(2)	−0.387(17)
	$\Delta\nu^{\text{st}}$ (mHz)		$\Delta\nu^{\text{dyn}}$ (mHz)
$^3D_1 - ^1S_0$	−0.15(5) <sup>b</sup>		−0.33(4)
$^3D_2 - ^1S_0$	10.1(8) <sup>b</sup>		−0.22(3)
$^1D_2 - ^1S_0$	66(17)		−0.11(2)

<sup>a</sup>These values are taken from Ref. [21].

<sup>b</sup>Extracted from the experimental results [23].

determined by so-called  $q$  factors, according to

$$\omega(x) = \omega' + qx, \quad (20)$$

where  $\omega'$  is the present laboratory value of the frequency,  $x = (\alpha/\alpha')^2 - 1$ , and the  $q$  factor is determined as

$$q = \left. \frac{d\omega}{dx} \right|_{x=0}. \quad (21)$$

From Eq. (20) we can easily obtain

$$\frac{\Delta\omega}{\omega} \approx Q \frac{\Delta\alpha}{\alpha}, \quad (22)$$

where  $Q \equiv 2q/\omega$ ,  $\Delta\omega \equiv \omega - \omega'$ , and  $\Delta\alpha \equiv \alpha - \alpha'$ .

### A. A simple estimate

In a single-electron approximation the relativistic energy shift (in a.u.) can be estimated as [42,43]

$$\Delta_a = \sqrt{\frac{-\varepsilon_a}{2}} (\alpha Z)^2 \left[ \frac{1}{j_a + 1/2} - C(Z, j_a, l_a) \right], \quad (23)$$

where  $a$  is the index for a single-electron state,  $\varepsilon_a$  is its energy,  $j_a$  and  $l_a$  are the total and orbital angular momenta of the state  $a$ , and  $C(Z, j_a, l_a)$  is a parameter introduced to simulate the effect of the Hartree-Fock exchange interaction and other many-body effects. An accurate value of  $C(Z, j_a, l_a)$  can be obtained only from many-body calculations, but  $C(Z, j_a, l_a) \approx 0.6$  [43] can be used for a rough estimate.

If we approximate a transition between many-electron states by a single-electron transition from state  $a$  in the lower level to state  $b$  in the upper level, the  $q$  factor can be approximated by [42]

$$q \approx \Delta_b - \Delta_a. \quad (24)$$

Using Eq. (24) we are able to roughly estimate the  $q$  (and  $Q$ ) factors for the  $^1S_0 - ^3D_J$  transitions. Taking into account that the main relativistic configurations are  $6s^2$  for  $^1S_0$ ,  $6s5d_{3/2}$  for  $^3D_{1,2}$ , and  $6s5d_{5/2}$  for  $^1D_2$ , we can approximate the  $^1S_0 - ^3D_{1,2}$  transitions by the single-electron  $6s - 5d_{3/2}$  transition and the  $^1S_0 - ^1D_2$  transition by the single-electron  $6s - 5d_{5/2}$  transition.

TABLE VI. The  $q$  and  $Q$  factors for the  $^1S_0 - ^3,^1D_J$  transitions are obtained in the CI, CI+MBPT, and CI+all-order approximations.

		$q$	$Q$
CI	$^1S_0$	—	
	$^3D_1$	-14 380	-2.44
	$^3D_2$	-14 572	-2.34
	$^3D_3$	-15 257	-2.15
	$^1D_2$	-16 515	-1.91
CI+MBPT	$^1S_0$	—	
	$^3D_1$	-14 951	-2.54
	$^3D_2$	-15 437	-2.48
	$^3D_3$	-17 223	-2.43
	$^1D_2$	-19 061	-2.20
CI+All	$^1S_0$	—	
	$^3D_1$	-14 854	-2.52
	$^3D_2$	-15 294	-2.46
	$^3D_3$	-16 873	-2.38
	$^1D_2$	-18 633	-2.15

For an estimate we substitute the Hartree-Fock energies  $\varepsilon_{6s} \approx -0.73$ ,  $\varepsilon_{5d_{3/2}} \approx -0.70$ , and  $\varepsilon_{5d_{5/2}} \approx -0.69$  a.u. to Eq. (23).

Then we obtain  $\Delta_{6s} \approx 0.065$ ,  $\Delta_{5d_{3/2}} \approx -0.016$ , and  $\Delta_{5d_{5/2}} \approx -0.042$  a.u.. It gives us the following transition  $q$  factors:

$$\begin{aligned}
 q(^1S_0 - ^3D_{1,2}) &\simeq \Delta_{5d_{3/2}} - \Delta_{6s} \approx -0.081 \text{ a.u.} \\
 &\approx -17\,777 \text{ cm}^{-1}, \\
 q(^1S_0 - ^1D_2) &\simeq \Delta_{5d_{5/2}} - \Delta_{6s} \approx -0.107 \text{ a.u.} \\
 &\approx -23\,484 \text{ cm}^{-1}.
 \end{aligned}$$

Taking into account that  $\omega(^1S_0 - ^3D_{1,2}) \simeq 12\,000 \text{ cm}^{-1}$  and  $\omega(^1S_0 - ^1D_2) = 17\,333 \text{ cm}^{-1}$  we obtain the following estimate:

$$Q(^1S_0 - ^3,^1D_J) \approx -3.$$

### B. Full-scale calculation

We carried out calculations in three approximations: CI, CI+MBPT, and CI+all-order. In each case three calculations (with  $x = 0, \pm 1/8$ ) were done. Using Eqs. (20)–(22), we found the  $q$  and  $Q$  factors for the transitions from the  $^3,^1D_J$  states to the ground state. The results are presented in Table VI.

The results obtained from the simple estimate above are in good agreement with those obtained from the full-scale calculation. Thus, if a high-accuracy calculation of the  $q$  factors

is not needed, Eq. (23) can be used for a quick estimate of these quantities.

The factors  $|Q| \approx 2\text{--}2.5$  presented in Table VI, though smaller than  $|Q| = 15$  found recently for an optical transition in Yb [44], are larger than the values for all currently operating clocks with the exception of the  $\text{Hg}^+$  and octupole  $\text{Yb}^+$  clocks [45]. Thus, the clocks based on the  $6s^2\ ^1S_0 - 5d6s\ ^3D_{1,2}$  transitions in  $\text{Lu}^+$  are good candidates for the search for the  $\alpha$ -variation.

## VI. CONCLUSION

To conclude, we carried out the calculations of the quadrupole moments and the corresponding quadrupole shifts, demonstrating the need to accurately suppress these effects. We provided the recommended value of the dc  $5d6s\ ^1D_2$

- [8] S. Kolkowitz, S. L. Bromley, T. Bothwell, M. L. Wall, G. E. Marti, A. P. Koller, X. Zhang, A. M. Rey, and J. Ye, *Nature (London)* **542**, 66 (2017).
- [9] T. E. Mehlstäubler, G. Grosche, C. Lisdat, P. O. Schmidt, and H. Denker, *Rep. Prog. Phys.* **81**, 064401 (2018).
- [10] D. Normile and D. Clery, *Science* **333**, 1820 (2011).
- [11] S. Kolkowitz, I. Pikovski, N. Langellier, M. D. Lukin, R. L. Walsworth, and J. Ye, *Phys. Rev. D* **94**, 124043 (2016).
- [12] A. Bauch, *Meas. Sci. Tech.* **14**, 1159 (2003).
- [13] T. L. Nicholson, S. L. Campbell, R. B. Hutson, G. E. Marti, B. J. Bloom, R. L. McNally, W. Zhang, M. D. Barrett, M. S. Safronova, G. F. Strouse *et al.*, *Nat. Commun.* **6**, 6896 (2015).
- [14] N. Huntemann, C. Sanner, B. Lipphardt, C. Tamm, and E. Peik, *Phys. Rev. Lett.* **116**, 063001 (2016).
- [15] J. Keller, T. Burgermeister, D. Kalincev, A. Didier, A. P. Kulosa, T. Nordmann, J. Kiethe, and T. E. Mehlstäubler, [arXiv:1803.08248](https://arxiv.org/abs/1803.08248) (2018).
- [16] K. Arnold, E. Hajiyev, E. Paez, C. H. Lee, M. D. Barrett, and J. Bollinger, *Phys. Rev. A* **92**, 032108 (2015).
- [17] K. J. Arnold and M. D. Barrett, *Phys. Rev. Lett.* **117**, 160802 (2016).
- [18] S. G. Porsev and A. Derevianko, *Phys. Rev. A* **74**, 020502(R) (2006).
- [19] I. Ushijima, M. Takamoto, M. Das, T. Ohkubo, and H. Katori, *Nat. Photonics* **9**, 185 (2015).
- [20] M. D. Barrett, *New J. Phys.* **17**, 053024 (2015).
- [21] E. Paez, K. J. Arnold, E. Hajiyev, S. G. Porsev, V. A. Dzuba, U. I. Safronova, M. S. Safronova, and M. D. Barrett, *Phys. Rev. A* **93**, 042112 (2016).
- [22] A. Kozlov, V. A. Dzuba, and V. V. Flambaum, *Phys. Rev. A* **90**, 042505 (2014).
- [23] K. J. Arnold, R. Kaewuam, A. Roy, T. R. Tan, and M. D. Barrett, *Nat. Commun.* **9**, 1650 (2018).
- [24] J.-S. Chen, S. M. Brewer, C. W. Chou, D. J. Wineland, D. R. Leibbrandt, and D. B. Hume, *Phys. Rev. Lett.* **118**, 053002 (2017).
- [25] D. J. Berkland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland, *J. Appl. Phys.* **83**, 5025 (1998).
- [26] P. Dubé, A. A. Madej, Z. Zhou, and J. E. Bernard, *Phys. Rev. A* **87**, 023806 (2013).
- [27] M. D. Barrett (private communication).
- [28] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, *Phys. Rev. A* **54**, 3948 (1996).
- [29] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. Jiang, *Phys. Rev. A* **80**, 012516 (2009).
- [30] V. A. Dzuba, M. G. Kozlov, S. G. Porsev, and V. V. Flambaum, *Zh. Eksp. Teor. Fiz.* **114**, 1636 (1998) [*Sov. Phys.–JETP* **87**, 885 (1998)].
- [31] R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950).
- [32] A. Dalgarno and J. T. Lewis, *Proc. R. Soc. London A* **233**, 70 (1955).
- [33] M. G. Kozlov and S. G. Porsev, *Eur. Phys. J. D* **5**, 59 (1999).
- [34] Yu. Ralchenko, A. Kramida, J. Reader, and the NIST ASD Team, NIST Atomic Spectra Database (version 4.1) <http://physics.nist.gov/asd>. National Institute of Standards and Technology, Gaithersburg, MD (2011).
- [35] W. Itano, *J. Res. Natl. Inst. Stand. Technol.* **105**, 829 (2000).
- [36] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956).
- [37] P. Dubé, A. A. Madej, J. E. Bernard, L. Marmet, J.-S. Boulanger, and S. Cundy, *Phys. Rev. Lett.* **95**, 033001 (2005).
- [38] N. Huntemann, M. Okhapkin, B. Lipphardt, S. Weyers, Chr. Tamm, and E. Peik, *Phys. Rev. Lett.* **108**, 090801 (2012).
- [39] J. W. Farley and W. H. Wing, *Phys. Rev. A* **23**, 2397 (1981).
- [40] J. R. P. Angel and P. G. H. Sandars, *Proc. R. Soc. London A* **305**, 125 (1968).
- [41] K. Beloy, U. I. Safronova, and A. Derevianko, *Phys. Rev. Lett.* **97**, 040801 (2006).
- [42] V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **77**, 012515 (2008).
- [43] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, *Phys. Rev. A* **59**, 230 (1999).
- [44] M. S. Safronova, S. G. Porsev, C. Sanner, and J. Ye, *Phys. Rev. Lett.* **120**, 173001 (2018).
- [45] V. V. Flambaum and V. A. Dzuba, *Can. J. Phys.* **87**, 25 (2009).