Clock-related properties of Lu^+

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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^+ 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^+ 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 $^{171}Yb^+$ [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^+ clock sympathetically cooled with Yb^+ 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^+ 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 $\lambda = 10.6\,\mu$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^+ [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 particulary the polarizability and the quadrupole shift.

Thus, further investigations of the clock-related properties of Lu^+ 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 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 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

$$H_{\rm eff}(E_n)|n\rangle = E_n|n\rangle, \tag{1}$$

with the effective Hamiltonian defined as

$$H_{\rm eff}(E) = H_{\rm FC} + \Sigma(E). \tag{2}$$

Here $H_{\rm FC}$ and Σ 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

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

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

The scalar static polarizability α_0 can be conventionally separated into three parts:

$$\alpha_0 = \alpha_0^v + \alpha^c + \alpha^{vc}. \tag{4}$$

Here α_0^v is the valence polarizability, α^c is the ionic core polarizability, and a small term α^{vc} accounts for possible excitations to the occupied valence shells. The valence part of the scalar polarizability, α_0^v, as well as the tensor polarizability, α_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 α^c and α^{vc} terms are evaluated using the RPA. The α^{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 sum-over-states formula, Eq. (3). Replacing the theoretical energies in the denominator of Eq. (3) for dominant contributions by the experimental ones changes the polarizability by less than 1%. The contributions of several lowest-lying intermediate states to $\alpha_0(0)$ of the $^1D_2$ state, calculated with the experimental and theoretical energies, are listed in columns α[A] and α[B] in Table I. The theoretical and experimental [34] transition frequencies are given in columns $\Delta E_{\rm th}$ and $\Delta E_{\rm expt}$ in $\rm cm^{-1}$. Final absolute values of the corresponding reduced electric-dipole MEs, calculated using the CI + all-order method and including RPA, σ, 2P, SR, and normalization corrections are listed in the column labeled "D" in a.u.

We also present the contribution of the intermediate states, not explicitly listed in the table, with fixed total angular momentum $J_n = 1 - 3$ in rows labeled "Other ($J_n = 1, 2, 3$)."

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 given (in $\rm cm^{-1}$) in columns $\Delta E_{\rm th}$ and $\Delta E_{\rm expt}$. We present the contribution of other (not explicitly listed in the table) intermediate states with fixed total angular momentum J_n in rows labeled "Other ($J_n = 1, 2, 3$)." In rows labeled "Total ($J_n = 1, 2, 3$)" we give the total contribution of *all* intermediate states with fixed total angular momentum J_n. In the row "Total val." we present the total value of α_0^v. The dominant contributions to the polarizabilities, listed in columns α[A] and α[B], are calculated with the experimental [34] and theoretical energies, respectively.

Contribution	$\Delta E_{\rm th}$	$\Delta E_{\rm expt}$	D	α[A]	α[B]
$^1D_2 - 6s6p\ ^3P_1^o$	10 826	11 171	0.326	0.28	0.29
$^1D_2 - 6s6p\ ^1P_1^o$	20 615	20 891	0.994	1.38	1.40
$^1D_2 - 5d6p\ ^3P_1^o$	33 038	32 717	0.144	0.02	0.02
$^1D_2 - 5d6p\ ^1P_1^o$	41 967	41 790	2.790	5.45	5.43
Other ($J_n = 1$)				0.64	0.64
Total ($J_n = 1$)				7.77	7.78
$^1D_2 - 6s6p\ ^3P_2^o$	14 815	15 121	0.445	0.38	0.39
$^1D_2 - 5d6p\ ^3F_2^o$	24 230	23 892	2.289	6.42	6.33
$^1D_2 - 5d6p\ ^1D_2^o$	28 399	28 126	4.017	16.79	16.63
$^1D_2 - 5d6p\ ^3D_2^o$	29 793	29 572	0.125	0.02	0.02
$^1D_2 - 5d6p\ ^3P_2^o$	34 204	33 869	1.980	3.39	3.35
Other ($J_n = 2$)				0.79	0.79
Total ($J_n = 2$)				27.78	27.50
$^1D_2 - 5d6p\ ^3F_3^o$	28 010	27 586	1.187	1.50	1.47
$^1D_2 - 5d6p\ ^3D_3^o$	31 678	31 401	0.352	0.12	0.11
$^1D_2 - 5d6p\ ^1F_3^o$	36 369	35 747	3.341	9.14	8.98
Other ($J_n = 3$)				5.75	5.75
Total ($J_n = 3$)				16.49	16.32
α_0^v				52.05	51.59
$\alpha^c + \alpha^{vc}$				3.74	3.74
Total				55.79	55.33
Recommended					55.3

TABLE II. The static scalar (α_0) and tensor (α_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)

[a]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 α_0^v is found as the sum of the values given in these rows.

The contributions from α^c and α^{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 α^{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, σ, 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 γ encapsulates all other electronic quantum numbers) is given by [35]

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

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

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

TABLE III. The energy levels (in cm^{-1}), reduced diagonal MEs of the $M1$ (in μ_0) and Q (in a.u.) operators, and electric quadrupole moments Θ (in a.u.) for the ^3D_J and $^1D_2$ states.

Level	Energy	Operator	ME	Θ
$6s5d\ ^3D_1$	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

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

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

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

where ω 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

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

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 Θ, defined as

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

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^+ 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 $\partial\mathcal{E}_z/\partial z = 1\ \mathrm{kV/cm^2} \approx 1.029 \times 10^{-15}$ a.u. [27] and

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

$$\frac{\Delta\nu}{\nu} \approx 6.3\times 10^{-15}. \tag{11}$$

Thus, at typical electric field gradients of $\sim$ 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

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

we obtain from Eq. (9)

$$\sum_M \langle \gamma J I F M|Q_0|\gamma J I F M\rangle = 0. \tag{13}$$

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 Lu^+ ion, for which $I > J$, averaging over all F states of a fixed $|M| \leqslant I + J$ 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 Yb^+ upper, $^2F^o_{7/2}$, 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]

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

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

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

Equation (14) can be expressed in terms of the dc polarizability α_0 of the $|0\rangle$ state as [18]

$$\Delta E \equiv \Delta E^{\rm st} + \Delta E^{\rm dyn}, \tag{16}$$

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

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

Here η 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 $\Delta E^{\rm st}$ 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 $\lambda = 10.6\,\mu$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 η can be approximated by [18]

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

Contributions of the intermediate odd-parity states to the dynamic fractional corrections η_1, η_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 η and the scalar polarizability α_0 for a given state, we estimate that η has the same relative uncertainly as α_0.

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

$$\Delta\nu = \Delta\nu^{\rm st} + \Delta\nu^{\rm dyn}. \tag{19}$$

The static and dynamic BBR shifts for the $6s5d\,{}^{1,3}D_J - 6s^2\,{}^1S_0$ 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 $\Delta\nu^{\rm st}$ for these transitions. For this reason the values of $\Delta\nu^{\rm st}$ 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 $\Delta\nu^{\rm st} = 66(17)$ mHz for the $^1D_2 - {}^1S_0$ transition.

In contrast with the scalar static polarizabilities, the η corrections for the ground and ^3D_J states differ by a factor of two, and we estimate the uncertainties of our values of $\Delta\nu^{\rm dyn}$ for the $^{3,1}D_J - {}^1S_0$ 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, $\Delta\nu = -0.48$ 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 **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 η_1, η_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.	η_1	η_2	η
$6s^2\ ^1S_0$	$6s6p\ ^3P_1^o$	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 μHz, 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 α, one can search for the α-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 α, one calculates the relativistic frequencies shifts,

TABLE V. The dynamic corrections $\Delta E^{\rm dyn}/h$ (h is the Planck constant) and $\Delta\nu^{\rm st\,(dyn)}$ to the BBR shifts for the $5d6s\ ^{3,1}D_J$ and $6s^2\ ^1S_0$ states and the $^{3,1}D_J - {}^1S_0$ transitions, respectively, at $T = 300$ K. Static scalar polarizabilities α_0 are listed. The uncertainties are given in parentheses.

	α_0 (a.u.)	η	$\Delta E^{\rm dyn}/h$ (mHz)
$6s^2\ ^1S_0$	63.0(0.8)[a]	0.00051(1)	−0.277(5)
$5d6s\ ^3D_1$	63.5(2.8)[a]	0.00110(5)	−0.603(38)
$5d6s\ ^3D_2$	62.1(2.6)[a]	0.00092(4)	−0.494(29)
$5d6s\ ^1D_2$	55.3(1.7)	0.00081(2)	−0.387(17)
	$\Delta\nu^{\rm st}$ (mHz)		$\Delta\nu^{\rm dyn}$ (mHz)
$^3D_1 - {}^1S_0$	−0.15(5)[b]		−0.33(4)
$^3D_2 - {}^1S_0$	10.1(8)[b]		−0.22(3)
$^1D_2 - {}^1S_0$	66(17)		−0.11(2)

[a]These values are taken from Ref. [21].
[b]Extracted from the experimental results [23].

determined by so-called q factors, according to

$$\omega(x) = \omega' + qx, \tag{20}$$

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

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

From Eq. (20) we can easily obtain

$$\frac{\Delta\omega}{\omega} \approx Q\,\frac{\Delta\alpha}{\alpha}, \tag{22}$$

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]

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

where a is the index for a single-electron state, ε_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]

$$q \approx \Delta_b - \Delta_a. \tag{24}$$

Using Eq. (24) we are able to roughly estimate the q (and Q) factors for the $^1S_0 - {}^{3,1}D_J$ 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 $^1S_0 - {}^{3,1}D_J$ 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:

$$q\left(^1S_0 - {}^3D_{1,2}\right) \simeq \Delta_{5d_{3/2}} - \Delta_{6s} \approx -0.081 \text{ a.u.} \approx -17\,777 \text{ cm}^{-1},$$

$$q\left(^1S_0 - {}^1D_2\right) \simeq \Delta_{5d_{5/2}} - \Delta_{6s} \approx -0.107 \text{ a.u.} \approx -23\,484 \text{ cm}^{-1}.$$

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

$$Q\left(^1S_0 - {}^{3,1}D_J\right) \approx -3.$$

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 $^{3,1}D_J$ 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 $|Q| \approx 2$–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 Hg^+ and octupole Yb^+ clocks [45]. Thus, the clocks based on the $6s^2\ ^1S_0 - 5d6s\ ^3D_{1,2}$ transitions in Lu^+ are good candidates for the search for the α-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 $5d6s\ ^1D_2$ polarizability and established the dominant contributions of the intermediate states to the polarizability. We determined the dynamic BBR shifts for the $6s^2\ ^1S_0$, $5d6s\ ^3D_{1,2}$, and $5d6s\ ^1D_2$ energy levels. The values of the dynamic BBR shifts at $T = 300$ K for the clock transitions are determined with 12%–18% uncertainties.

We note that the differential polarizability of the $6s^2\ ^1S_0 - 5d6s\ ^1D_2$ transition is negative (so the micromotion effect can be canceled at the magic radio frequency). The $5d6s\ ^1D_2$ state has very small quadrupole moment which may eliminate a need for hyperfine averaging. These features make the $6s^2\ ^1S_0 - 5d6s\ ^1D_2$ transition a good candidate for creating a clock in its own right.

We confirm the observation of Ref. [23] that the $Lu^+\ 6s^2\ ^1S_0 - 5d6s\ ^3D_1$ transition is the only known clock transition where the dynamic part of the BBR frequency shift is much larger than the static part. We also considered the third-order contribution to this differential polarizability and estimated that the resulting BBR frequency shift is negligible. Finally, we calculated the sensitivity of the Lu^+ clock transitions to the variation of the fine-structure constant and related dark matter searches.

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