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# Anomalously small blackbody radiation shift in Tl<sup>+</sup> frequency standard

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The operation of atomic clocks is generally carried out at room temperature, whereas the definition of the second refers to the clock transition in an atom at absolute zero. This implies that the clock transition frequency should be corrected in practice for the effect of finite temperature of which the leading contributor is the blackbody radiation (BBR) shift. In the present work, we used configuration interaction + coupled-cluster method to evaluate polarizabilities of the  $6s^2\ ^1S_0$  and  $6s6p\ ^3P_0$  states of Tl<sup>+</sup> ion; we find  $\alpha_0(^1S_0) = 19.6$  a.u. and  $\alpha_0(^3P_0) = 21.4$  a.u.. The resulting BBR shift of the  $6s6p\ ^3P_0 - 6s^2\ ^1S_0$  Tl<sup>+</sup> transition at 300 K is  $\Delta\nu_{\text{BBR}} = -0.0157(16)$  Hz. This result demonstrates that near cancellation of the  $^1S_0$  and  $^3P_0$  state polarizabilities in divalent B<sup>+</sup>, Al<sup>+</sup>, In<sup>+</sup> ions of group IIIB [Safronova *et al.*, PRL 107, 143006 (2011)] continues for much heavier Tl<sup>+</sup>, leading to anomalously small BBR shift for this system. This calculation demonstrates that the BBR contribution to the fractional frequency uncertainty of the Tl<sup>+</sup> frequency standard at 300 K is  $1 \times 10^{-18}$ . We find that Tl<sup>+</sup> has the smallest fractional BBR shift among all present or proposed frequency standards with the exception of Al<sup>+</sup>.

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## I. INTRODUCTION

Recent advances in atomic and optical physics have led to unprecedented improvements in the accuracy of optical frequency standards that are essential for many applications including measurements of the fundamental constants and search of their variation with time, testing of physics postulates, inertial navigation, magnetometry, tracking of deep-space probes, and others [1]. An optical clock with a record low fractional frequency uncertainty of  $8.6 \times 10^{-18}$ , based on quantum logic spectroscopy of an Al<sup>+</sup> ion was demonstrated in 2010 [2].

Any definition of the second should be based on a clock decoupled from its particular environment. Thermal fluctuations of the electromagnetic field, i.e. blackbody radiation (BBR), are pervasive and can only be suppressed by cooling the clock. The BBR at any non-zero temperature induces small shifts in atomic energy levels through the AC Stark effect. The operation of atomic clocks is generally carried out at room temperature and the clock transition frequency should be corrected in practice for the BBR shift. Experimental measurements of the BBR shifts are sufficiently difficult that no direct measurement has yet been reported for optical frequency standards. At room temperature, the BBR shift of a clock transition turns out to make one of the largest irreducible contributions to the uncertainty budget of optical atomic clocks [3]. The present status of the theoretical and experimental determinations of the BBR shifts in all frequency standards was recently reviewed in [3, 4].

The BBR frequency shift of a clock transition can be related to the difference of the static electric-dipole polarizabilities between the two clock states [5]. Recent work [6] demonstrated that the polarizabilities of ground

$ns^2\ ^1S_0$  and metastable  $nsnp\ ^3P_0$  states are nearly equal to each other in B<sup>+</sup>, Al<sup>+</sup>, and In<sup>+</sup>, all of which are group IIIB ions. As a result, these three ions have anomalously small BBR shifts of the  $ns^2\ ^1S_0 - nsnp\ ^3P_0$  clock transitions. The fractional BBR shifts for these ions are at least 10 times smaller than those of any other present or proposed optical frequency standards at the same temperature, and are less than 0.3% of the Sr clock shift.

Optical frequency standard based on  $^{204}\text{Tl}^+$   $6s^2\ ^1S_0\ m_F = 0 - 6s6p\ ^3P_0\ m_{F'} = 0$  transition was proposed in Ref. [7]. The radioactive isotope of  $^{204}\text{Tl}$  has a half-life of 3.78 years, a spin of 2, and a very small magnetic moment of 0.0908 nuclear magnetons making it ideal object for very high-resolution laser spectroscopy [7]. Because of its small nuclear magnetic moment the natural linewidth of the clock transition in  $^{204}\text{Tl}^+$  is expected to be orders of magnitude smaller than estimated for stable Tl isotopes [7]. The BBR in this frequency standard have not been previously estimated. Since three group IIIB ions exhibit very small BBR shifts, it is very interesting to evaluate if this trend holds for much heavier Tl<sup>+</sup>.

The BBR frequency shift of the clock transition can be related to the difference of the static electric-dipole polarizabilities between the clock states,  $\Delta\alpha_0$ , by [5]

$$\Delta\nu_{\text{BBR}} = -\frac{1}{2}(831.9\text{ V/m})^2 \left(\frac{T(K)}{300}\right)^4 \Delta\alpha_0(1 + \eta), \quad (1)$$

where  $\eta$  is a small dynamic correction due to the frequency distribution and only the electric-dipole transition part of the contribution is considered. The M1 and E2 contributions have been estimated for Al<sup>+</sup> and found to be negligible [6]. Therefore, the calculation of the BBR shift reduces to accurate calculation of the static polar-

izabilities of the clock states and dynamic correction  $\eta$ .

In this work, we evaluate polarizabilities of the  $6s^2\ ^1S_0$  and  $6s6p\ ^3P_0$  states in  $\text{TI}^+$ , corresponding BBR shift and its uncertainty. Dynamic correction to the BBR shift is evaluated and found negligible. We also calculate a number of electric-dipole matrix elements in  $\text{TI}^+$  for transitions between low-lying levels. We note that our calculation of all of these properties is independent on the particular isotope number well within the quoted level of precision. Therefore, all these results apply to any  $\text{TI}^+$  isotope.

## II. METHOD

Correlation corrections between a few valence electrons can be accurately treated by the configuration interaction (CI) method. Since the valence-valence correlations are very large, the CI method provides better description of these correlations than the perturbative approaches. However, excitations of the core [ $1s^2, \dots, 5d^{10}$ ] electrons can not be directly included in the CI approach due to enormous size of such problem. An elegant approach to the inclusion of the core-valence correlations within the CI framework was developed in [8], where core-valence correlations were incorporated into the CI by constructing an effective Hamiltonian using the second-order many-body perturbation theory (CI+MBPT). Recently, we have developed the relativistic CI+all-order method [9] combining CI with coupled-cluster (CC) approach. This method, first suggested in [10], was successfully applied to the calculation of divalent atom properties in Refs. [6, 9]. The coupled-cluster method used here is known to describe the core-core and core-valence correlations very well as demonstrated by its great success in predicting alkali-metal atom properties [11]. Therefore, combination of the CI and all-order coupled-cluster methods allows to account for all dominant correlations to all orders. To evaluate uncertainty of our results, we use all three of the approaches and compare the results of the CI, CI+MBPT, and CI+all-order calculations. We refer the reader to Refs. [6, 8, 9] for the description of the methods and outline only main points of the calculations below.

We start with solving Dirac-Fock (DF) equations

$$\hat{H}_0 \psi_c = \varepsilon_c \psi_c,$$

where  $H_0$  is the relativistic DF Hamiltonian [8, 9] and  $\psi_c$  and  $\varepsilon_c$  are single-electron wave functions and energies. The self-consistent calculations were performed for the [ $1s^2, \dots, 5d^{10}$ ] closed core and the  $6s$ ,  $7s$ ,  $6p$ ,  $7p$ , and  $6d$  orbitals. We have constructed the B-spline basis set consisting of  $N = 35$  orbitals for each of the  $s$ ,  $p_{1/2}$ ,  $p_{3/2}$ , ... partial waves up to  $l \leq 5$ . The core and the  $6s$ ,  $7s$ ,  $6p$ ,  $7p$ , and  $6d$  orbitals expanded as the linear combinations of B-splines were replaced by the exact DF functions; the orthogonalization procedure was preformed after the replacement. Tests were carried out to demonstrate that

this procedure improves the numerical accuracy in comparison with unmodified  $N = 35$  B-spline basis set. The basis set is formed in a spherical cavity with radius 60 a.u. The CI space is effectively complete and includes  $20sp$  and  $21dfg$  orbitals. All MBPT and all-order terms were summed over the entire  $N = 35$ ,  $l \leq 5$  basis set.

The multiparticle relativistic equation for three valence electrons is solved within the CI framework [12] to find the wave functions and the low-lying energy levels:

$$H_{\text{eff}}(E_n)\Phi_n = E_n\Phi_n.$$

The effective Hamiltonian is defined as

$$H_{\text{eff}}(E) = H_{\text{FC}} + \Sigma(E),$$

where  $H_{\text{FC}}$  is the Hamiltonian in the frozen-core approximation and the energy-dependent operator  $\Sigma(E)$  takes into account virtual core excitations. The  $\Sigma(E)$  part of the effective Hamiltonian is constructed using the second-order perturbation theory in the CI+MBPT approach [8] and linearized coupled-cluster single-double method in the CI+all-order approach [9]. The  $\Sigma(E) = 0$  in the pure CI calculation. Construction of the effective Hamiltonian in CI+MBPT and CI+all-order approximations is described in detail in Refs. [8, 9].

## III. RESULTS

Comparison of the energy levels (in  $\text{cm}^{-1}$ ) obtained in the CI, CI+MBPT, and CI+all-order approximations with experimental values [13, 14] is given in Table I. Corresponding relative differences of these three calculations with experiment are given in the last three columns in %. Two-electron binding energies are given in the first row of Table I, energies in other rows are counted from the ground state. We also observed significant, by a factor of 4 or better, improvement in the precision of the energy levels with CI+all-order method in comparison with the CI+MBPT one. For example, CI+MBPT value for the two-electron binding energy differs from experiment by 1.8%, while our all-order value differs from the experiment by only 0.4% (see line one of Table I). The experimental value of the two-electron binding energy is obtained as the sum of the  $\text{TI}^+$  and  $\text{TI}^{2+}$  ionization limits given in [13],  $164765(5)\ \text{cm}^{-1}$  and  $240600\ \text{cm}^{-1}$ . Ref. [13] notes that the ionization limit for  $\text{TI}^{2+}$ , derived from the first 3 members of the  $^2S$  series was shifted by  $300\ \text{cm}^{-1}$  to give effective quantum number for  $5g\ ^2G$  that is nearly hydrogenic. Therefore, there is some uncertainty ( $\lesssim 0.1\%$ ) associated with the two-electron binding energy in  $\text{TI}^+$ .

We also compared the transition energies between the  $6s6p\ ^3P_0$  level and 4 levels relevant to the calculation of the  $6s6p\ ^3P_0$  polarizability. These values, calculated in the CI+all-order approximation are compared with experiment in Table II. We find that these transition energies are substantially more accurate than the energy levels counted from the ground state listed in Table I.

TABLE I: Comparison between experimental [13, 14] and theoretical energy levels in  $\text{cm}^{-1}$ . Two-electron binding energies are given in the first row, energies in other rows are counted from the ground state. Results of the CI, CI+MBPT, and CI+all-order calculations are given in columns labeled CI, MBPT, and All. Corresponding relative differences of these three calculations with experiment are given in the last three columns in %.

State	Expt.	CI	MBPT	All	Differences (%)		
					CI	MBPT	All
$6s^2\ ^1S_0$	405365	376102	412676	407125	-7	1.8	0.4
$6s7s\ ^3S_1$	105229	92945	108031	106028	-12	2.7	0.8
$6s7s\ ^1S_0$	108000	96304	110845	108904	-11	2.6	0.8
$6s6d\ ^1D_2$	115166	101238	118678	116194	-12	3.1	0.9
$6s6d\ ^3D_1$	116152	103334	119000	116857	-11	2.5	0.6
$6s6d\ ^3D_2$	116436	103555	119339	117284	-11	2.5	0.7
$6s6d\ ^3D_3$	116831	103911	119688	117758	-11	2.5	0.8
$6p^2\ ^3P_0$	117408	108495	120875	118450	-8	3.0	0.9
$6p^2\ ^3P_1$	125338	114961	129401	126440	-8	3.2	0.9
$6p^2\ ^3P_2$	128817	117721	132754	129839	-9	3.1	0.8
$6s8s\ ^3S_1$	133568	120147	136369	134187	-10	2.1	0.5
$6s8s\ ^1S_0$	134292	121089	137132	134950	-10	2.1	0.5
$6s6p\ ^3P_0$	49451	41719	52320	50288	-16	5.8	1.7
$6s6p\ ^3P_1$	52394	44743	55114	53060	-15	5.2	1.3
$6s6p\ ^3P_2$	61728	61728	65044	62669	-14	5.4	1.5
$6s6p\ ^1P_1$	75663	75663	76866	76145	-7	1.6	0.6
$6s7p\ ^3P_0$	119361	119361	122299	120155	-11	2.5	0.7
$6s7p\ ^3P_1$	119576	119576	122602	120472	-11	2.5	0.8
$6s7p\ ^3P_2$	122209	122029	124873	122675	-11	2.3	0.5
$6s7p\ ^1P_1$	122379	122379	126014	124019	-9	3.0	1.3
$6s5f\ ^3F_2$	136216	136216	138873	136600	-10	2.0	0.3
$6s5f\ ^3F_3$	136115	136115	138868	136577	-10	2.0	0.4
$6s5f\ ^3F_4$	136230	136230	138870	136595	-10	1.9	0.3
$6s5f\ ^1F_3$	136263	136263	138997	136756	-10	2.0	0.4

In the present calculation, the  $\text{TI}^+$  scalar polarizability  $\alpha_0$  is separated into a valence polarizability  $\alpha_0^v$ , ionic core polarizability  $\alpha_c$ , and a small term  $\alpha_{vc}$  (that modifies ionic core polarizability due to the presence of two valence electrons). The ionic core polarizability is evaluated in the random-phase approximation (RPA), an approach that is expected to provide core values accurate to better than 5% [4]. We approximate the vc term by adding vc contributions from the individual electrons, i.e.  $\alpha_{vc}(6s^2) = 2\alpha_{vc}(6s)$ , and  $\alpha_{vc}(6s6p) = \alpha_{vc}(6s) + \alpha_{vc}(6p)$ . For consistency, this term is also calculated in RPA. We note that  $\alpha_{vc}$  contributions are small, but their contribution to the  $\Delta\alpha(^3P_0 - ^1S_0)$  polarizability difference is significant, 15%, due to severe cancellation of the valence polarizabilities of these two states. The valence polarizability is determined by solving the inhomogeneous equation of perturbation theory in the valence space, which is approximated as

$$(E_v - H_{\text{eff}})|\Psi(v, M')\rangle = D_{\text{eff},q}|\Psi_0(v, J, M)\rangle \quad (2)$$

for a state  $v$  with the total angular momentum  $J$  and projection  $M$  [15]. The wave function  $\Psi(v, M')$ , where

TABLE II: Comparison between experimental [13, 14] and CI+all-order transition energies in  $\text{cm}^{-1}$ . The relative differences are given in the last column in percent.

Transition	Expt.	CI+all-order	Dif. (%)
$6s6p\ ^3P_0 - 6s7s\ ^3S_1$	55778	55739	0.07%
$6s6p\ ^3P_0 - 6s6d\ ^3D_1$	66701	66569	0.20%
$6s6p\ ^3P_0 - 6p^2\ ^3P_1$	75887	76152	-0.35%
$6s6p\ ^3P_0 - 6s8s\ ^3S_1$	84117	83899	0.26%

$M' = M + q$ , is composed of parts that have angular momenta of  $J' = J, J \pm 1$  from which the scalar and tensor polarizability of the state  $|v, J, M\rangle$  can be determined [15]. The effective dipole operator  $D_{\text{eff}}$  includes RPA corrections.

Unless stated otherwise, we use atomic units (a.u.) for all matrix elements and polarizabilities throughout this paper: the numerical values of the elementary charge,  $e$ , the reduced Planck constant,  $\hbar = h/2\pi$ , and the electron mass,  $m_e$ , are set equal to 1. The atomic unit for polarizability can be converted to SI units via  $\alpha/h$  [ $\text{Hz}/(\text{V}/\text{m})^2$ ]= $2.48832 \times 10^{-8}\alpha$  (a.u.). The conversion coefficient is  $4\pi\epsilon_0 a_0^3/h$  in SI units and the Planck constant  $h$  is factored out in order to provide direct conversion into frequency units;  $a_0$  is the Bohr radius and  $\epsilon_0$  is the electric constant.

While we do not use the sum-over-state approach in the calculation of the polarizabilities, it is useful to establish which levels give the dominant contributions. We evaluate several leading contributions to polarizabilities by combining our values of the E1 matrix elements and energies according to the sum-over-states formula for the valence polarizability [4]:

$$\alpha_0^v = \frac{2}{3(2J+1)} \sum_n \frac{|\langle v||D||n\rangle|^2}{E_n - E_v} \quad (3)$$

where  $J$  is the total angular momentum of state  $v$ ,  $D$  is the electric dipole operator, and  $E_i$  is the energy of the state  $i$ .

The breakdown of the contributions to the  $6s^2\ ^1S_0$  and  $6s6p\ ^3P_0$  polarizabilities  $\alpha_0$  of  $\text{TI}^+$  in a.u. is given in Table III. Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled “ $D$ ” in  $a_0 e$ . To demonstrate the size of the correlation corrections, we list valence results obtained in the CI, CI+MBPT, and CI+all-order approximations. The contribution of the other terms listed in the row “Other” is obtained by subtracting the sum of the contributions that are calculated separately from the total valence polarizability result obtained by the direct solution of the Eq. (2). With the exception of the last column labeled CI+all<sup>B</sup>, we use the theoretical energies obtained in the respective approximations. To obtain data listed in the last column, we combine CI+all-order E1 matrix elements and experimental energies. The polarizability of the ground state changes by 0.5% as expected from the

TABLE III: Contributions to the  $6s^2\ ^1S_0$  and  $6s6p\ ^3P_0$  polarizabilities in a.u. The dominant contributions to the valence polarizabilities are listed separately with the corresponding E1 matrix elements given in columns labeled  $D$ . The remaining valence contribution is given in row Other. The contribution from the core and vc terms are given by  $\alpha_c$  and  $\alpha_{vc}$ , respectively. The dominant contributions to  $\alpha_0$  listed in columns CI+all<sup>A</sup> and CI+all<sup>B</sup> are calculated with CI + all-order energies and NIST [13, 14] energies, respectively. The differences of the  $^3P_0$  and  $^1S_0$  polarizabilities calculated in different approximations are given in the last row.

State	Contribution	CI		CI+MBPT		CI+all <sup>A</sup>		CI+all <sup>B</sup>
		$D$	$\alpha_0$	$D$	$\alpha_0$	$D$	$\alpha_0$	$\alpha_0$
$6s^2\ ^1S_0$	$6s^2\ ^1S_0 - 6s6p\ ^3P_1$	0.424	0.589	0.658	1.149	0.597	0.984	0.997
	$6s^2\ ^1S_0 - 6s6p\ ^1P_1$	2.789	16.131	2.619	13.057	2.646	13.450	13.535
	Other		0.269		0.143		0.155	0.155
	$\alpha_c$		4.983		4.983		4.983	4.983
	$\alpha_{vc}$		-0.071		-0.071		-0.071	-0.071
	Total		21.901		19.261		19.501	19.599
$6s6p\ ^3P_0$	$6s6p\ ^3P_0 - 6s7s\ ^3S_1$	1.044	3.113	0.975	2.499	0.980	2.519	2.517
	$6s6p\ ^3P_0 - 6s6d\ ^3D_1$	2.007	9.563	1.893	7.860	1.897	7.912	7.897
	$6s6p\ ^3P_0 - 6p^2\ ^3P_1$	1.616	5.219	1.557	4.603	1.562	4.690	4.706
	Other		1.782		1.630		1.660	1.660
	$\alpha_c$		4.983		4.983		4.983	4.983
	$\alpha_{vc}$		-0.338		-0.338		-0.338	-0.338
	Total		24.322		21.236		21.426	21.425
$\Delta\alpha_0(^3P_0 - ^1S_0)$			2.421		1.975		1.925	1.826

TABLE IV: Contributions to dynamic corrections  $\eta$  for  $6s^2\ ^1S_0$  and  $6s6p\ ^3P_0$  states.

State	Transition	$y_n$	$\eta$
$\eta(6s^2\ ^1S_0)$	$6s^2\ ^1S_0 - 6s6p\ ^3P_1$	363	0.000099
	$6s^2\ ^1S_0 - 6s6p\ ^1P_1$	251	0.000015 0.000114
$\eta(6s6p\ ^3P_0)$	$6s6p\ ^3P_0 - 6s7s\ ^3S_1$	268	0.000031
	$6s6p\ ^3P_0 - 6s6d\ ^3D_1$	320	0.000068
	$6s6p\ ^3P_0 - 6p^2\ ^3P_1$	364	0.000031 0.000130
$\Delta\eta(^3P_0 - ^1S_0)$			0.000016

accuracy of the  $6s^2\ ^1S_0 - 6s6p\ ^1P_1$  transition energy listed in Table I. The polarizability of the excited  $6s6p\ ^3P_0$  state remains the same to four significant figures. Such remarkable agreement is due to excellent, 0.07%, accuracy of the CI+all-order  $6s6p\ ^3P_0 - 6s7s\ ^3S_1$  transition energy and opposite signs of the difference between CI+all-order  $6s6p\ ^3P_0 - 6s6d\ ^3D_1$  and  $6s6p\ ^3P_0 - 6p^2\ ^3P_1$  transition energies and experiment (see Table II). We note that while the change in the ground state polarizability is only 0.5%, the corresponding change in the final polarizability difference  $\Delta\alpha(^3P_0 - ^1S_0)$  is 5%.

To the best of our knowledge, there is only one experimental measurement of the  $6s6p\ ^1P_1$  and  $6s6p\ ^3P_1$  lifetimes,  $\tau(6s6p\ ^1P_1) = 0.59(4)$  ns and  $\tau(6s6p\ ^3P_1) = 39(2)$  ns carried out using a beam-foil excitation tech-

nique [16]. Our corresponding CI+all-order matrix elements are  $D(6s^2\ ^1S_0 - 6s6p\ ^1P_1) = 2.646$  a.u. and  $D(6s^2\ ^1S_0 - 6s6p\ ^3P_1) = 0.597$  a.u. To evaluate the uncertainties of these values, we compared the CI+MBPT and CI+all-order results for these matrix elements (see Table III), and took the difference between these two calculations (1% for  $^1P_1$  and 10% for  $^3P_1$ ) as the uncertainty in the core-valence correlations. We expect all other missing corrections to be smaller than these differences. Therefore, all other uncertainties should not exceed the 1% and 10%, respectively. Conservatively, we add uncertainties in core-valence correlations and all other contributions in quadrature, giving  $D(6s^2\ ^1S_0 - 6s6p\ ^1P_1) = 2.646(37)$  a.u. and  $D(6s^2\ ^1S_0 - 6s6p\ ^3P_1) = 0.597(84)$  a.u. Correlation corrections are very large for the  $^1S_0 - ^3P_1$  intercombination line, resulting in much higher uncertainty. The contribution of this transition to polarizability is negligible.

We combine CI+all-order E1 matrix elements from Table III with experimental energies to obtain  $\tau(6s6p\ ^1P_1) = 0.488(14)$  ns and  $\tau(6s6p\ ^3P_1) = 29(8)$  ns lifetimes. The resonance  $^1P_1$  lifetime differs with the experiment by  $2.5\sigma$ , where  $\sigma$  is a combined uncertainty of our calculation and measurement [16]. The value for the  $^3P_1$  lifetime is consistent within uncertainty estimate with the measured value. Authors of Ref. [16] note that due to the nonselective nature of beam-foil excitation, the level populations (and hence the decay curves) are affected by cascade repopulation. Thus, cascades can distort the decay curves of shorter-lived levels such as the  $6s^2\ ^1S_0 - 6s6p\ ^1P_1$  resonance transition. Additional

TABLE V: BBR shifts at  $T = 300K$  in  $B^+$ ,  $Al^+$ ,  $In^+$ , and  $Tl^+$ .  $B^+$ ,  $Al^+$ , and  $In^+$  values are taken from Ref. [6]. Polarizabilities  $\alpha_0$  and their differences  $\Delta\alpha_0$  are given in a.u.; clock frequencies  $\nu_0$  and the BBR shifts  $|\Delta\nu_{\text{BBR}}|$  are given in Hz. Uncertainties in the values of  $\Delta\nu_{\text{BBR}}/\nu_0$  are given in column labeled ‘‘Uncertainty’’.

Ion	$\alpha_0(^1S_0)$	$\alpha_0(^3P_0)$	$\Delta\alpha_0$	$\Delta\nu_{\text{BBR}}$ (Hz)	$\nu_0$ (Hz)	$ \Delta\nu_{\text{BBR}}/\nu_0 $	Uncertainty
$B^+$	9.624	7.772	-1.85(19)	0.0159(16)	$1.119 \times 10^{15}$	$1.42 \times 10^{-17}$	$1 \times 10^{-18}$
$Al^+$	24.048	24.543	0.495(50)	-0.00426(43)	$1.121 \times 10^{15}$	$3.8 \times 10^{-18}$	$4 \times 10^{-19}$
$In^+$	24.01	26.02	2.01(20)	-0.0173(17)	$1.267 \times 10^{15}$	$1.36 \times 10^{-17}$	$1 \times 10^{-18}$
$Tl^+$	19.60	21.43	1.83(18)	-0.0157(16)	$1.483 \times 10^{15}$	$1.06 \times 10^{-17}$	$1 \times 10^{-18}$

analysis was used to evaluate such lifetimes.

In recent work [17], we have demonstrated that the same  $6s6p\ ^1P_1$  lifetime measured in another Hg-like ion,  $Pb^{2+}$  by the same beam-foil excitation approach [18] is inconsistent with the 2010 very accurate (0.6%) experimental value of the ground state polarizability [19]. The  $6s^2\ ^1S_0$  polarizability is dominated by the  $6s^2\ ^1S_0 - 6s6p\ ^1P_1$  resonance transition. Our theoretical lifetime in the  $6s6p\ ^1P_1$  Hg-like ion,  $Pb^{2+}$ , calculated by the same approach as the  $Tl^+$  result, is 0.301 ns [17]. Our calculation is in agreement with the polarizability measurement [19], but 20% lower than the beam-foil measurement 0.380(21)nm. This difference is similar to the 17% difference in  $Tl^+$ . Further experimental investigations of the  $6s6p\ ^1P_1$  lifetimes in Hg-like ions are needed to resolve the discrepancy.

We have also calculated the dynamic correction  $\eta$  of both clock states. The total dynamic correction  $\eta$  in Eq. (1) is the difference of individual corrections,  $\Delta\eta(^3P_0 - ^1S_0) = \eta(^3P_0) - \eta(^1S_0)$ . The dynamic correction  $\eta$  of the state  $v$  is evaluated using the formula [5]

$$\eta = \sum_n \frac{(80/63)\pi^2}{\alpha_0 T} \frac{|\langle v || D || n \rangle|^2}{(2J+1)y_n^3} \left( 1 + \frac{21\pi^2}{5y_n^2} + \frac{336\pi^4}{11y_n^4} \right),$$

where  $y_n = \omega_{nv}/T$ ;  $\alpha_0$  is the static dipole polarizability of the state  $v$ , and  $J$  the total angular momentum of the state  $v$ . We list the dominant contributions to  $\eta$  of the clock states calculated using CI+all-order E1 matrix elements and experimental energies in Table IV. The sum in the expression for  $\eta$  above converges very rapidly making all other contributions negligible. The values of  $\eta$  for the  $6s\ ^1S_0$  and  $6s6p\ ^3P_0$  state are almost equal, and their difference listed in the last row gives only 0.0016% contribution to the BBR shift.

#### IV. EVALUATION OF THE UNCERTAINTY AND CONCLUSION

We use Table III to evaluate the uncertainty to the BBR shift due to the core-valence correlation corrections by comparing the CI, CI+MBPT, and CI+all-order results for  $\Delta\alpha_0(^3P_0 - ^1S_0)$  listed in the last row of Table III. The difference between the CI and CI+MBPT results is 23%, which is expected owing to poor agreement of CI energies with experiment. The difference between the

CI+MBPT and CI+all-order results is only 3%. As we noted above, the use of the experimental energies changes CI+all-order value by 5%.

We studied the effect of the Breit interaction by repeating the CI+all-order calculation with the one-body part of the Breit interaction incorporated into the DF equations and construction of the basis set on the same footing with the Coulomb interaction. We find that the Breit interaction affects both  $^1S_0$  and  $^3P_0$  polarizabilities by approximately the same amount, -0.5%. As a result, the correction to the BBR shift due to the Breit interaction is negligible (0.6%) at the present level of accuracy.

To evaluate the uncertainty in the  $\alpha_{vc}$  contribution to the polarizability, we calculate this term in both DF and RPA approximations. The difference between these results is taken to be the uncertainty. We find that the uncertainty of the  $vc$  term contributes 2.4% to the uncertainty in the BBR shift. The ionic core polarizability  $\alpha_c$  is the same for both states and does not contribute to the BBR shift.

Based on the comparison of the CI, CI+MBPT, and CI+all-order data, estimated of the accuracy of the  $\alpha_{vc}$  terms, and estimated effect of the Breit interaction, we place an upper bound on the uncertainty of our  $\Delta\alpha_0(^3P_0 - ^1S_0)$  polarizability difference and the corresponding BBR shift of  $Tl^+$  at 10%.

Our final result for the BBR shift of the  $6s^2\ ^1S_0 - 6s6p\ ^3P_0$  transition in  $Tl^+$  is  $\Delta\nu_{\text{BBR}} = -0.0157(16)$  Hz at 300 K. The corresponding relative BBR shift at 300 K is  $|\Delta\nu_{\text{BBR}}/\nu_0| = 1.1(1) \times 10^{-17}$ . Our final results are summarized in Table V, where we list the clock state polarizabilities, their difference  $\Delta\alpha_0$ , BBR shift at  $T = 300$  K,  $^1S_0 - ^3P_0$  clock frequencies  $\nu_0$ , absolute value of the relative BBR shift  $|\Delta\nu_{\text{BBR}}/\nu_0|$ , and the uncertainty in the relative BBR shift of  $Tl^+$ . The  $Tl^+$  values are compared with the results obtained for  $B^+$ ,  $Al^+$ , and  $In^+$  ions in Ref. [6]. The results listed in Table V demonstrate that near cancelation of the  $^1S_0$  and  $^3P_0$  state polarizabilities in divalent  $B^+$ ,  $Al^+$ ,  $In^+$  ions of group IIIB [6] continues for much heavier  $Tl^+$ , leading to anomalously small BBR shift for this system. This calculation demonstrates that the BBR contribution to the fractional frequency uncertainty of the  $Tl^+$  frequency standard at 300 K is  $1 \times 10^{-18}$ . We find that  $Tl^+$  has the smallest fractional BBR shift among all present or proposed frequency standards with the exception of  $Al^+$ .

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