

Anomalously small blackbody radiation shift in the Tl^+ 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 the Tl^+ 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^+ 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^+ , Al^+ , and In^+ ions of group IIIB [M. S. Safronova *et al.*, *Phys. Rev. Lett.* **107**, 143006 (2011)] 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 1×10^{-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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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 the 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 8.6×10^{-18} , based on quantum logic spectroscopy of an Al^+ 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 nonzero 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 Refs. [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^+ , Al^+ , and In^+ , 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}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 an 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 has 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^+ .

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]

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

where η 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^+ and found to be negligible [6]. Therefore, the calculation of the BBR shift reduces to accurate calculation of the static polarizabilities of the clock states and dynamic correction η .

In this work, we evaluate polarizabilities of the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ states in Tl^+ , 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 Tl^+ for transitions between low-lying levels. We note that our calculation of all of these properties is independent of the particular isotope number well within the quoted level of precision. Therefore, all these results apply to any Tl^+ 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 Ref. [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 the coupled-cluster (CC) approach. This method, suggested in Ref. [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 ψ_c and ε_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 $s, p_{1/2}, p_{3/2}, \dots$ partial waves with $l \leq 5$. 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 performed 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 two 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_{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 perturba-

TABLE I. Comparison between experimental [13,14] and theoretical energy levels in 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
$6s^2 1S_0$	405 365	376 102	412 676	407 125	-7	1.8	0.4
$6s 7s 3S_1$	105 229	929 45	108 031	106 028	-12	2.7	0.8
$6s 7s 1S_0$	108 000	963 04	110 845	108 904	-11	2.6	0.8
$6s 6d 1D_2$	115 166	101 238	118 678	116 194	-12	3.1	0.9
$6s 6d 3D_1$	116 152	103 334	119 000	116 857	-11	2.5	0.6
$6s 6d 3D_2$	116 436	103 555	119 339	117 284	-11	2.5	0.7
$6s 6d 3D_3$	116 831	103 911	119 688	117 758	-11	2.5	0.8
$6p^2 3P_0$	117 408	108 495	120 875	118 450	-8	3.0	0.9
$6p^2 3P_1$	125 338	114 961	129 401	126 440	-8	3.2	0.9
$6p^2 3P_2$	128 817	117 721	132 754	129 839	-9	3.1	0.8
$6s 8s 3S_1$	133 568	120 147	136 369	134 187	-10	2.1	0.5
$6s 8s 1S_0$	134 292	121 089	137 132	134 950	-10	2.1	0.5
$6s 6p 3P_0$	494 51	417 19	523 20	502 88	-16	5.8	1.7
$6s 6p 3P_1$	523 94	447 43	551 14	530 60	-15	5.2	1.3
$6s 6p 3P_2$	617 28	617 28	650 44	626 69	-14	5.4	1.5
$6s 6p 1P_1$	756 63	756 63	768 66	761 45	-7	1.6	0.6
$6s 7p 3P_0$	119 361	119 361	122 299	120 155	-11	2.5	0.7
$6s 7p 3P_1$	119 576	119 576	122 602	120 472	-11	2.5	0.8
$6s 7p 3P_2$	122 209	122 029	124 873	122 675	-11	2.3	0.5
$6s 7p 1P_1$	122 379	122 379	126 014	124 019	-9	3.0	1.3
$6s 5f 3F_2$	136 216	136 216	138 873	136 600	-10	2.0	0.3
$6s 5f 3F_3$	136 115	136 115	138 868	136 577	-10	2.0	0.4
$6s 5f 3F_4$	136 230	136 230	138 870	136 595	-10	1.9	0.3
$6s 5f 1F_3$	136 263	136 263	138 997	136 756	-10	2.0	0.4

tion 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 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 TI^+ and TI^{2+} ionization limits given in Ref. [13], $164\,765(5) \text{ cm}^{-1}$ and $240\,600 \text{ cm}^{-1}$. Reference [13] notes that the ionization

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

Transition	Expt.	CI+all-order	Difference (%)
$6s6p\ ^3P_0$ - $6s7s\ ^3S_1$	55 778	55 739	0.07%
$6s6p\ ^3P_0$ - $6s6d\ ^3D_1$	66 701	66 569	0.20%
$6s6p\ ^3P_0$ - $6p^2\ ^3P_1$	75 887	76 152	-0.35%
$6s6p\ ^3P_0$ - $6s8s\ ^3S_1$	84 117	83 899	0.26%

limit for Tl^{2+} , derived from the first three 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 Tl^+ .

We also compared the transition energies between the $6s6p\ ^3P_0$ level and four 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.

In the present calculation, the Tl^+ scalar polarizability α_0 is separated into a valence polarizability α_0^v , ionic core polarizability α_c , and a small term α_{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 α_{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 $M' = M + q$, 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_{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 α/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 ϵ_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 α_0 of Tl^+ 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_0e . 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^B, 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 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 technique [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

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 α_c and α_{vc} , respectively. The dominant contributions to α_0 listed in columns CI+all^A and CI+all^B 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 ^A		CI+all ^B
		D	α_0	D	α_0	D	α_0	α_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
	α_c		4.983		4.983		4.983	4.983
	α_{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
	α_c		4.983		4.983		4.983	4.983
	α_{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

$\tau(6s6p\ ^1P_1) = 0.488(14)$ ns and $\tau(6s6p\ ^3P_1) = 29(8)$ ns lifetimes. The resonance 1P_1 lifetime differs with the experiment by 2.5σ , where σ is the 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 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

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

State	Transition	y_n	η
$\eta(6s^2\ ^1S_0)$	$6s^2\ ^1S_0$ - $6s6p\ ^3P_1$	363	0.000099
	$6s^2\ ^1S_0$ - $6s6p\ ^1P_1$	251	0.000015
	Total		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
	Total		0.000130
$\Delta\eta(^3P_0 - ^1S_0)$			0.000016

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 η of both clock states. The total dynamic correction η in Eq. (1) is the difference of individual corrections, $\Delta\eta(^3P_0 - ^1S_0) = \eta(^3P_0) - \eta(^1S_0)$. The dynamic correction η 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 $y_n = \omega_{nv}/T$; α_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 η of the clock states calculated using CI+all-order $E1$ matrix elements and experimental energies in Table IV. The sum in the expression for η above converges very rapidly making all other contributions negligible. The values of η for the $6s^2\ ^1S_0$ and $6s6p\ ^3P_0$ states 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%.

TABLE V. BBR shifts at $T = 300$ K in B^+ , Al^+ , In^+ , and Tl^+ . B^+ , Al^+ , and In^+ values are taken from Ref. [6]. Polarizabilities α_0 and their differences $\Delta\alpha_0$ are given in a.u.; clock frequencies ν_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)	ν_0 (Hz)	$ \Delta\nu_{\text{BBR}}/\nu_0 $	Uncertainty
B^+	9.624	7.772	-1.85(19)	-0.0159(16)	1.119×10^{15}	1.42×10^{-17}	1×10^{-18}
Al^+	24.048	24.543	0.495(50)	-0.00426(43)	1.121×10^{15}	3.8×10^{-18}	4×10^{-19}
In^+	24.01	26.02	2.01(20)	-0.0173(17)	1.267×10^{15}	1.36×10^{-17}	1×10^{-18}
Tl^+	19.60	21.43	1.83(18)	-0.0157(16)	1.483×10^{15}	1.06×10^{-17}	1×10^{-18}

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 α_{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 α_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 accuracy of the α_{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 differences $\Delta\alpha_0$, BBR shift at $T = 300$ K, $^1S_0-^3P_0$ clock frequencies ν_0 , absolute values of the relative BBR shift $|\Delta\nu_{\text{BBR}}/\nu_0|$, and the uncertainties in the relative BBR shift. 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 cancellation 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 1×10^{-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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