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 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$^+$. Optical frequency standard based on $^{204}$Tl is 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 $^{204}$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]

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

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$^+$ 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 $\eta$.

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 perturbative approaches. However, excitations of the core \([1s^2, \ldots, 5d^{10}]\) 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

\[ \hat{H}_0 \psi_c = e_c \psi_c, \]

where \(H_0\) is the relativistic DF Hamiltonian [8,9] and \(\psi_c\) and \(e_c\) are single-electron wave functions and energies. The self-consistent calculations were performed for the \([1s^2, \ldots, 5d^{10}]\) 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 \(s, p_{1/2}, p_{3/2}, \ldots\) 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 \(H_{\text{FC}}\) 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 perturba-

\[
\begin{array}{cccccc}
\text{State} & \text{Expt.} & \text{CI} & \text{MBPT} & \text{All} & \text{Differences (%)} \\
\hline
6s^2 \text{\textit{S}}_0 & 405.365 & 376.102 & 412.676 & 407.125 & -7 & 1.8 & 0.4 \\
6s^7 \text{\textit{S}}_3 & 105.229 & 929.45 & 108.031 & 106.028 & -12 & 2.7 & 0.8 \\
6s^7 \text{\textit{S}}_5 & 108.000 & 936.04 & 110.845 & 108.904 & -11 & 2.6 & 0.8 \\
6s^6 \text{\textit{P}}_2 & 115.166 & 101.238 & 118.678 & 116.194 & -12 & 3.1 & 0.9 \\
6s^6 \text{\textit{P}}_3 & 116.152 & 103.334 & 119.000 & 116.857 & -11 & 2.5 & 0.6 \\
6s^6 \text{\textit{D}}_0 & 116.436 & 103.555 & 119.339 & 117.284 & -11 & 2.5 & 0.7 \\
6s^6 \text{\textit{D}}_3 & 116.831 & 103.911 & 119.688 & 117.758 & -11 & 2.5 & 0.8 \\
6p^2 \text{\textit{P}}_1 & 117.408 & 108.495 & 120.875 & 118.450 & -8 & 3.0 & 0.9 \\
6p^2 \text{\textit{P}}_3 & 125.338 & 114.961 & 129.401 & 126.440 & -8 & 3.2 & 0.9 \\
6p^2 \text{\textit{P}}_5 & 128.817 & 117.721 & 132.754 & 129.839 & -9 & 3.1 & 0.8 \\
6s^8 \text{\textit{S}}_1 & 133.568 & 120.147 & 136.369 & 134.187 & -10 & 2.1 & 0.5 \\
6s^8 \text{\textit{S}}_3 & 134.292 & 121.089 & 137.132 & 134.950 & -10 & 2.1 & 0.5 \\
6s^6 \text{\textit{P}}_0 & 494.51 & 417.19 & 523.20 & 502.88 & -16 & 5.8 & 1.7 \\
6s^6 \text{\textit{P}}_1 & 523.94 & 447.43 & 551.14 & 530.60 & -15 & 5.2 & 1.3 \\
6s^6 \text{\textit{P}}_2 & 617.28 & 617.28 & 650.44 & 626.69 & -14 & 5.4 & 1.5 \\
6s^6 \text{\textit{P}}_3 & 756.63 & 756.63 & 768.66 & 761.45 & 7 & 1.6 & 0.5 \\
6s^7 \text{\textit{P}}_0 & 119.361 & 119.361 & 122.299 & 120.155 & -11 & 2.5 & 0.7 \\
6s^7 \text{\textit{P}}_1 & 119.576 & 119.576 & 122.602 & 120.472 & -11 & 2.5 & 0.8 \\
6s^7 \text{\textit{P}}_2 & 122.209 & 122.029 & 124.873 & 122.675 & -11 & 2.3 & 0.5 \\
6s^7 \text{\textit{P}}_3 & 122.379 & 122.379 & 126.014 & 124.019 & -9 & 3.0 & 1.3 \\
6s^5 \text{\textit{F}}_3 & 136.216 & 136.216 & 138.873 & 136.600 & -10 & 2.0 & 0.3 \\
6s^5 \text{\textit{F}}_5 & 136.115 & 136.115 & 138.668 & 136.577 & -10 & 2.0 & 0.4 \\
6s^5 \text{\textit{F}}_7 & 136.230 & 136.230 & 138.870 & 136.595 & -10 & 1.9 & 0.3 \\
6s^5 \text{\textit{F}}_9 & 136.263 & 136.263 & 138.997 & 136.756 & -10 & 2.0 & 0.4 \\
\end{array}
\]
ANOMALOUSLY SMALL BLACKBODY RADIATION SHIFT ...

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.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Expt.</th>
<th>CI+all-order</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6s6p (^3)P(_0)-6s7s (^3)S(_1)</td>
<td>55778</td>
<td>55739</td>
<td>0.07%</td>
</tr>
<tr>
<td>6s6p (^3)P(_0)-6s6d (^3)D(_1)</td>
<td>66701</td>
<td>66669</td>
<td>0.20%</td>
</tr>
<tr>
<td>6s6p (^3)P(_0)-6s6p (^3)P(_1)</td>
<td>75887</td>
<td>76152</td>
<td>−0.35%</td>
</tr>
<tr>
<td>6s6p (^3)P(_0)-6s8s (^3)S(_1)</td>
<td>84117</td>
<td>83899</td>
<td>0.26%</td>
</tr>
</tbody>
</table>

limit for Tl\(^{2+}\), derived from the first three members of the \(^3\)S series was shifted by 300 cm\(^{-1}\) to give effective quantum number for 5\(^2\)G that is nearly hydrogenic. Therefore, there is some uncertainty (≤ 0.1%) associated with the two-electron binding energy in Tl\(^{2+}\).

We also compared the transition energies between the 6s6p \(^3\)P\(_0\) level and four levels relevant to the calculation of the 6s6p \(^3\)P\(_0\) 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 \(\alpha_0\) 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 \(v\)c 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 \(\Delta\alpha(6p^2 - 5d^2)\) 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

\[
(E_v - H_{eff})|\Psi(v, M')\rangle = D_{eff, q}|\Psi_0(v, J, M)\rangle
\]

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 \(v, J, M\) 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 \(\alpha/h|Hz/(V/m)^2| = 2.48832 \times 10^{-19}\) (a.u.) The conversion coefficient is \(4\pi \varepsilon_0 \alpha_0/\hbar\) in SI units and the Planck constant \(h\) is factored out in order to provide direct conversion into frequency units; \(\alpha_0\) is the Bohr radius and \(\varepsilon_0\) 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]

\[
\alpha_0^v = \frac{2}{3(2J + 1)} \sum_i |\langle v | D || n \rangle|^2 E_n - E_v'^, \tag{3}
\]

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\(^2\) 5S\(_0\) and 6s6p \(^3\)P\(_0\) polarizabilities \(\alpha_0\) 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 ”\(Dn\)” in \(\alpha_0\). 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\(^R\), 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\(^2\) 5S\(_0\)-6s6p \(^3\)P\(_1\) transition energy listed in Table I. The polarizability of the excited 6s6p \(^3\)P\(_0\) state remains the same to four significant figures. Such remarkable agreement is due to excellent, 0.07%, accuracy of the CI+all-order 6s6p \(^3\)P\(_0\)-6s7s \(^3\)S\(_1\) transition energy and opposite signs of the difference between CI+all-order 6s6p \(^3\)P\(_0\)-6s6d \(^3\)D\(_1\) and 6s6p \(^3\)P\(_0\)-6s6p \(^3\)P\(_1\) 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 \(\Delta\alpha(6p^2 - 5d^2)\) is 5%.

To the best of our knowledge, there is only one experimental measurement of the 6s6p \(^3\)P\(_1\) and 6s6p \(^3\)P\(_3\) lifetimes, \(\tau(6s6p \(^3\)P\(_1\)) = 0.59(4)\) ns and \(\tau(6s6p \(^3\)P\(_3\)) = 39(2)\) ns carried out using a beam-foil excitation technique [16]. Our corresponding CI+all-order matrix elements are \(D(6s\(^2\) 5S\(_0\)-6s6p \(^3\)P\(_1\)) = 2.646\) a.u. and \(D(6s\(^2\) 5S\(_0\)-6s6p \(^3\)P\(_3\)) = 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 \(^3\)P\(_1\) and 10% for \(^3\)P\(_3\)) 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\(^2\) 5S\(_0\)-6s6p \(^3\)P\(_1\)) = 2.646(37)\) a.u. and \(D(6s\(^2\) 5S\(_0\)-6s6p \(^3\)P\(_3\)) = 0.597(84)\) a.u. Correlation corrections are very large for the \(^3\)S\(_0\)-\(^3\)P\(_1\) 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 $\alpha_c$ and $\alpha_{vc}$, respectively. The dominant contributions to $\alpha_c$ listed in columns CI+all$^4$ and CI+all$^d$ 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.

<table>
<thead>
<tr>
<th>State</th>
<th>Contribution</th>
<th>CI</th>
<th>CI+MBPT</th>
<th>CI+all$^4$</th>
<th>CI+all$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D$</td>
<td>$\alpha_c$</td>
<td>$D$</td>
<td>$\alpha_c$</td>
</tr>
<tr>
<td>$6s^2 , ^1S_0$</td>
<td>$6s^2 , ^1S_0 - 6s6p , ^1P_1$</td>
<td>0.424</td>
<td>0.589</td>
<td>0.658</td>
<td>1.149</td>
</tr>
<tr>
<td></td>
<td>$6s^2 , ^1S_0 - 6s6p , ^1P_1$</td>
<td>2.789</td>
<td>16.131</td>
<td>2.619</td>
<td>13.057</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0.269</td>
<td>0.143</td>
<td>0.143</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td>$\alpha_c$</td>
<td>4.983</td>
<td>4.983</td>
<td>4.983</td>
<td>4.983</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{vc}$</td>
<td>-0.071</td>
<td>-0.071</td>
<td>-0.071</td>
<td>-0.071</td>
</tr>
<tr>
<td>$6s6p , ^3P_0$</td>
<td>$6s6p , ^3P_0 - 6s7s , ^3S_1$</td>
<td>1.044</td>
<td>3.113</td>
<td>0.975</td>
<td>2.499</td>
</tr>
<tr>
<td></td>
<td>$6s6p , ^3P_0 - 6s6d , ^3D_1$</td>
<td>2.007</td>
<td>9.563</td>
<td>1.893</td>
<td>7.860</td>
</tr>
<tr>
<td></td>
<td>$6s6p , ^3P_0 - 6p^2 , ^3P_1$</td>
<td>1.616</td>
<td>5.219</td>
<td>1.557</td>
<td>4.603</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>1.782</td>
<td>1.630</td>
<td>1.630</td>
<td>1.660</td>
</tr>
<tr>
<td></td>
<td>$\alpha_c$</td>
<td>4.983</td>
<td>4.983</td>
<td>4.983</td>
<td>4.983</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{vc}$</td>
<td>-0.338</td>
<td>-0.338</td>
<td>-0.338</td>
<td>-0.338</td>
</tr>
<tr>
<td>$\Delta \alpha_0(, ^1P_0 - , ^1S_0)$</td>
<td></td>
<td>2.421</td>
<td>1.975</td>
<td>1.925</td>
<td>1.826</td>
</tr>
</tbody>
</table>

$\tau(6s6p \, ^1P_1) = 0.488(14)$ 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 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 Ti$^{2+}$ 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 Ti$^{2+}$. 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, $\Delta \eta(\, ^1P_0 - \, ^1S_0) = \eta(\, ^1P_0) - \eta(\, ^1S_0)$. The dynamic correction $\eta$ of the state $v$ is evaluated using the formula [5]

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

where $y_n = \omega_{\alpha_0}/T$, $\alpha_0$ 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 $6s^2 \, ^1S_0$ 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 $\Delta \alpha_0(\, ^1P_0 - \, ^1S_0)$ 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 $Ti^+$. $B^+$, $Al^+$, and $In^+$ values are taken from Ref. [6]. Polarizabilities $\alpha_0$ and their differences $\Delta \alpha_0$ are given in a.u.; clock frequencies $v_0$ and the BBR shifts $|\Delta \nu_{BBR}|$ are given in Hz. Uncertainties in the values of $\Delta \nu_{BBR}/v_0$ are given in column labeled Uncertainty.

| Ion   | $\alpha_0(1S_0)$ | $\alpha_0(3P_0)$ | $\Delta \alpha_0$ | $\Delta \nu_{BBR}$ (Hz) | $v_0$ (Hz) | $|\Delta \nu_{BBR}/v_0|$ | 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} |
| $Ti^+$| 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 $S_0$ and $P_0$ 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 $\alpha_{vc}$ contribution accounts for the uncertainty in the $vc$ part by RFBR Grant No. RFBR Grant No. 11-02-00943. The work of M.G.K. was supported in part by US NSF Grants No. PHY-1068699 and No. PHY-0758088. The work of M.G.K. was supported in part by RFBR Grant No. 11-02-00943.

Our final result for the BBR shift of the $6s^2 1S_0$ → $6s6p 3P_0$ transition in $Ti^+$ is $\Delta \nu_{BBR} = −0.0157(16)$ Hz at 300 K. The corresponding relative BBR shift at 300 K is $|\Delta \nu_{BBR}/v_0| = 1.1(1) × 10^{−17}$. 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, $S_0$-$P_0$ clock frequencies $v_0$, absolute values of the relative BBR shift $|\Delta \nu_{BBR}/v_0|$, and the uncertainties in the relative BBR shift. The $Ti^+$ 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 $S_0$ and $P_0$ state polarizabilities in divalent $B^+$, $Al^+$, $In^+$ ions of group III [6] continues for much heavier $Ti^+$, leading to anomalously small BBR shift for this system. This calculation demonstrates that the BBR contribution to the fractional frequency uncertainty of the $Ti^+$ frequency standard at 300 K is $1 × 10^{−18}$. We find that $Ti^+$ has the smallest fractional BBR shift among all present or proposed frequency standards with the exception of $Al^+$.

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