Blackbody radiation shifts in optical atomic clocks

M. S. Safronova[1], M. G. Kozlov, and Charles W. Clark

Abstract—**A review of recent theoretical calculations of black-body radiation (BBR) shifts in optical atomic clocks is presented. We summarize previous results for monovalent ions that were obtained by a relativistic all-order single-double method, where all single and double excitations of the Dirac-Fock wave function are included to all orders of perturbation theory. A recently developed method for accurate calculations of BBR shifts in divalent atoms is then presented. This approach combines the relativistic all-order method and the configuration interaction method, which provides for accurate treatment of correlation corrections in atoms with two valence electrons. Calculations of the BBR shifts in B^+, Al^+, and In^+ have enabled us to reduce the present fractional uncertainties in the frequencies of their clock transitions as measured at room temperature: to 4×10^{-19} for Al^+ and 10^{-18} for B^+ and In^+. These uncertainties approach recent estimates of the limits of precision of currently proposed optical atomic clocks. We discuss directions of future theoretical developments for reducing clock uncertainties due to blackbody radiation shifts.**

I. INTRODUCTION

The International System of Units (SI) defines the unit of time, the second, as "the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom," meaning, to be precise, "a cesium atom at rest at a temperature of 0 K" [1]. However, in light of recent advances in optical measurements beyond the 10 digits of precision in this microwave-based definition, the SI governance body has recommended a number of other radiation sources for attention, notably certain optical transitions of trapped cold atoms and ions such as Ca, H, Sr^+, Hg^+, In^+, Yb^+, Sr, and Rb [1], [2], [3]. In 2010, one such transition, $^{27}Al^+$ $3s^2$ $^1S_0$ - $3s3p$ $^3P_0$, was used to construct a quantum-logic optical clock with an estimated fractional frequency uncertainty of 8.6×10^{-18} [4]. This is a 10 million-fold improvement over the precision of the definition of the second. Development of such precise frequency standards opens the way to applications such as precise measurements of time variation of the fundamental constants, testing of physics postulates, geodesy, inertial navigation, magnetometry, and tracking of deep-space probes [5], and potentially to a more precise definition of the second.

Any definition of the second should be based on a clock decoupled from its particular environment. Thermal fluctuations of the electromagnetic field - "blackbody radiation" (BBR) are pervasive and can only be suppressed by cooling the clock. Through the AC Stark effect, the BBR at any non-zero temperature induces small shifts in atomic energy levels. At room temperature, the differential BBR shift of the two

levels of a clock transition turns out to make one of the largest irreducible contributions to the uncertainty budget of optical atomic clocks. Thus, measured clock transition frequencies must be corrected in practice for the effect of the BBR shift, which is quite difficult to measure directly.

In this paper, we review the current status of the theoretical calculations of BBR shifts in optical frequency standards. We consider the most recent developments in improving the accuracy of BBR shifts in Ca^+ and Al^+. In the latter case, our recent calculations reduce the fractional frequency uncertainty to 4×10^{-19}, which is close to the fundamental limits of cooled ion frequency standards due to effects such as micromotion in the trap [6], [7]. We present new calculations of BBR shifts for B^+ and In^+, which are candidates for quantum-logic spectroscopy as used with Al^+ [8]. We also discuss future possibilities for improvement of theoretical calculations of BBR shifts in various systems.

The overall BBR shift of the clock frequency is the difference between BBR shifts of the initial and final levels involved in the transition. It is related to the difference of the static electric-dipole polarizabilities between the clock states, $\Delta\alpha_0$, by [9]

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

where η is a small dynamic correction due to the frequency distribution of the blackbody radiation field. Evaluation of η requires knowledge of the electric-dipole matrix elements of the transitions that make the dominant contributions to the polarizabilities. Higher multipolar contributions to the BBR shift are suppressed by powers of the fine structure constant, α, and are insignificant in present uncertainty budgets. For example, magnetic-dipole (M1) contributions are suppressed by a factor of α^2 [9]; we estimate the M1 contribution to the Al^+ BBR shift to be less than 10^{-5} Hz, which is negligible at the present level of accuracy [10].

For optical *vs.* microwave transitions, the polarizabilities of the two clock states are completely independent, in principle. Theoretical evaluation of the BBR shift requires accurate calculation of the polarizabilities of the individual states. Only the scalar part of the polarizability contributes to the BBR shift, since any tensor component of the polarizability averages out due to the isotropy of blackbody radiation.

Useful figure of merit for the frequency standard is the fractional BBR shift, $\Delta\nu_{\mathrm{BBR}}/\nu_0$, where ν_0 is the absolute transition frequency. A summary of the fractional BBR shifts and their uncertainties at $T = 300$ K is given in Table I for various atomic transitions [9], [10], [11], [12], [13], [14], [15], [16], [17]. We also give the fractional BBR shifts in Rb and Cs microwave frequency standards [11], [12] to demonstrate

[1]Email: msafrono@udel.edu

TABLE I

SUMMARY OF THE FRACTIONAL BBR SHIFTS $\Delta\nu_{\mathrm{BBR}}/\nu_0$ AND THEIR UNCERTAINTIES AT $T = 300$ K IN VARIOUS FREQUENCY STANDARDS. ν_0 IS THE ABSOLUTE TRANSITION FREQUENCY IN Hz.

Atom	Clock transition	ν_0 (Hz)	$\Delta\nu_{\mathrm{BBR}}/\nu_0$	Uncertainty in $\Delta\nu_{\mathrm{BBR}}/\nu_0$	Reference
Rb	$5s\ (F = 2 - F = 1)$	8.34×10^9	-1.25×10^{-14}	4×10^{-17}	Safronova *et al.* 2010 [11]
Cs	$6s\ (F = 4 - F = 3)$	9.19×10^9	-1.7×10^{-14}	3×10^{-17}	Simon *et al.* 1998 [12]
Ca$^+$	$4s - 3d_{5/2}$	4.11×10^{14}	9.2×10^{-16}	1×10^{-17}	Safronova *et al.* 2011 [13]
Sr$^+$	$5s - 4d_{5/2}$	4.45×10^{14}	5.6×10^{-16}	2×10^{-17}	Jiang *et al.* 2009 [14]
Mg	$3s^2\ {}^1\mathrm{S}_0 - 3s3p\ {}^3\mathrm{P}_0$	6.55×10^{14}	-3.9×10^{-16}	1×10^{-17}	Porsev *et al.* 2006 [9]
Ca	$4s^2\ {}^1\mathrm{S}_0 - 4s4p\ {}^3\mathrm{P}_0$	4.54×10^{14}	-2.6×10^{-16}	4×10^{-17}	Porsev *et al.* 2006 [9]
Sr	$5s^2\ {}^1\mathrm{S}_0 - 5s5p\ {}^3\mathrm{P}_0$	4.29×10^{14}	-5.5×10^{-15}	7×10^{-17}	Porsev *et al.* 2006 [9]
Yb	$6s^2\ {}^1\mathrm{S}_0 - 6s6p\ {}^3\mathrm{P}_0$	5.18×10^{14}	-2.6×10^{-15}	3×10^{-16}	Porsev *et al.* 2006 [9]
Hg	$6s^2\ {}^1\mathrm{S}_0 - 6s6p\ {}^3\mathrm{P}_0$	1.13×10^{15}	-1.6×10^{-16}		Hachisu *et al.* 2008 [15]
B$^+$	$2s^2\ {}^1\mathrm{S}_0 - 2s2p\ {}^3\mathrm{P}_0$	1.12×10^{15}	1.42×10^{-17}	1×10^{-18}	Safronova *et al.* 2011 [10]
Al$^+$	$3s^2\ {}^1\mathrm{S}_0 - 3s3p\ {}^3\mathrm{P}_0$	1.12×10^{15}	-3.8×10^{-18}	4×10^{-19}	Safronova *et al.* 2011 [10]
In$^+$	$5s^2\ {}^1\mathrm{S}_0 - 5s5p\ {}^3\mathrm{P}_0$	1.27×10^{15}	-1.36×10^{-17}	1×10^{-18}	Safronova *et al.* 2011 [10]
Yb$^+$	$6s - 5d\ {}^2\mathrm{D}_{3/2}$	6.88×10^{14}	-5.1×10^{-16}	1×10^{-16}	Tamm *et al.* 2009 [16]
Yb$^+$	$6s - 4f^{13}6s^2\ {}^2\mathrm{F}_{7/2}$	6.42×10^{14}	-2.5×10^{-16}	1×10^{-16}	Hosaka *et al.* 2009 [17]

their size relative to the BBR shifts in optical frequency standards. Only the values with the smallest (to the best of our knowledge) uncertainty are listed for each frequency standard. With the exception of the Cs value [12], all data are results of the theoretical calculations.

From the theoretical standpoint, the number of the valence electrons (and the presence of core holes) defines the most accurate theoretical approach that can be used. For example, calculations of the BBR shift in Ca$^+$ and Sr$^+$ have the same degree of complexity, but the treatment of Sr is considerably more involved than that of Sr$^+$. The main sources of uncertainties in these cases also differ. Most of the present optical clock proposals involve either monovalent or divalent systems, with Yb$^+$, Hg$^+$, and Ag being notable exceptions due to low-lying excitation energies of their subvalence electrons. We discuss monovalent and divalent systems separately, and outline possible approaches for treating other systems.

II. MONOVALENT IONS: CA$^+$ AND SR$^+$

Both Ca$^+$ and Sr$^+$ ions are monovalent systems with atomic structure similar to that of their alkali neighbors, K and Rb. However, in the ions, the lowest nd states lie below the lowest np state, leading to the possibility of using these low-lying metastable nd states for the development of optical frequency standards.

The overall BBR shift of the Ca$^+$ $4s - 3d_{5/2}$ and Sr$^+$ $5s - 4d_{5/2}$ clock transition frequencies is calculated as the difference between the BBR shifts of the individual levels involved in the transition. For example, in the case of Ca$^+$, the BBR shift is given by

$$\Delta\nu_{\mathrm{BBR}}(4s - 3d_{5/2}) = -\frac{1}{2}[\alpha_0(3d_{5/2}) - \alpha_0(4s)]$$
$$\times\ (831.9\ \mathrm{V/m})^2 \left(\frac{T(\mathrm{K})}{300}\right)^4. \quad (2)$$

The polarizability difference, $\Delta\alpha_0$, is negative when the upper state polarizability is smaller than the lower state polarizability. A negative polarizability difference means the

frequency shift is positive. Both Ca$^+$ and Sr$^+$ polarizabilities can be obtained using the same approaches as for the alkali-metal atoms, owing to their similar electronic structure. The most accurate calculations of the relevant ns and $nd_{5/2}$ polarizabilities in these systems have been recently carried out using the relativistic all-order method [13], [14].

The relativistic all-order method including single, double, and partial valence triple excitations has been applied to accurate calculations of energies, transition amplitudes, hyperfine constants, static and dynamic electric-dipole polarizabilities, quadrupole and octupole polarizabilities, magic wavelengths, atomic quadrupole moments, C_3 and C_6 coefficients, isotope shifts and other properties of a large number of monovalent atoms and ions as well as the calculation of parity-violating amplitudes and EDM enhancement factors. We refer the reader to the review [18] and references therein for a detailed description of this method, its applications, and extensions. The accuracy of this approach is well understood, which enables accurate estimation of the uncertainties in calculations of the clock state polarizabilities and the resulting BBR shifts.

The valence scalar $\alpha_0(v)$ polarizability of Ca$^+$ or Sr$^+$ in an excited state v is given by (in a.u.)

$$\alpha_0(v) = \frac{2}{3(2j_v + 1)} \sum_{nlj} \frac{|\langle v||D||nlj\rangle|^2}{E_{nlj} - E_v}, \quad (3)$$

Unless stated otherwise, we use atomic units (a.u.) for all matrix elements and polarizabilities throughout this paper. We note that atomic units for α are converted to SI units via $\alpha/h[\mathrm{Hz}/(V/m)^2] = 2.48832 \times 10^{-8}\alpha[a.u.]$, where the conversion coefficient is $4\pi\epsilon_0 a_0^3/h$ and the Planck constant h is factored out.

The ionic core polarizability has to be added to the valence term given by Eq. (3) and corrected for the presence of the respective valence electron (term VC). This core correction VC term is small and is calculated in the random phase approximation (RPA). This partitioning of the core and valence polarizability contributions is discussed in detail in [19].

While the sum over the excited states in Eq. (3) converges

TABLE II

CONTRIBUTIONS TO THE $3d_{5/2}$ SCALAR POLARIZABILITY OF Ca^+ IN a_0^3. UNCERTAINTIES ARE GIVEN IN PARENTHESIS. THE FINAL RESULTS ARE COMPARED WITH OTHER THEORY [20], [21], [22].

Contribution	α_0
$4p_{3/2}$	22.78(25)
$np_{3/2}$	0.03
$4f_{5/2}$	0.12
$nf_{5/2}$	0.17
$4f_{7/2}$	2.39(5)
$5f_{7/2}$	0.77(1)
$6f_{7/2}$	0.35(1)
$7f_{7/2}$	0.19(1)
$(8-12)f_{7/2}$	0.31(1)
$(13-26)f_{7/2}$	1.39(4)
$nf_{7/2}$	0.27(15)
Core	3.26(3)
VC	-0.23(1)
Total	31.8(3)
Ref. [20]	32.0(1.1)
Ref. [21]	32.73
Ref. [22]	29.5(1.0)

rapidly for the lower state, this is not the case for the upper $nd_{5/2}$ state, where the contribution of highly-excited $nf_{7/2}$ states is large and has to be treated accurately. This problem has been recently resolved in [13] by performing the all-order calculation for n up to $n = 26$, resulting in factor of 3 improvement in the accuracy of $3d_{5/2}$ polarizability over previous calculation (see [20] and references therein). In previous work, contributions from highly-excited states were calculated in the Dirac-Hartree-Fock (DHF) approximation and adjusted for missing correlation using a semi-empirical procedure resulting in the larger uncertainty [20]. We refer the reader to Ref. [13] for further details of the most recent polarizability calculations.

We list contributions to the Ca^+ $3d_{5/2}$ polarizability (in a.u.) [13] in Table II. The final result is compared with other calculations [20], [21], [22].

Substituting the values for the $4s$ and $3d_{5/2}$ static polarizabilities, 76.1(5) a.u. and 31.8(3) a.u., respectively, into Eq. (2) yields 0.3815(44) Hz [13] for the BBR shift. The dynamic corrections were evaluated in [13] to be $\eta = 0.0012$ and $\eta = 0.0044$ for the $4s$ and $3d_{5/2}$ states, respectively, following Ref. [9]. The resulting dynamic correction to the BBR shift is only 0.1%, -0.0004 Hz.

Mitroy and Zhang [21] used non-relativistic configuration interaction with a semi-empirical core potential (CICP) approach. The CICP values are in good agreement with our results taking into account the accuracy of both calculations. The comparison with coupled-cluster calculations of Ref. [22] is discussed in detail in [13]. In summary, the present value of the BBR shift, 0.3811(44) Hz, is consistent with other calculations, 0.380(14) Hz [20], 0.37(1) Hz [22], and 0.368 Hz [21], but is three times more accurate.

The all-order calculation of the BBR shift of the Sr^+ $4s - 3d_{5/2}$ clock transition is similar to that for the Ca^+. The dynamic contribution is more significant in Sr^+, where it contributes nearly 1% (-0.002 Hz) to the BBR shift of 0.250(9) Hz.

In comparison with the Ca^+, the lower accuracy of the calculated Sr^+ BBR shift is due to greater cancelation between polarizabilities of the upper and lower clock states. The individual uncertainties in the Sr^+ $5s$ and $4d_{5/2}$ static polarizabilities, 91.3(9) a.u. and 62.0(5) a.u., respectively, are about 1% which is similar to that of the corresponding states in Ca^+.

Further reduction of the theoretical uncertainty would be very difficult as it would require predicting a number of E1 matrix elements to significantly better than 0.5%. On the other hand, experimental measurement of the DC Stark shift of the clock transition would be essentially equivalent to the measurement of the BBR shift, in particularly for Ca^+, where dynamic correction contributes only 0.1%. Very accurate measurements of the ground state static polarizabilities would also lead to the improvement of the BBR shift values.

III. DIVALENT SYSTEMS

A. Mg, Ca, Sr, Hg, and Yb

While the all-order approach produced accurate results for BBR shifts for optical clocks based on the monovalent ions, such as Ca^+ and Sr^+, it can not be straightforwardly extended to the BBR calculations in divalent systems, such as Sr or Al^+. The main difficulties of such an extension are outlined in [23]. The correlation corrections associated with the interaction of valence electrons are very large and are described poorly by perturbative treatments. On the other hand, the configuration interaction (CI) method is well suited for the accurate treatment of valence-valence correlations as long as number of the valence electrons is small. However, core excitations are neglected or only a small number of them are included, leading to a significant loss of accuracy for heavy atoms. Therefore, an approach that combines configuration interaction with many-body perturbation theory (MBPT) was developed in Ref. [24]. The CI+MBPT approach allows one to incorporate core excitations in the CI method by constructing an effective Hamiltonian that incorporates certain perturbation theory terms. The CI method is then applied to the modified H^{eff} to obtain improved energies and wave functions. The CI+MBPT method was used in Refs. [9], [15] to calculate BBR shifts in ns^2 $^1S_0 - nsnp$ $^3P_0$ clock transitions in Mg, Ca, Sr, Yb, and Hg. Where available, experimental data was used for the dipole matrix element associated with dominant contributions. The Sr BBR shift was later investigated in more detail in Ref. [25] using the same approach. Table I lists the results of these calculations.

The CI+MBPT approach includes only a limited number of the core-valence excitation terms (mostly to second order) and it deteriorates in accuracy for heavier, more complicated systems. Moreover, the BBR shifts are particularly large in Sr and Yb, requiring higher precision of the calculation (or measurements) to achieve the same ultimate clock uncertainty.

CI+all-order method developed in [23], [26] includes higher-order correlations beyond second order in a systematic way, resulting in higher accuracy of the resulting atomic properties. We have applied this method to the calculation of the BBR shifts in B^+, Al^+, and In^+. This calculation is

described in Section III-B. The same approach may be also used to calculate BBR shifts in all other divalent systems.

The Sr case requires very high accuracy of the BBR calculations (see [25] for detailed analysis of the Sr case) since fractional BBR shift in this system is the largest among all optical cases listed in Table I. Therefore, more all-order corrections, such as triple excitations [18] and all-order corrections to the effective dipole operation may have to be included to significantly reduce the uncertainty.

Until recently, attempts to apply CI+all-order approach to treat Yb resulted in the failure of the convergence procedure used in the the all-order part of the method. Specifically, we found that the iteration procedure in the all-order method fails to converge for the Yb^{2+} core equations owing to extremely large contributions from the $4f$ shell. This all-order core calculation is necessary for the future use in the CI+all-order Yb calculation. Recently, this problem was resolved by using the reduced linear equation (RLE) stabilizer procedure [27]. Therefore, Yb BBR shift value may be improved with the use of the CI+all-order method described in the next section.

B. Al^+, B^+, and In^+

While the BBR shift in Al^+ frequency standards is anomalously small, its contribution becomes significant at the current level of precision. As noted above, the BBR frequency shift of the clock transition can be related to the difference of the static electric-dipole polarizabilities between the final and initial clock states. Owing to severe (98%) cancellation between the static polarizabilities of the two clock states in this frequency standard, accurate calculation of the BBR shift in Al^+ is very difficult and required development of new all-order methodology. We developed a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with a few valence electrons [23]. This method combines the all-order approach currently used in precision calculations of properties of monovalent atoms with the configuration-interaction (CI) approach that is applicable for many-electron systems. In this work, we have extended this method to accurate calculation of the ground and excited state polarizabilities of divalent ions. The resulting polarizabilities are used to evaluate the BBR shifts at 300K in the $ns^2 - nsnp$ $^3P_0$ clock transitions in Al^+, B^+, and In^+. Frequency-dependent corrections are also evaluated and found to be negligible in all three cases.

In the combined CI + all-order approach used in this work, core excitations are incorporated in the CI method by constructing an effective Hamiltonian using fully converged all-order method mentioned in Section III-A. This approach is described in detail in [23]. Its application to the polarizability calculations is described in [10]. The valence part of the polarizability is determined by solving the inhomogeneous equation of perturbation theory in the valence space [28]. The ionic core contribution to the polarizability is calculated separately in the random-phase approximation (RPA). The small valence-core (VC) term that corrects the ionic core polarizability for the presence of the valence electrons is also calculated in the RPA. DHF calculations are carried out as well for both of these contributions to evaluate their uncertainties.

We note that in our approach the ionic core contribution is the same for both clock states and so it does not contribute to the BBR shift. On the other hand, the VC contribution differs between the two clock states. It is negligible for B^+. It is the largest for the $^3P_0$ polarizability of In^+ to which it contributes only 0.5%. However, its contribution to the BBR shift is much larger, 1.8% and 5% in Al^+ and In^+, respectively, owing to the large degree of cancelation between $^1S_0$ and $^3P_0$ polarizabilities. Our estimate of the dominant uncertainty in this term is the difference of the DHF and RPA values; we assume that all other uncertainties do not exceed this dominant uncertainty. Adding these uncertainties in quadrature, we estimate that the VC term leads to 0.6% and 2% uncertainties in the BBR shifts for Al^+ and In^+, respectively.

TABLE III
PERCENTAGE DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED ENERGY LEVELS THE B^+ AND Al^+ (IN %). EXPERIMENTAL ENERGY LEVELS E ARE GIVEN IN cm^{-1}. THE TWO-ELECTRON BINDING ENERGIES ARE LISTED IN THE FIRST ROW FOR EACH ION; ALL OTHER LEVELS ARE MEASURED FROM THE GROUND STATE. THE THREE RIGHTMOST COLUMNS ARE RESULTS OF THE DIFFERENT METHODS LABELED IN THE TEXT.

Ion	Term	E_{expt}	CI	CI+MBPT	CI+All
B^+	$2s^2$ $^1S_0$	508818	0.2	0.007	-0.001
	$2p^2$ $^3P_0$	98911	-1.0	-0.114	-0.005
	$2p^2$ $^3P_1$	98920	-1.0	-0.116	-0.007
	$2p^2$ $^3P_2$	98933	-1.1	-0.124	-0.015
	$2p^2$ $^1D_2$	102363	-0.8	-0.188	-0.113
	$2p^2$ $^1S_0$	127661	-0.5	-0.264	-0.223
	$2s3s$ $^3S_1$	129774	0.2	0.010	0.014
	$2s3s$ $^1S_0$	137622	-0.2	-0.116	-0.093
	$2s3d$ $^3D_1$	150650	0.2	-0.005	-0.004
	$2s3d$ $^3D_2$	150650	0.2	-0.006	-0.004
	$2s3d$ $^3D_3$	150650	0.2	-0.006	-0.005
	$2s2p$ $^3P_0$	37336	-0.7	-0.028	0.043
	$2s2p$ $^3P_1$	37342	-0.7	-0.040	0.037
	$2s2p$ $^3P_2$	37358	-0.8	-0.054	0.020
	$2s2p$ $^1P_1$	73397	-1.3	-0.395	-0.272
	$2s3p$ $^3P_0$	143989	0.1	0.004	0.009
	$2s3p$ $^3P_2$	143990	0.1	0.003	0.008
	$2s3p$ $^3P_1$	143993	0.1	0.002	0.008
	$2s3p$ $^1P_1$	144103	0.04	-0.016	-0.004
Al^+	$3s^2$ $^1S_0$	381308	1.2	0.043	0.006
	$3p^2$ $^1D_2$	85481	2.3	0.071	-0.022
	$3s4s$ $^3S_1$	91275	1.4	0.068	0.015
	$3p^2$ $^3P_0$	94085	1.6	0.036	0.008
	$3p^2$ $^3P_1$	94147	1.6	0.032	0.004
	$3p^2$ $^3P_2$	94269	1.6	0.024	-0.004
	$3s4s$ $^1S_0$	95351	1.4	0.053	0.003
	$3s3d$ $^3D_3$	95549	1.4	-0.002	-0.026
	$3s3d$ $^3D_2$	95551	1.4	-0.002	-0.026
	$3s3d$ $^3D_1$	95551	1.4	-0.001	-0.025
	$3s3p$ $^3P_0$	37393	3.1	0.151	0.007
	$3s3p$ $^3P_1$	37454	3.1	0.140	0.008
	$3s3p$ $^3P_2$	37578	3.1	0.120	-0.017
	$3s3p$ $^1P_1$	59852	0.4	-0.175	-0.141
	$3s4p$ $^3P_0$	105428	1.4	0.068	0.020
	$3s4p$ $^3P_1$	105442	1.4	0.067	0.020
	$3s4p$ $^3P_2$	105471	1.4	0.065	0.018
	$3s4p$ $^1P_1$	106921	1.3	0.046	0.007

In order to establish the accuracy of our approach to the calculation of valence polarizability, we also perform CI and CI+MBPT [24] calculations carried out with the same

TABLE IV

PERCENTAGE DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED
ENERGY LEVELS THE IN$^+$ (IN %). EXPERIMENTAL ENERGY LEVELS E
ARE GIVEN IN CM^{-1}. THE TWO-ELECTRON BINDING ENERGY IS LISTED IN
THE FIRST ROW; ALL OTHER LEVELS ARE MEASURED FROM THE GROUND
STATE. THE THREE RIGHTMOST COLUMNS ARE RESULTS OF THE
DIFFERENT METHODS LABELED IN THE TEXT.

Ion	Term	E_{expt}	CI	CI+MBPT	CI+All
In$^+$	$5s^2\ ^1S_0$	378299	5.8	-1.1	-0.25
	$5s6s\ ^3S_1$	93923	8.8	-1.5	-0.42
	$5s6s\ ^1S_0$	97030	8.1	-1.5	-0.48
	$5p^2\ ^1D_2$	97628	10.5	-2.3	-0.66
	$5p^2\ ^3P_0$	101608	7.0	-1.8	-0.42
	$5s5d\ ^3D_1$	102088	8.6	-1.4	-0.30
	$5s5d\ ^3D_2$	102174	8.6	-1.4	-0.30
	$5s5d\ ^3D_3$	102308	8.6	-1.4	-0.31
	$5p^2\ ^3P_1$	103249	7.2	-1.9	-0.44
	$5p^2\ ^3P_2$	105565	7.3	-1.9	-0.45
	$5s5p\ ^3P_0$	42276	13.2	-3.7	-1.08
	$5s5p\ ^3P_1$	43351	13.0	-3.6	-0.97
	$5s5p\ ^3P_2$	45830	13.0	-3.6	-1.06
	$5s5p\ ^1P_1$	63038	4.2	-0.4	-0.09
	$5s6p\ ^3P_0$	107662	8.1	-1.4	-0.34
	$5s6p\ ^3P_1$	107842	8.0	-1.4	-0.34
	$5s6p\ ^3P_2$	108430	8.0	-1.4	-0.35
	$5s6p\ ^1P_1$	109780	7.4	-1.3	-0.35

parameters (configuration space, basis set, number of partial waves, etc.). No core excitations are added in the pure divalent CI approach. Comparison of the CI, CI+MBPT, and CI+all-order values allows us to evaluate the importance of the various correlation corrections, thereby establishing the upper bound on the uncertainty of our calculations.

Tables III and IV present the comparison of the experimental energies of Al$^+$, B$^+$, and In$^+$ with those calculated in the CI, CI+MBPT, and CI+all-order approximations. The first and second column give state identification and the term value taken from the NIST critically evaluated experimental data [29]. Percentage differences between experimental and calculated energy levels

$$\epsilon = \frac{E_{\text{expt}} - E_{\text{th}}}{E_{\text{expt}}}$$

the In$^+$ (in %). Experimental term values E are given in cm^{-1}. Theoretical values calculated in the CI, CI+MBPT, and CI+all-order approximations are listed in the respectively labeled columns. Two-electron binding energies are given in the first row for each ion; all other levels are counted from the ground state as in [29]. Significant improvement of the energy values is observed for Al$^+$ and In$^+$ with the CI+all-order method as expected owing to the more complete inclusion of the correlation corrections in comparison with the CI and CI+MBPT approaches. The CI+all-order energies are within a few cm^{-1} of the experimental values for B$^+$ and Al$^+$ for most of the levels. The accuracy of the In$^+$ energy levels is sufficient for the purposes of the present work, i.e. replacing our theoretical energies by the experimental values in the dominant polarizability contributions leads to only a 1% change in the value of the BBR shift. The accuracy of the CI+MBPT method for B$^+$ is already at the level of our numerical precision for most of the transitions.

The breakdown of the contributions to the $ns^2\ ^1S_0$ and $nsnp\ ^3P_0$ polarizabilities α_0 of B$^+$ ($n = 2$), Al$^+$ ($n = 3$), and In$^+$ ($n = 5$) is given in Table V. Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled "D" in units of a_0e. The ionic core polarizability and VC term that corrects it for the presence of the valence electrons are listed in rows labeled "Core" and "VC". The final polarizability values are listed in rows labeled "Total". We subtract the values of the terms listed separately in Table V from our total valence polarizability values to obtain the remaining contributions that are listed in the rows labeled "Other". Our dominant contributions for Al$^+$ are in excellent agreement with CI calculations with a semi-empirical core potential (CICP) of Mitroy *et al.* [30]. Note that Al$^+$ is anomalous in this table for the near equality (within 2%) of the polarizabilities of its upper and lower states, especially since the polarizability of the lower state is completely dominated by the contribution from a single transition, whereas the upper state has substantial contributions from three different configurations.

We note that the oscillator strengths f_{gn} can be obtained from the reduced matrix elements to compare with standard tabulations by using

$$f_{gn} = \frac{2D_{gn}^2 \Delta E_{ng}}{3(2J_g + 1)}, \tag{4}$$

where $\Delta E_{ng} = E_n - E_g$ and $J_g = 0$ for the present clock states [19].

We investigate the uncertainty due to the inclusion of the core excitations by comparing the difference $\Delta\alpha_0$ calculated in the CI, CI+MBPT, CI+all-order approximations. These results are summarized in Table V. We find that the entire contribution of core excitations to the BBR shift, estimated as the difference of the CI+all-order and CI values $\Delta\alpha_0$ is only 3%, 5%, and 16% for B$^+$, Al$^+$, and In$^+$, respectively. The difference between CI+MBPT and CI+all-order values is 0.4% for B$^+$ and Al$^+$, and 1.7% for In$^+$. Therefore, we place an upper bound on the uncertainty of our BBR values at 10% for all three cases.

Our final results are summarized in Table VI [10], where we list the polarizability difference $\Delta\alpha_0$, BBR shift at $T = 300$ K, relative BBR shift $\Delta\nu_{\text{BBR}}/\nu_0$, and the uncertainty in the relative BBR shift for B$^+$, Al$^+$, and In$^+$. We find that dynamic corrections are very small for both states and nearly equal foe both states. Their contributions to BBR shift are thus negligible for all three ions. Our BBR shift value in Al$^+$ $\Delta\nu_{\text{BBR}} = -0.00426(43)$ Hz is in agreement with CICP value of Mitroy *et al.* [30] and recent coupled-cluster calculation [31]. It is also consistent with the experimental measurement $\Delta\nu_{\text{BBR}} = -0.008(3)$ Hz from Ref. [32]. The values of η for Al$^+$ are in agreement with those of [30].

IV. OTHER SYSTEMS

While the ground state of Yb$^+$ is a single-particle configuration, $4f^{14}6s\ ^2S_{1/2}$, the first excited configuration in this system is a one-hole two-particle state, i.e. $4f^{13}6s^2\ ^2F_{7/2}$. Both this configuration and the next excited configuration,

TABLE V
CONTRIBUTIONS TO THE $ns^2\ ^1S_0$ AND $nsnp\ ^3P_0$ POLARIZABILITIES α_0 OF B^+, AL^+, AND IN^+ IN a_3^0. ABSOLUTE VALUES OF THE CORRESPONDING REDUCED ELECTRIC-DIPOLE MATRIX ELEMENTS ARE LISTED IN COLUMN LABELED "D" IN $a_0 e$. FINAL POLARIZABILITY VALUES ARE LISTED IN ROWS LABELED "TOTAL".

Ion	State	Contr.	D	α_0
B^+	$2s^2\ ^1S_0$	$2s^2\ ^1S_0 - 2s2p\ ^1P_1$	2.118	8.918
		$2s^2\ ^1S_0 - 2s3p\ ^1P_1$	0.320	0.104
		Other		0.582
		Core		0.020
		VC		0.000
		Total		9.624
B^+	$2s2p\ ^3P_0$	$2s2p\ ^3P_0 - 2p^2\ ^3P_1$	1.354	3.216
		$2s2p\ ^3P_0 - 2s3s\ ^3S_1$	0.476	0.754
		$2s2p\ ^3P_0 - 2s3d\ ^3D_1$	1.175	1.517
		Other		2.267
		Core		0.020
		VC		-0.001
		Total		7.772
Al^+	$3s^2\ ^1S_0$	$3s^2\ ^1S_0 - 3s3p\ ^1P_1$	3.113	23.661
		$3s^2\ ^1S_0 - 3s4p\ ^1P_1$	0.045	0.003
		Other		0.138
		Core		0.265
		VC		-0.019
		Total		24.048
Al^+	$3s3p\ ^3P_0$	$3s3p\ ^3P_0 - 3s4s\ ^3S_1$	0.900	2.197
		$3s3p\ ^3P_0 - 3p^2\ ^3P_0$	1.836	8.687
		$3s3p\ ^3P_0 - 3s3d\ ^3D_1$	2.236	12.568
		Other		0.836
		Core		0.265
		VC		-0.010
		Total		24.543
In^+	$5s^2\ ^1S_0$	$5s^2\ ^1S_0 - 5s5p\ ^1P_1$	2.977	20.554
		$5s^2\ ^1S_0 - 5s6p\ ^1P_1$	0.123	0.020
		Other		0.261
		Core		3.220
		VC		-0.041
		Total		24.014
In^+	$5s5p\ ^3P_0$	$5s5p\ ^3P_0 - 5s6d\ ^3S_1$	1.015	2.921
		$5s5p\ ^3P_0 - 5s5d\ ^3D_1$	2.189	11.755
		$5s5p\ ^3P_0 - 5p^2\ ^3P_1$	1.664	6.649
		Other		1.645
		Core		3.220
		VC		-0.170
		Total		26.019

TABLE VI
BBR SHIFTS AT $T = 300K$ IN B^+, AL^+, AND IN^+. $\Delta\alpha_0$ IS GIVEN IN a_3^0; THE BBR SHIFTS $\Delta\nu_{BBR}$ ARE GIVEN IN HZ.

Ion	$\Delta\alpha_0$	$\Delta\nu_{BBR}$ (Hz)	$|\Delta\nu_{BBR}/\nu_0|$	Uncertainty
B^+	-1.851	0.0159(16)	1.42×10^{-17}	1×10^{-18}
Al^+	0.495	-0.00426(43)	3.8×10^{-18}	4×10^{-19}
In^+	2.01	-0.0173(17)	1.36×10^{-17}	1×10^{-18}

$4f^{14}5d\ ^2D$, are metastable, as electric-dipole transitions to the ground state are forbidden. Therefore, Yb^+ is particularly well suited for the development of optical-frequency standards since two different types of transitions (quadrupole and octupole) may be used [2], [16], [17].

While the single-particle states of Yb^+ such as the ground and the $4f^{14}5d\ ^2D$ configurations can be treated with the all-order approach, the results may not be as accurate as for monovalent systems, such as Cs or even heavier Ra^+ owing to very large correlation corrections and mixing of the one-hole two-particle configuration. However, accuracy of the BBR shift for the quadupole transition may be improved with the all-order approach such as described above for Ca^+. Such calculations have not yet yet been performed owing to the convergence issue in the Yb^{2+} core equations described in Section III-A that was resolved only recently [27].

At the present time, there is no approach that can produce accurate predictions of the properties of actual one-hole two-particle configurations such as $4f^{13}6s^2\ ^2F_{7/2}$ in Yb^+. The best possible theoretical approach may be to develop a CI+MBPT method that can treat one-hole two-particle configurations. The particle-hole formalism provides more efficient treatment of the states with more-than-half filled shells. It is particularly useful for almost-filled shells with no more than one hole. Generalization of the CI+MBPT approach to systems with holes requires significant modifications. The main problem here is avoiding double counting of the correlation corrections.

The Hg^+ case is similar to that of Yb^+, but since the Hg^+ trap is operated at cryogenic temperatures [33], the BBR shift is negligible.

V. CONCLUSION

In summary, we have reviewed the present status of BBR shift calculations for a number of optical frequency standards. Recent calculations of BBR shifts in Ca^+, B^+, Al^+, and In^+ are described in more detail. Our calculations of the BBR shifts in B^+, Al^+, and In^+ reduce the ultimate uncertainties due to this effect at room temperature to the 10^{-18} level for B^+ and In^+ and to 4×10^{-19} for Al^+. These uncertainties approach recent estimates of the feasible precision of currently proposed optical atomic clocks. Possible theoretical approaches that may reduce uncertainties due to BBR shifts in other systems are discussed.

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Marianna Safronova is an Associate Professor at the Department of Physics and Astronomy at the University of Delaware, working in the field of Theoretical Atomic Physics. She has received her Ph. D. from the Physics Department of the University of Notre Dame in 2001. Her Theoretical Atomic physics group focuses on the development of methodologies for high-precision atomic calculations and their applications. Her research involves both the study of the fundamental physics problems (fundamental symmetries) and applications of atomic physics to future technological developments (such as quantum computing and optical atomic clocks).

Mikhail G. Kozlov is a Leading scientific collaborator at the Molecular beam laboratory, Neutron Research Division, Petersburg Nuclear Physics Institute, Russia. He is also a member of the Foundational Questions Institute (FQXi). Dr. Kozlov received his Ph. D. from the Department of Physics of the Leningrad State University, Russia, in 1982. His research interests include development of new methods in atomic and molecular theory, parity non-conservation, time-reversal violation, and permanent electric dipole moments of atoms and molecules, space-time variation of fundamental constants, and quantum chaos.

Charles W. Clark is a NIST Fellow at the National Institute of Standards and Technology in Gaithersburg, Maryland and is Co-Director of the Joint Quantum Institute of NIST and the University of Maryland (UMD). He received his Ph. D. in physics from the University of Chicago in 1979. He is also an Affiliate Professor at the Institute for Physical Science and Technology (UMD), Program Manager for Atomic, Molecular and Quantum Physics at the Office of Naval Research, and Visiting Professor at the National University of Singapore. His research interests include dynamics of ultracold atoms, physical implementation of quantum information processing, far-ultraviolet radiometry with synchrotron radiation sources, quantitative tomographic imaging and neutron optics and detection.