Precision calculation of blackbody radiation shifts for metrology at the 18$^{\text{th}}$ decimal place

M. S. Safronova
University of Delaware
Newark, DE, 19716
Email: msafrono@udel.edu

M. G. Kozlov
PNPI
Gatchina, Russia
Email: mgk@mf1309.spb.edu

Charles W. Clark
Joint Quantum Institute
NIST and University of Maryland
Email: charles.clark@nist.gov

Abstract—We developed a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with few valence electrons, and applied it to calculate polarizabilities and the blackbody radiation (BBR) shifts of atomic frequency standards. We have performed the calculations of the BBR shifts in B$^+$, Al$^+$, and In$^+$ that allowed to reduce the ultimate uncertainties due to this effect at room temperature to 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.

I. INTRODUCTION

Recent advances in atomic and optical physics led to unprecedented improvements in the accuracy of the optical frequency standards. In 2010, the construction of optical clock with a fractional frequency inaccuracy of 8.6×10^{-18}, based on quantum logic spectroscopy of an Al+ ion, was reported [1]. Development of more precise frequency standards will open ways to more sensitive quantum-based standards for applications such as measurements of the fundamental constants and testing of physics postulates, inertial navigation, magnetometry, and tracking of deep-space probes.

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. Experimental measurements of the BBR shifts are difficult.

While the BBR shift in Al$^+$ frequency standards is anomalously small, its contribution becomes significant at the current level of precision. 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 [2]. 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.

II. CALCULATION OF POLARIZABILITIES

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 [3]

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

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 magnetic-dipole contributions are suppressed by a factor of α^2 [3]. We estimated that the contribution to the Al$^+$ BBR shift due to the $^3P_0 - ^3P_1$ M1 transition is below 10^{-5} Hz and is negligible at the present level of accuracy. The evaluation of the dynamic correction η requires the knowledge of the electric-dipole matrix for transitions giving the dominant contributions to the polarizabilities.

In the combined CI + all-order approach used in the present work, core excitations are incorporated in the CI method by constructing an effective Hamiltonian using fully converged all-order excitation coefficients. This approach is described in detail in [2]. Its application to the polarizability calculations is described in [4]. The valence part of the polarizability is determined by solving the inhomogeneous equation of perturbation theory in the valence space [5]. The ionic core part of 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 the uncertainty associated with this term.

We note that 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 is different for the two clock states. It is negligible for B$^+$. It is the largest for the

Ion	Level	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

Ion	Level	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

order values allows us to evaluate the importance of the various correlation corrections, therefore establishing the upper bound on the uncertainty of our calculations. Unless stated otherwise, we use atomic units (a.u.) for all matrix elements and polarizabilities throughout this paper.

Tables I and II presents the comparison of the experimental energies of Al$^+$, B$^+$, and In$^+$ with those calculated in the CI, CI+MBPT, and CI+all-order approximations. Relative differences of the B$^+$, Al$^+$, and In$^+$ calculated energy levels and NIST data (in %) are presented. CI, CI+MBPT, and CI+all-order data are listed in columns labeled "CI", "CI+MBPT", and "CI+All", respectively. Experimental energy levels are listed for reference in cm^{-1}. Two-electron binding energy is listed in the first row. All other levels are counted from the ground state. 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 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 of B$^+$ ($n = 2$), Al$^+$ ($n = 3$), and In$^+$ ($n = 5$) is given in Table III. Absolute values of the corresponding reduced electric-dipole matrix elements

$^3P_0$ 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. We estimate the dominant uncertainty in this term as the difference of the DHF and RPA values, and assume that all other uncertainties do not exceed this dominant uncertainty. Adding these two uncertainties in quadrature, we estimate that VC term leads to the 0.6% and 2% uncertainties in the BBR shifts for Al$^+$ and In$^+$.

In order to establish the accuracy of our approach to the calculation of valence polarizability, we also perform the CI and CI+MBPT [6] calculations carried out with the same 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-

TABLE III

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_0e. 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
		Othe		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

reduced matrix elements by using

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

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

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 III. We find that the entire contribution of core excitations to the BBR shift, estimated as the difference of the $\Delta\alpha_0$ CI+all-order and CI values 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.

III. BBR SHIFTS

Our final results are summarized in Table IV [4], where we list the polarizability difference $\Delta\alpha_0$, BBR shift at $T = 300K$, relative BBR shift $\Delta\nu_{\mathrm{BBR}}/\nu_0$, 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 cancel each other contributions. Their contributions to BBR shift are negligible for all three ions. Our BBR shift value in Al$^+$ $\Delta\nu_{\mathrm{BBR}} = -0.00426(43)$ Hz is in agreement with CICP value of Mitroy *et al.* [7] and recent coupled-cluster calculation [8]. It is also consistent with experimental measurement $\Delta\nu_{\mathrm{BBR}} = -0.008(3)$ Hz from Ref. [9]. The values of η for Al$^+$ are in agreement with [7].

TABLE IV

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

Ion	$\Delta\alpha_0$	$\Delta\nu_{\mathrm{BBR}}$ (Hz)	$|\Delta\nu_{\mathrm{BBR}}/\nu_0|$	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}

are listed in column labeled "D" in 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". Final polarizability values are listed in rows labeled "Total". We subtract the values of the terms listed separately in Table III 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.* [7].

The oscillator strengths f_{gn} can be obtained from the

IV. CONCLUSION

In summary, we have performed the calculations of the BBR shifts in B$^+$, Al$^+$, and In$^+$ that allowed to reduce the ultimate uncertainties due to this effect at room temperature to 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 [10]. This work demonstrated the success of the CI+all-order method in accurate determination of the polarizabilities and BBR shifts.

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