

## Precision Calculation of Blackbody Radiation Shifts for Optical Frequency Metrology

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We show that three group IIIB divalent ions,  $B^+$ ,  $Al^+$ , and  $In^+$ , have anomalously small blackbody radiation (BBR) shifts of the  $ns^2\ ^1S_0 - nsnp\ ^3P_0^o$  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. We have developed a hybrid configuration-interaction + coupled-cluster method that provides accurate treatment of correlation corrections in such ions and yields a rigorous upper bound on the uncertainty of the final results. We reduce the BBR contribution to the fractional frequency uncertainty of the  $Al^+$  clock to  $4 \times 10^{-19}$  at  $T = 300$  K. We also reduce the uncertainties due to this effect at room temperature to  $10^{-18}$  level for  $B^+$  and  $In^+$  to facilitate further development of these systems for metrology and quantum sensing.

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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 [1]. Recent advances in atomic and optical physics have led to unprecedented improvements in the accuracy of optical frequency standards, which could lead to redefinition of a second [2]. For example, in 2010, the most accurate clock to date was demonstrated, an optical clock based on quantum logic spectroscopy of an  $Al^+$  ion [3]. Its fractional frequency uncertainty of  $8.6 \times 10^{-18}$  is equivalent to a shift of 1 s in  $3.7 \times 10^9$  years.

The definition of the second refers to a clock transition in an atom at a temperature of absolute zero [2], whereas all present optical atomic clocks operate at room temperature (with the exception of  $Hg^+$  [4]). Thus, the transition of a working optical clock must be corrected for the effect of finite temperature, to which the leading contributor is the blackbody radiation (BBR) shift of the transition frequency. In fact, the three largest systematic uncertainties in the  $Al^+$  clock frequency are due to excess micromotion of the trapped ion, its secular motion, and the BBR shift [3]. The corresponding fractional frequency uncertainties associated with these three effects were evaluated [3] to be  $6 \times 10^{-18}$ ,  $5 \times 10^{-18}$ , and  $3 \times 10^{-18}$ . If the motional effects could be sufficiently suppressed by experimental techniques, the BBR shift, which is, in principle, calculable, will become the main source of uncertainty.

Experimental measurements of the BBR shifts are sufficiently difficult that no direct measurement has yet been reported for optical frequency standards, and even the measurement of differential Stark shifts has only been carried out with uncertainties greater than 10%. While BBR shifts can be strongly suppressed by lowering the temperature, it is desirable to attain the highest accuracy that is possible without using cryogenic techniques. In this work, we have calculated the BBR shifts in  $Al^+$ ,  $B^+$ , and  $In^+$  frequency standards with 10% accuracy, which removes the BBR shift as a significant source of uncertainty in the present experiments. Our present work calculates the BBR shift uncertainty at constant temperature (300 K). Imperfect temperature control is a source of additional experimental uncertainty. Small BBR shifts are also favorable because they translate to small uncertainties due to imperfect temperature control.

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]. It happens that polarizabilities of the two  $Al^+$  clock states are nearly equal (within 2%). This is a source of difficulty in the calculation and the determination of its uncertainty. Because of this cancellation, the BBR shift in  $Al^+$  frequency standard [3] is at least an order of magnitude smaller than that estimated for any other atomic frequency standard to date [6–9]. Precise knowledge of the BBR shift and its uncertainty is essential for further improvement of the accuracy of the  $Al^+$  optical frequency standard. Here we report the development of a new method of first-principles calculation that

reduces the relative uncertainty due to the BBR shift at 300 K in  $\text{Al}^+$  to  $4 \times 10^{-19}$ .

In this work, we have also investigated other divalent group IIIB ions,  $\text{B}^+$  and  $\text{In}^+$ , which have been suggested as potential optical frequency standards [10–13]. No published values of their BBR shifts exist at the present time to the best of our knowledge. We find that  $\text{B}^+$  and  $\text{In}^+$  have unusually small BBR shifts due to the same type of cancellation that we find in  $\text{Al}^+$ .  $\text{Al}^+$  remains the species with the smallest BBR shift yet investigated, but  $\text{In}^+$  and  $\text{B}^+$  are superior in terms of the BBR shift to any other present frequency standards.

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

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]

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

where  $\eta$  is a small dynamic correction due to the frequency distribution and only the electric-dipole transition part of the contribution is considered. In this equation,  $\Delta\alpha_0$  in atomic units has to be multiplied by the numerical factor from the previous paragraph.

Precision calculations for divalent atoms require an accurate treatment of the strong valence-valence correlations; low-order perturbation theory does not give results of competitive accuracy for neutral atoms or singly charged ions. As a solution to this problem, we developed an *ab initio* theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in divalent atoms [14]. This method combines the all-order approach currently used in precision calculations of properties of monovalent atoms [15] with the configuration-interaction (CI) approach that is applicable for many-electron systems. Here we report the extension of this method to calculate ground and excited state polarizabilities of divalent ions.

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 [14]. Therefore, the core-core and core-valence sectors of the correlation corrections for divalent systems are treated with the same accuracy as in the all-order approach for monovalent atoms. Then, the CI method is used to treat

valence-valence correlations. For divalent systems, only two-particle configuration space needs to be considered, so the configuration space can be made numerically complete. The valence part of the polarizability is determined by solving the inhomogeneous equation of perturbation theory in the valence space, which is approximated as

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

for a state  $\nu$  with the total angular momentum  $J$  and projection  $M$  [16]. The wave function  $\Psi(\nu, M')$ , 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  $|\nu, J, M\rangle$  can be determined [16]. The construction of the effective Hamiltonian  $H_{\text{eff}}$  using the all-order approach is described in [14]. The effective dipole operator  $D_{\text{eff}}$  includes random phase approximation (RPA) corrections. The calculations are carried out with a finite  $B$ -spline basis set [17], with several lower orbitals replaced by exact Dirac-Hartree-Fock (DHF) functions.

In order to establish the accuracy of our approach, we also perform the CI and CI + MBPT 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. In the CI + MBPT method, core excitations are incorporated by constructing an effective Hamiltonian using second-order many-body perturbation theory [18]. Comparison of the CI, CI + MBPT, and CI + all-order values allows us to evaluate the importance of the various correlation corrections, therefore establishing the upper bound on the uncertainty of our calculations.

Table I presents the comparison of the experimental energies of  $\text{Al}^+$  levels with those calculated in the CI, CI + MBPT, and CI + all-order approximations. The Supplemental Material contains the analogous data for  $\text{B}^+$  and  $\text{In}^+$  [19]. Significant improvement of the energy values is observed for  $\text{Al}^+$  and  $\text{In}^+$  with the CI + all-order method as expected due to the more complete inclusion of the correlation corrections than in the CI and CI + MBPT approaches. For most levels, the CI + all-order energies are within a few  $\text{cm}^{-1}$  of the experimental values for  $\text{B}^+$  and  $\text{Al}^+$ . The accuracy of the  $\text{In}^+$  energy levels is sufficient for the purposes of the present work: replacing our theoretical energies by the experimental values in the dominant polarizability contributions changes the BBR shift by only 1%.

The breakdown of the contributions to the  $3s^2 \ ^1S_0$  and  $3s3p \ ^3P_0^o$  polarizabilities  $\alpha$  of  $\text{Al}^+$  is given in Table II. The Supplemental Material contains the analogous data for  $\text{B}^+$  and  $\text{In}^+$  [19]. While we do not use the sum-over-state approach in the calculations of the polarizabilities, it is useful to establish which terms give the dominant contributions. We evaluate several dominant contributions to polarizabilities by combining our values of the  $E1$  matrix elements and energies as  $2D^2/3\Delta E$  according to the sum-over-states formula [20] with

TABLE I. Comparison of calculated and experimental energies of  $\text{Al}^+$  in  $\text{cm}^{-1}$ . Column 1: level designation. Column 2: experimental energies. The entry for the ground state  $3s^2$  is its two-electron binding energy; all excited state entries are energies measured from the ground state. Columns 3–5: differences of experimental from theoretical values in CI, CI + MBPT, and CI + all-order approximations. For example, the CI  $3s^2$  energy is  $381\,308 - 4718 = 376\,591 \text{ cm}^{-1}$ .

Level	Experimental	CI	CI + MBPT	CI + All
$3s^2 \ ^1S_0$	381 308	4718	163	23
$3p^2 \ ^1D_2$	85 481	1984	61	-19
$3s4s \ ^3S_1$	91 275	1290	62	14
$3p^2 \ ^3P_0$	94 085	1499	34	7
$3p^2 \ ^3P_1$	94 147	1499	30	4
$3p^2 \ ^3P_2$	94 269	1498	23	-4
$3s4s \ ^1S_0$	95 351	1359	50	3
$3s3d \ ^3D_3$	95 549	1353	-2	-25
$3s3d \ ^3D_2$	95 551	1354	-2	-24
$3s3d \ ^3D_1$	95 551	1354	-1	-24
$3s3p \ ^3P_0^o$	37 393	1155	56	3
$3s3p \ ^3P_1^o$	37 454	1154	52	3
$3s3p \ ^3P_2^o$	37 578	1153	45	-6
$3s3p \ ^1P_1^o$	59 852	255	-105	-84

$J = 0$ . We find that a single transition,  $ns^2 \ ^1S_0 - nsn p \ ^1P_1^o$ , contributes 92.9%, 99.4%, and 98.7% to the valence ground state polarizability for  $\text{B}^+$ ,  $\text{Al}^+$ , and  $\text{In}^+$ , respectively. Three transitions,  $nsnp \ ^3P_0^o - np^2 \ ^3P_1$ ,  $nsnp \ ^3P_0^o - ns(n+1)s \ ^3S_1$ , and  $nsnp \ ^3P_0^o - ns(n+1)d \ ^3D_1$  contribute 70.8%, 98.7%, and 92.8% to the  $^3P_0^o$  polarizability for  $\text{B}^+$ ,  $\text{Al}^+$ , and  $\text{In}^+$ , respectively. Therefore, both  $\text{Al}^+$  and  $\text{In}^+$  polarizabilities could be calculated more precisely if experimental values of the dipole matrix elements were

TABLE II. Contributions to the  $3s^2 \ ^1S_0$  and  $3s3p \ ^3P_1^o$  polarizabilities  $\alpha_0$  of  $\text{Al}^+$  in a.u. Absolute values of the corresponding reduced electric-dipole matrix elements are listed in column labeled “ $D$ ” in a.u. Contributions labeled “Other,” “Core,” and “VC” are described in the text. Final polarizability values are listed in rows labeled “Total.”

State	Contributions	$D$	$\alpha_0$
$3s^2 \ ^1S_0$	$3s^2 \ ^1S_0 - 3s3p \ ^1P_1^o$	3.113	23.661
	$3s^2 \ ^1S_0 - 3s4p \ ^1P_1^o$	0.045	0.003
	Other		0.138
	Core		0.265
	VC		-0.019
	Total		24.048
$3s3p \ ^3P_0^o$	$3s3p \ ^3P_0^o - 3s4s \ ^3S_1$	0.900	2.197
	$3s3p \ ^3P_0^o - 3p^2 \ ^3P_0$	1.836	8.687
	$3s3p \ ^3P_0^o - 3s3d \ ^3D_1$	2.236	12.568
	Other		0.836
	Core		0.265
	VC		-0.010
	Total		24.543

known to high precision. We subtract the values of the terms listed separately in Table II from our total valence polarizability values to obtain the remaining contributions that are listed in the rows labeled “Other.” Our dominant contributions for  $\text{Al}^+$  are in excellent agreement with CI calculations with a semiempirical core potential (CICP) [8].

The ionic core polarizability and valence-core (VC) term that corrects it for the presence of the valence electrons are listed in rows labeled “Core” and “VC.” 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  $\text{B}^+$ . It is the largest for the  $^3P_0^o$  polarizability of  $\text{In}^+$  to which it contributes only 0.5%. However, its contribution to the BBR shift is much larger, 1.8% and 5% in  $\text{Al}^+$  and  $\text{In}^+$ , respectively, owing to the large degree of cancellation between  $^1S_0$  and  $^3P_0^o$  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  $\text{Al}^+$  and  $\text{In}^+$ .

There are three other major sources of uncertainties in our calculations of the BBR shift. One is the omission of the Breit interaction in our calculations. We have estimated the main part of the Breit correction by incorporating the one-body part of the Breit interaction into the basis set orbitals on the same footing with Coulomb interaction. All calculations were then repeated with the modified basis set. The change in the  $\text{Al}^+$  BBR shift was found to be only 1.4%. The two other main sources of uncertainty are incompleteness of treatment of core excitations via the effective Hamiltonian technique described above (for example, our all-order method is restricted to single and double excitations), and limiting the treatment of the effective dipole operator  $D_{\text{eff}}$  to the RPA method [16]. The second issue is unlikely to cause large errors as RPA is expected to be the dominant

TABLE III. The values of the  $ns^2 \ ^1S_0$  and  $nsnp \ ^3P_0^o$  polarizabilities  $\alpha_0$  in  $\text{B}^+$ ,  $\text{Al}^+$ , and  $\text{In}^+$  calculated in CI, CI + MBPT, and CI + all-order approximations in a.u. CI + all-order values are taken as final.

Ion		CI	CI + MBPT	CI + all
$\text{B}^+$	$\alpha_0(2s^2 \ ^1S_0)$	9.575	9.613	9.624
	$\alpha_0(2s2p \ ^3P_0^o)$	7.779	7.769	7.772
	$\Delta\alpha_0$	-1.796	-1.844	-1.851
$\text{Al}^+$	$\alpha_0(3s^2 \ ^1S_0)$	24.405	24.030	24.048
	$\alpha_0(3s3p \ ^3P_0^o)$	24.874	24.523	24.543
	$\Delta\alpha_0$	0.469	0.493	0.495
$\text{In}^+$	$\alpha_0(5s^2 \ ^1S_0)$	26.27	23.83	24.01
	$\alpha_0(5s5p \ ^3P_0^o)$	28.60	25.87	26.02
	$\Delta\alpha_0$	2.33	2.04	2.01

TABLE IV. BBR shifts at  $T = 300$  K in  $B^+$ ,  $Al^+$ , and  $In^+$ .  $\Delta\alpha_0$  is given in a.u.; clock frequencies  $\nu_0$  and the BBR shifts  $\Delta\nu_{\text{BBR}}$  are given in Hz. Uncertainties in the values of  $\Delta\nu_{\text{BBR}}/\nu_0$  are given in the column labeled ‘‘Uncertainty.’’

Ion	$\Delta\alpha_0$	$\eta(^1S_0)$	$\eta(^3P_0)$	$\Delta\nu_{\text{BBR}}$ (Hz)	$\nu_0$ (Hz)	$ \Delta\nu_{\text{BBR}}/\nu_0 $	Uncertainty
$B^+$	-1.851	0.000 14	0.000 14	0.015 9(16)	$1.119 \times 10^{15}$	$1.42 \times 10^{-17}$	$1 \times 10^{-18}$
$Al^+$	0.495	0.000 22	0.000 24	-0.004 26(43)	$1.121 \times 10^{15}$	$3.8 \times 10^{-18}$	$4 \times 10^{-19}$
$In^+$	2.01	0.000 18	0.000 19	-0.017 3(17)	$1.267 \times 10^{15}$	$1.36 \times 10^{-17}$	$1 \times 10^{-18}$

contribution for these E1 matrix elements. Moreover, we have verified that our *ab initio* CI + all-order method reproduces the recommended values [5] of clock state polarizabilities of Mg, Ca, and Sr [21]. 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.

Our final results are summarized in Table IV, where we list the polarizability difference  $\Delta\alpha_0$ , dynamic corrections  $\eta$ , BBR shift at  $T = 300$  K,  $^1S_0 - ^3P_0$  clock frequencies  $\nu_0$ , relative BBR shift  $\Delta\nu_{\text{BBR}}/\nu_0$ , and the uncertainty in the relative BBR shift for  $B^+$ ,  $Al^+$ , and  $In^+$ . Dynamic corrections are very small for both states and nearly cancel each other. Their contributions to the BBR shift are negligible for all three ions. We estimated that contribution to the 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.

Our BBR shift value in  $Al^+$ ,  $\Delta\nu_{\text{BBR}} = -0.00426(43)$  Hz, is in agreement with CICIP value of Ref. [8]  $\Delta\nu_{\text{BBR}} = -0.0042(32)$  and is consistent with experimental measurement  $\Delta\nu_{\text{BBR}} = -0.008(3)$  Hz from Ref. [7]. The values of  $\eta$  for  $Al^+$  are in agreement with [8].

Our value for the  $Al^+$  BBR shift is in agreement with that of the coupled-cluster calculation  $\Delta\nu_{\text{BBR}} = -0.0041(7)$  Hz [9]. Although the uncertainty in that calculation was estimated at 17%, the individual state polarizabilities, and more significantly, their difference  $\Delta\alpha_0$ , varied considerably with choice of basis set. Specifically, the single-double coupled-cluster (CCSD) values of  $\Delta\alpha_0$  with increasing basis sets are reported to be 0.165, 0.058, 0.897, 0.427, and 0.406 (in a.u.). Although the last two numbers are close, this sequence in itself does not demonstrate convergence (twice the difference in the last two values was taken to be the basis set error). Heavy dependence of the polarizability on the choice of basis set is a well-known problem in coupled-cluster methods (see [20] and references therein). This issue was exacerbated in [9] by the use of different methods for the lower and upper clock states. In our work, on the other hand, large basis sets

were used in all all-order or perturbation theory calculations (385 orbitals with  $l < 6$ ), and the CI space was saturated until the error was negligible at the present level of accuracy. The same approach and basis sets were used in all our calculations. In addition to the polarizabilities, the only other numerical result reported in Ref. [9] is the  $3s^2 - 3s3p \ ^3P_0$  clock transition energy. Its reported value of  $37\,326(95)$   $\text{cm}^{-1}$  differs from the experimental value  $37\,393$   $\text{cm}^{-1}$  by  $67$   $\text{cm}^{-1}$ . Our CI + all-order value  $37\,390$   $\text{cm}^{-1}$  agrees with experiment to  $3$   $\text{cm}^{-1}$ , and even our CI + MBPT value agrees to  $56$   $\text{cm}^{-1}$  (see line  $3s3p \ ^3P_0$  in Table I). Most of our other energy levels also agree with experiment to a few  $\text{cm}^{-1}$ .

We also calculated frequency-dependent polarizabilities of clock states at 1126 nm using the same approach; our values are  $\alpha_0(\omega)[^1S_0] = 24.58$  a.u. and  $\alpha_0(\omega)[^3P_0] = 25.13$  a.u. The resulting frequency-dependent polarizability difference  $\Delta\alpha_0(\omega) = 0.549(55)$  a.u. is in agreement with theoretical CICIP value  $0.54(41)$  a.u. [8] and is  $1.6\sigma$  from the experimental value  $1.08(34)$  a.u. [7].

In summary, our calculations of the BBR shifts reduce the uncertainties in the fractional frequency shift at room temperature to  $10^{-18}$  in  $B^+$  and  $In^+$  and to  $4 \times 10^{-19}$  in  $Al^+$ . These uncertainties approach recent estimates of the feasible precision of currently proposed optical atomic clocks [4]. This work introduces a novel computational approach that can be used for a variety of problems of importance to atomic, nuclear, and high-energy physics, as well as quantum chemistry (study of parity violation, searches for electron dipole moment, study of degenerate gases, determination of nuclear magnetic moments, search for variation of fundamental constants, etc.).

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