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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 $ns^2\ ^1S_0 - nsn p\ ^3P_0^o$ 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, considers all relevant states in the same systematic way, 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 4×10^{-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. These uncertainties approach recent estimates of the feasible precision of currently proposed optical atomic clocks.

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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 8.6×10^{-18} is equivalent to a shift of 1 second in 3.7 billion 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 6×10^{-18} , 5×10^{-18} , and 3×10^{-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 suf-

ficiently 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. Due to 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 300K in Al^+ to 4×10^{-19} .

In this work, we have also investigated other divalent group IIIB ions, B^+ and 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 B^+ and In^+ have unusually small BBR shifts due to the same type of cancellation that we find in Al^+ . Al^+ remains the species with the smallest BBR shift yet investigated, but In^+ and 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 paper: the numerical values of the elementary charge, e , the reduced Planck constant, $\hbar = h/2\pi$, and the electron mass, m_e , are set equal to 1. The atomic unit for polarizability can be converted to SI units via α/h [$Hz/(V/m)^2$] $=2.48832 \times 10^{-8} \alpha$ (a.u.). The conversion coefficient is $4\pi\epsilon_0 a_0^3/h$ in SI units and the Planck constant h is factored out in order to provide direct conversion into frequency units; a_0 is the Bohr radius and ϵ_0 is the electric constant.

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 η 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

TABLE I: Comparison of calculated and experimental energies of Al^+ in 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 $381308 - 4718 = 376591 \text{ cm}^{-1}$.

Level	Expt.	CI	CI+MBPT	CI+All
$3s^2 \ ^1S_0$	381308	4718	163	23
$3p^2 \ ^1D_2$	85481	1984	61	-19
$3s4s \ ^3S_1$	91275	1290	62	14
$3p^2 \ ^3P_0$	94085	1499	34	7
$3p^2 \ ^3P_1$	94147	1499	30	4
$3p^2 \ ^3P_2$	94269	1498	23	-4
$3s4s \ ^1S_0$	95351	1359	50	3
$3s3d \ ^3D_3$	95549	1353	-2	-25
$3s3d \ ^3D_2$	95551	1354	-2	-24
$3s3d \ ^3D_1$	95551	1354	-1	-24
$3s3p \ ^3P_0^o$	37393	1155	56	3
$3s3p \ ^3P_1^o$	37454	1154	52	3
$3s3p \ ^3P_2^o$	37578	1153	45	-6
$3s3p \ ^1P_1^o$	59852	255	-105	-84

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

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

for a state v with the total angular momentum J and projection M [16]. The wave function $\Psi(v, M')$, where $M' = M + q$, is composed of parts that have angular momenta of $J' = J, J \pm 1$ from which the scalar and tensor polarizability of the state $|v, J, M\rangle$ can be determined [16]. The construction of the effective Hamiltonian H_{eff} using the all-order approach is described in [14]. The effective dipole operator D_{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 II: Contributions to the $3s^2\ ^1S_0$ and $3s3p\ ^3P_0^\circ$ polarizabilities α_0 of 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	Contr.	D	α_0
$3s^2\ ^1S_0$	$3s^2\ ^1S_0 - 3s3p\ ^1P_1^\circ$	3.113	23.661
	$3s^2\ ^1S_0 - 3s4p\ ^1P_1^\circ$	0.045	0.003
	Other		0.138
	Core		0.265
	VC		-0.019
	Total		24.048
$3s3p\ ^3P_0^\circ$	$3s3p\ ^3P_0^\circ - 3s4s\ ^3S_1$	0.900	2.197
	$3s3p\ ^3P_0^\circ - 3p^2\ ^3P_0$	1.836	8.687
	$3s3p\ ^3P_0^\circ - 3s3d\ ^3D_1$	2.236	12.568
	Other		0.836
	Core		0.265
	VC		-0.010
	Total		24.543

Table I presents the comparison of the experimental energies of Al^+ levels with those calculated in the CI, CI+MBPT, and CI+all-order approximations. The supplementary material contains the analogous data for B^+ and In^+ [19]. Significant improvement of the energy values is observed for Al^+ and 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 cm^{-1} of the experimental values for B^+ and Al^+ . The accuracy of the 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 $3s3p\ ^3P_0^\circ$ polarizabilities α of Al^+ is given in Table II. The supplementary material contains the analogous data for B^+ and 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 $J = 0$. We find that a single transition, $ns^2\ ^1S_0 - nsnp\ ^1P_1^\circ$, contributes 92.9%, 99.4%, and 98.7% to the valence ground state polarizability for B^+ , Al^+ , and In^+ , respectively. Three transitions, $nsnp\ ^3P_0^\circ - np^2\ ^3P_1$, $nsnp\ ^3P_0^\circ - ns(n+1)s\ ^3S_1$, and $nsnp\ ^3P_0^\circ - ns(n+1)d\ ^3D_1$ contribute 70.8%, 98.7%, and 92.8% to the $^3P_0^\circ$ polarizability for B^+ , Al^+ , and In^+ , respectively. Therefore, both Al^+ and In^+ polarizabilities could be calculated more precisely if experimental values of the dipole matrix elements were known

TABLE III: The values of the $ns^2\ ^1S_0$ and $nsnp\ ^3P_0^\circ$ polarizabilities α_0 in B^+ , Al^+ , and 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
B^+	$\alpha_0(2s^2\ ^1S_0)$	9.575	9.613	9.624
	$\alpha_0(2s2p\ ^3P_0^\circ)$	7.779	7.769	7.772
	$\Delta\alpha_0$	-1.796	-1.844	-1.851
Al^+	$\alpha_0(3s^2\ ^1S_0)$	24.405	24.030	24.048
	$\alpha_0(3s3p\ ^3P_0^\circ)$	24.874	24.523	24.543
	$\Delta\alpha_0$	0.469	0.493	0.495
In^+	$\alpha_0(5s^2\ ^1S_0)$	26.27	23.83	24.01
	$\alpha_0(5s5p\ ^3P_0^\circ)$	28.60	25.87	26.02
	$\Delta\alpha_0$	2.33	2.04	2.01

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 Al^+ are in excellent agreement with CI calculations with a semi-empirical core potential (CICP) [8].

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”. 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 $^3P_0^\circ$ 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 cancellation between 1S_0 and $^3P_0^\circ$ 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^+ .

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 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_{eff} to the RPA method

TABLE IV: BBR shifts at $T = 300\text{K}$ in B^+ , Al^+ , and In^+ . $\Delta\alpha_0$ is given in a.u.; clock frequencies ν_0 and the BBR shifts $\Delta\nu_{\text{BBR}}$ are given in Hz. Uncertainties in the values of $\Delta\nu_{\text{BBR}}/\nu_0$ are given in column labeled “Uncertainty”.

Ion	$\Delta\alpha_0$	$\eta(^1S_0)$	$\eta(^3P_0)$	$\Delta\nu_{\text{BBR}}$ (Hz)	ν_0 (Hz)	$ \Delta\nu_{\text{BBR}}/\nu_0 $	Uncertainty
B^+	-1.851	0.00014	0.00014	0.0159(16)	1.119×10^{15}	1.42×10^{-17}	1×10^{-18}
Al^+	0.495	0.00022	0.00024	-0.00426(43)	1.121×10^{15}	3.8×10^{-18}	4×10^{-19}
In^+	2.01	0.00018	0.00019	-0.0173(17)	1.267×10^{15}	1.36×10^{-17}	1×10^{-18}

[16]. The second issue is unlikely to cause large errors as RPA is expected to be the dominant 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 η , BBR shift at $T = 300\text{ K}$, $^1S_0-^3P_0^o$ clock frequencies ν_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 $^3P_0^o-^3P_1^o$ 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 η 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 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/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 $3s^2-3s3p\ ^3P_0^o$ clock transition energy. Its reported value of $37326(95)\text{ cm}^{-1}$ differs from the experimental value 37393 cm^{-1} by 67 cm^{-1} . Our CI+all-order value 37390 cm^{-1} agrees with experiment to 3 cm^{-1} , and even our CI+MBPT value agrees to 56 cm^{-1} (see line $3s3p\ ^3P_0^o$ in Table I). Most of our other energy levels also agree with experiment to a few cm^{-1} .

We also calculated frequency-dependent polarizabilities of clock states at 1126 nm using the same approach; our values are $\alpha_0(\omega)[^1S_0] = 24.58\text{ a.u.}$ and $\alpha_0(\omega)[^3P_0] = 25.13\text{ a.u.}$ The resulting frequency-dependent polarizability difference $\Delta\alpha_0(\omega) = 0.549(55)\text{ a.u.}$ is in agreement with theoretical CICIP value $0.54(41)\text{ a.u.}$ [8] and is 1.6σ from the experimental value $1.08(34)\text{ a.u.}$ [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 4×10^{-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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