

## Blackbody-radiation shift in a $^{43}\text{Ca}^+$ ion optical frequency standard

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Motivated by the prospect of an optical frequency standard based on  $^{43}\text{Ca}^+$ , we calculate the blackbody-radiation (BBR) shift of the  $4s_{1/2}-3d_{5/2}$  clock transition, which is a major component of the uncertainty budget. The calculations are based on the 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. Additional calculations are conducted for the dominant contributions in order to evaluate some omitted high-order corrections and estimate the uncertainties of the final results. The BBR shift obtained for this transition is 0.38(1) Hz. The tensor polarizability of the  $3d_{5/2}$  level is also calculated and its uncertainty is evaluated as well. Our results are compared with other calculations.

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The definition for the International System of Units (SI) of time, the second, is based on the microwave transition between the two hyperfine levels of the ground state of  $^{133}\text{Cs}$ . The advancements in experimental techniques such as laser frequency stabilization, atomic cooling and trapping, etc. have made the realization of the SI unit of time possible to 15 digits. 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. A number of groups [1,2] have accurately calculated the BBR shift at room temperature affecting the Cs microwave frequency standard. A significant further improvement in frequency standards is possible with the use of optical transitions. The frequencies of feasible optical clock transitions are five orders of magnitude larger than the relevant microwave transition frequencies, thus making it theoretically possible to reach relative uncertainty of  $10^{-18}$ . The ability to develop more precise optical frequency standards will open ways to improve global positioning system (GPS) measurements and tracking of deep-space probes, perform more accurate measurements of the physical constants and tests of fundamental physics such as searches for nonlinearity of quantum mechanics, gravitational waves, etc.

One of the promising schemes for the optical frequency standard with a single  $^{43}\text{Ca}^+$  ion trapped in a Paul trap was proposed by Champenois *et al.* [3]. A major advantage of using  $^{43}\text{Ca}^+$  ions is that the radiation required for cooling, repumping, and clock transition is easily produced by non-bulky solid state or diode lasers. In this work, we calculate the shift in a  $^{43}\text{Ca}^+$  optical clock transition due to blackbody radiation. The clock transition involved is  $4s_{1/2} \rightarrow 3d_{5/2}$   $F=6$   $m_F=0$ .

The accuracy of optical frequency standards is limited by the frequency shift in the clock transitions caused by the interaction of the ion with external fields. One such shift in

the atomic levels is caused by external magnetic fields (Zeeman shift). The first-order Zeeman shift can be eliminated by using isotopes with half-integer nuclear spin [3]. The second-order Zeeman shift depends on the choice of hyperfine sub-levels involved in the optical transition. The particular transition scheme used to minimize second-order Zeeman shift in  $^{43}\text{Ca}^+$  is  $4s_{1/2} \rightarrow 3d_{5/2}$   $F=6$   $m_F=0$ . The effect of this shift on the clock transition is of the order of  $-0.09(9)$  Hz at  $0.1 \mu\text{T}$  at room temperature [3]. There are some additional shifts in the clock transition frequency due to the second-order Doppler effect. These are on the order of mHz for ions at room temperature [3,4]. There have been a number of accurate calculations of the Zeeman and Doppler shifts [3,4]; however, there has been no accurate study of the BBR shift in this optical transition. As we show here, the BBR shift is the major component in the uncertainty budget of this frequency standard at room temperature.

The frequency-dependent electric field  $E$  radiated by a black body at temperature  $T$  is given by the Planck's radiation law. The frequency shift of an ionic state due to such an electric field can be related to the state's static scalar polarizability  $\alpha_0$  by

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

where  $\eta$  is a small "dynamic" correction [5]. We estimate that this dynamic correction is negligible with comparison to the present 3% accuracy of our calculations. The effect of the tensor part of the polarizability average out due to the isotropic nature of the electric field radiated by the blackbody. However, for completeness, we also present results for the static tensor polarizability of the  $3d_{5/2}$  state.

The overall BBR shift of the clock transition frequency is calculated as the difference between the BBR shifts of the individual levels involved in the transition:

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

Therefore, the evaluation of the BBR shift involves accurate calculation of static scalar polarizabilities for the  $4s_{1/2}$  ground and  $3d_{5/2}$  excited states. We use the relativistic single-double (SD) all-order method to find the electric-dipole matrix elements used in the calculation of dominant contributions to the polarizability values. The relativistic all-order method is one of the most accurate methods currently being used in atomic structure calculations. We refer the reader to Refs. [6,7] for the detailed description of this approach.

The calculation of the static scalar polarizability of an atom can be separated into the calculations of the ionic core contribution  $\alpha_{\text{core}}$  and a valence contribution. The static ionic core polarizability values were calculated using random-phase approximation (RPA) in Ref. [8]. The valence scalar and tensor polarizabilities of an atom in a state  $v$  are expressed as the sums over all intermediate states  $k$  allowed by the electric-dipole selection rules:

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

$$\alpha_2 = -4C \sum_k (-1)^{j_v + j_k + 1} \begin{Bmatrix} j_v & 1 & j_k \\ 1 & j_v & 2 \end{Bmatrix} \frac{\langle k||D||v \rangle^2}{E_k - E_v},$$

$$C = \left( \frac{5j_v(2j_v - 1)}{6(j_v + 1)(2j_v + 1)(2j_v + 3)} \right)^{1/2}, \quad (4)$$

where  $\langle k||D||v \rangle$  are the reduced electric-dipole ( $E1$ ) matrix elements and  $E_i$  is the energy of a state  $i$ . In these equations, and hereafter, we use the conventional system of atomic units, a.u., in which  $e, m_e, 4\pi\epsilon_0$  and the reduced Planck constant  $\hbar$  have the numerical value 1. Polarizability in a.u. has the dimensions of volume, and its numerical values presented here are thus expressed in units of  $a_0^3$ , where  $a_0 \approx 0.052918 \text{ nm}$  is the Bohr radius. The atomic units for  $\alpha$  can be converted to SI units via  $\alpha/h[\text{Hz}/(\text{V/m})^2] = 2.48832 \times 10^{-8} \alpha [\text{a.u.}]$ , where the conversion coefficient is  $4\pi\epsilon_0 a_0^3/h$  and Planck constant  $h$  is factored out. Experimental energies from Ref. [9] have been used for the dominant contributions to the polarizability.

We use the  $B$ -spline method to reduce infinite sums in Eqs. (3) and (4) to a finite number of terms [10] with 70 splines of order 11 for each angular momentum constrained to a spherical cavity with  $R=220 \text{ a.u.}$  The particular choice of such a large cavity ensures that all valence orbitals of interest are enclosed. In our case, the relevant excited states up to  $12d$  states fit inside this cavity. We also separate the polarizability calculation into two parts, the main term  $\alpha_{\text{main}}$  containing the first few contributions from the states that fit inside the cavity, with the remaining part designated by  $\alpha_{\text{tail}}$ . The main contribution is calculated using the all-order matrix elements obtained in the present work and experimental

TABLE I. Contributions to the  $4s_{1/2}$  scalar ( $\alpha_0$ ) static polarizabilities in  $^{43}\text{Ca}^+$  and their uncertainties in units of  $a_0^3$ . The values of corresponding  $E1$  matrix elements are given in  $ea_0$ .

Contribution	$\langle k  D  4s_{1/2} \rangle$	$\alpha_0$
$4s_{1/2}-4p_{1/2}$	2.898	24.4(5)
$4s_{1/2}-5p_{1/2}$	0.076	0.007
$4s_{1/2}-6p_{1/2}$	0.085	0.007
$4s_{1/2}-4p_{3/2}$	4.099	48.4(1.0)
$4s_{1/2}-5p_{3/2}$	0.091	0.010
$4s_{1/2}-6p_{3/2}$	0.112	0.012
$\alpha_{\text{core}}$		3.25(17)
$\alpha_{\text{tail}}$		0.006(6)
$\alpha_{\text{total}}$		76.1(1.1)

energies [9]. The tail contribution is evaluated in the Dirac-Fock (DF) approximation. We included as many states as practical in  $\alpha_{\text{main}}$  for the  $3d_{5/2}$  state in order to reduce the uncertainty in the remainder.

Table I shows the contributions from the individual transitions to the  $\alpha_0$  of the  $4s_{1/2}$  ground state of  $^{43}\text{Ca}^+$ . The main contributions are listed separately along with the respective values of the electric-dipole matrix elements. The tail contributions are grouped together as  $\alpha_{\text{tail}}$ . The total contribution of the  $4s_{1/2}-4p_{1/2}$  and  $4s_{1/2}-4p_{3/2}$  transitions is overwhelmingly dominant. We use our *ab initio* SD all-order value for these matrix elements based on the comparison of the all-order results for alkali-metal atoms with experiment [7] and assign these values 1% uncertainty.

The lifetimes of the  $4p_{1/2}$  and  $4p_{3/2}$  states have been measured by Jin and Church [11] using a variant of the collinear laser-beam-ion-beam spectroscopy technique in 1993. The experimental results,  $\tau(4p_{1/2})=7.098(20) \text{ ns}$  and  $\tau(4p_{3/2})=6.924(19) \text{ ns}$  [11], were found to be in significant disagreement with perturbation theory calculations at that time. By 1993, similar discrepancies were found between other measurements carried out using the same technique and theoretical calculations of light alkali-metal atom lifetimes. These disagreements in alkali-metal atoms were resolved a few years later when new measurements became available (see [7,12] and references therein). In all cases, new experimental results were found to be in excellent agreement with precise theoretical calculations. Recently, excellent agreement was also found between experimental and theoretical calculations of the  $3d$  lifetimes in  $\text{Ca}^+$  [13]. Just as in the case of earlier comparison of theory and experiment for alkali-metal atoms, we find significant discrepancy between our present calculations yielding  $\tau(4p_{1/2})=6.875 \text{ ns}$ ,  $\tau(4p_{3/2})=6.686 \text{ ns}$ , and measurements of Ref. [11]. It is interesting to make a direct comparison of the  $4p_j-4s$  theoretical and experimental matrix elements. The contributions of the  $4p-3d$  transitions into the  $4p$  lifetimes are small, as shown by comparison of our theory values for the Einstein  $A$  coefficients  $A_{ab}$  for the transitions to the  $4s$  state,  $A_{4p_{1/2}4s}=136.0 \times 10^6 \text{ s}^{-1}$  and  $A_{4p_{3/2}4s}=139.7 \times 10^6 \text{ s}^{-1}$ , and for the transitions to the  $3d_j$  states,  $A_{4p_{1/2}3d_{3/2}}=9.452 \times 10^6 \text{ s}^{-1}$ ,  $A_{4p_{3/2}3d_{3/2}}=0.997 \times 10^6 \text{ s}^{-1}$ , and  $A_{4p_{3/2}3d_{5/2}}=8.877 \times 10^6 \text{ s}^{-1}$ . The lifetimes are

calculated as inverse of the sum of the appropriate  $A$  coefficients,  $\tau_a = 1/\sum_b A_{ab}$ . Therefore, we can infer the ‘‘experimental’’ values for the  $A_{4p,4s}^{\text{expt}}$  and, correspondingly, the values of the reduced matrix elements  $\langle 4p_j || d || 4s \rangle^{\text{expt}}$  by combining the experimental lifetimes from [11] with our results for  $A_{4p_j,3d_j}$ . The resulting values are  $\langle 4p_{1/2} || d || 4s \rangle^{\text{expt}} = 2.849(4)$  and  $\langle 4p_{3/2} || d || 4s \rangle^{\text{expt}} = 4.023(6)$ . While the uncertainties of these values include the uncertainties in the theoretical values of the  $4p-3d$  matrix elements, their contributions are negligible. Our theoretical values differ from these experimental matrix elements by 1.7% and 1.9% for the  $4p_{1/2}-4s$  and  $4p_{3/2}-4s$  transitions, respectively. Our theoretical values for these transitions in K agree with experiment values within experimental uncertainties (0.13%). We note some differences between the contributions of the various correlation correction terms in the K and  $\text{Ca}^+$  calculations of these matrix elements. Therefore, it would very interesting to see a new measurement of these matrix elements in  $\text{Ca}^+$  to determine if the discrepancies between the theoretical and experimental values of the  $4p$  lifetimes will be resolved as in the case of the alkali-metal atoms.

Our all-order SD values are used for other main term contributions as well but their contribution is negligible. The uncertainty of the core contribution is taken to be 5% based on the comparison of the RPA approximation with experimental values for noble gases.

Table II shows the detailed breakdown of the contributions to the  $3d_{5/2}$  state polarizabilities. In this case, the allowed transitions are to  $np_{3/2}$  and  $nf_{5/2,7/2}$  states. The two dominant contributions come from the  $3d_{5/2}-4p_{3/2}$  and  $3d_{5/2}-4f_{7/2}$  transitions. The sum of the contribution from the  $3d_{5/2}-nf$  transitions converges more slowly than the  $ns-np$  sums; therefore, we include in the main term the nine lowest  $3d_{5/2}-nf_j$  transitions for each  $j$ . In addition to the SD all-order calculations, we carry out semiempirical scaling procedure for the two lowest  $3d_{5/2}-np_{3/2}$  transitions and the three lowest  $3d_{5/2}-nf$  transitions to evaluate some classes of the correlation corrections omitted by the current all-order calculation.

We also conduct additional more complicated *ab initio* calculations that partially include triple excitation (SDpT) since those appear to be important for these types of transitions. The scaling procedure and SDpT calculations are described in Refs. [7,13,15]. We conducted a more detailed study of the uncertainties in the values of the final matrix elements for the first transition in each sum, i.e.,  $3d_{5/2}-4p_{3/2}$ ,  $3d_{5/2}-4f_{5/2}$ , and  $3d_{5/2}-4f_{7/2}$ . They are determined as the maximum difference between the final results and the *ab initio* and scaled SDpT values. The remaining uncertainties for the  $3d_{5/2}-nf$  contributions are determined as the differences between the final values (either scaled SD or SDpT) and the *ab initio* SD values. The all-order calculation of such a large number of matrix elements and evaluation of their uncertainties makes the calculation of the  $3d_{5/2}$  state polarizability much more challenging than the calculation of the ground state polarizability.

The tail contribution of the  $3d_{5/2}$  state is almost 5% of the total polarizability. Such a large tail leads to a large uncertainty in the total polarizability. In order to evaluate the un-

TABLE II. Contributions to the  $3d_{5/2}$  scalar ( $\alpha_0$ ) and tensor ( $\alpha_2$ ) static polarizabilities in  $^{43}\text{Ca}^+$  and their uncertainties in units of  $a_0^3$ . The values of corresponding  $E1$  matrix elements are given in  $ea_0$ .

Contribution	$\langle k    D    3d_{5/2} \rangle$	$\alpha_0$	$\alpha_2$
$3d_{5/2}-4p_{3/2}$	3.306	22.78(25)	-22.78(25)
$3d_{5/2}-5p_{3/2}$	0.148	0.011(2)	-0.011(2)
$3d_{5/2}-6p_{3/2}$	0.095	0.004	-0.004
$3d_{5/2}-4f_{5/2}$	0.516	0.120(3)	0.137(3)
$3d_{5/2}-5f_{5/2}$	0.319	0.039(2)	0.044(2)
$3d_{5/2}-6f_{5/2}$	0.224	0.018(1)	0.020(1)
$3d_{5/2}-7f_{5/2}$	0.169	0.010	0.011
$3d_{5/2}-8f_{5/2}$	0.134	0.006	0.007
$3d_{5/2}-9f_{5/2}$	0.110	0.004	0.004
$3d_{5/2}-10f_{5/2}$	0.093	0.003	0.003
$3d_{5/2}-11f_{5/2}$	0.079	0.002	0.002
$3d_{5/2}-12f_{5/2}$	0.069	0.002	0.002
$3d_{5/2}-4f_{7/2}$	2.309	2.392(53)	-0.854(19)
$3d_{5/2}-5f_{7/2}$	1.428	0.773(33)	-0.276(12)
$3d_{5/2}-6f_{7/2}$	1.000	0.350(12)	-0.125(4)
$3d_{5/2}-7f_{7/2}$	0.757	0.191(7)	-0.068(3)
$3d_{5/2}-8f_{7/2}$	0.600	0.117(4)	-0.042(2)
$3d_{5/2}-9f_{7/2}$	0.492	0.077(3)	-0.028(1)
$3d_{5/2}-10f_{7/2}$	0.414	0.054(2)	-0.019(1)
$3d_{5/2}-11f_{7/2}$	0.354	0.039(1)	-0.014(1)
$3d_{5/2}-12f_{7/2}$	0.308	0.029(1)	-0.011
$\alpha_{\text{core}}$		3.25(17)	
$\alpha_{\text{tail}}$		1.7(1.1)	-0.5(3)
$\alpha_{\text{total}}$		32.0(1.1)	-24.5(4)

certainty in the tail, we calculated the last few main terms using the DF approximation and compared the results with our all-order values. We found that the DF approximation overestimates the polarizability contributions by about 60% relative to the all-order value. To improve our accuracy, we scaled the tail contribution with this ratio and took the difference of the DF and scaled DF result to be the uncertainty of the tail value. The uncertainties from all terms are added in quadrature to obtain the uncertainties of the final polarizability values.

We also list the contributions from various transitions to the  $3d_{5/2}$  tensor polarizability in Table II. The  $3d_{5/2}-4p_{3/2}$  transition also gives the dominant contribution to the tensor polarizability. The tail contribution is less important for  $\alpha_2$  and the uncertainty in  $\alpha_2$  calculation is less than that of  $\alpha_0$ .

We use the scalar polarizability values to evaluate the shift of a clock transition due to blackbody radiation at 300 K. The final shift in the clock transition for a  $^{43}\text{Ca}^+$  ion is found to be  $(0.380 \pm 0.013)$  Hz. The overall uncertainty of the result is dominated by the contribution of highly excited  $nf_{7/2}$  states to  $3d_{5/2}$  polarizability.

Blackbody radiation also shifts the hyperfine splittings of the ground and excited states [1,2] although this is third-order effect and thus expected to be small. For completeness, we have calculated this effect which is proportional to the

difference in the atomic polarizabilities between the two ground hyperfine structure states  $F$  of the atom. This is exactly the sort of calculation that is involved in the determination of the BBR shift in the microwave standard. The  $F$ -dependent polarizability can be written as the sum of three terms, each involving a reduced hyperfine matrix element and two reduced electric-dipole matrix elements [1,2]. We estimated the magnitude of the frequency shift of the ground state hyperfine transition using DF values of these reduced matrix elements. For consistency, we used the same set of  $B$ -splines. Further details of the method can be found in Refs. [1,2]. The frequency shift in the ground-state hyperfine transition of  $^{43}\text{Ca}^+$  at room temperature is calculated to be  $4.2 \times 10^{-6}$  Hz. The magnitude of this third-order correction is approximately  $10^{-5}$  times lower than the second-order BBR shift and hence can be neglected. The effect of electric field on the frequency of the  $3d_{5/2}$  state hyperfine transition is even smaller and; therefore, is not expected to affect the BBR shift of the clock transition.

In Table III, we compare our polarizability and BBR shift results with previous theoretical studies. In the work done by Champenois *et al.* [3], only first few transitions were included in the Stark shift calculations. The required oscillator strengths were taken from the Kurucz database [16] in Ref. [3] and from Ref. [17] in Ref. [4]. Our value for the ground state polarizability differs from that of Theodosiou [14] in part because of his omission of the core polarizability contribution in [14] and his use of the Jin and Church [11] values of the  $4s-4p$  matrix elements. Our all-order values are

TABLE III. Comparison of static scalar polarizabilities for  $4s_{1/2}$  and  $3d_{5/2}$  states and blackbody radiation shift for the  $4s_{1/2}-3d_{5/2}$  transition of  $^{43}\text{Ca}^+$  ion at  $T=300$  K. The polarizability values are in  $a_0^3$  and BBR shift is in Hz.

	Present work	Ref. [3]	Ref. [4]	Ref. [14]
$\alpha_0(4s_{1/2})$	76.1(1.1)	76	73	70.89(15)
$\alpha_0(3d_{5/2})$	32.0(1.1)	31	23	
BBR shift	0.38(1)	0.39(27)	0.4	

in good agreement with those predicted by Champenois *et al.* [3] and Kajita *et al.* [4]. We have significantly improved the accuracy of the BBR shift in comparison to these calculations by using all-order values for the dominant terms and also by including the tail and core contributions.

We have increased the accuracy of the polarizability values as compared to any other previous calculations by using a more accurate dipole-matrix element values calculated using relativistic all-order single-double method making the BBR shift value accurate enough to evaluate the performance of a  $\text{Ca}^+$  single-ion frequency standard at room temperature.

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