

Blackbody Radiation Shifts and Theoretical Contributions to Atomic Clock Research

(Invited Paper)

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Abstract—A review of the theoretical calculations of the blackbody radiation (BBR) shifts in various systems of interest to the atomic clock research is presented. The calculations for monovalent systems, such as Ca⁺, Sr⁺, and Rb are carried out using 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. New method for accurate calculations of BBR shifts for divalent systems such as Sr is discussed. The new approach combines the relativistic all-order method and the configuration interaction method. The evaluation of the uncertainty of the BBR shift values is discussed in detail.

I. INTRODUCTION

The current definition of a second in the International System of Units (SI) is based on the microwave transition between the two hyperfine levels ($F = 4$ and $F = 3$) of the ¹³³Cs ground state. The present relative standard uncertainty of Cs microwave frequency standard is around 4×10^{-16} [1]. 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. The BBR shift at room temperature affecting the Cs microwave frequency standard has been calculated to high accuracy (0.35%) in Refs. [2], [3] implying 6×10^{-17} fractional uncertainty. These calculations are in agreement with 0.2% measurement [4].

A significant further improvement in frequency standards is possible with the use of optical transitions as the frequencies of feasible optical clock transitions are five orders of magnitude larger than the relevant microwave transition frequencies. Significant recent progress in optical spectroscopy and measurement techniques has led to the achievement of relative standard uncertainties in optical frequency standards that are comparable to the Cs microwave benchmark. In 2006, the International Committee for Weights and Measures (CIPM) recommended that the following transitions frequencies shall be used as secondary representations of the second [5]:

ground-state hyperfine microwave transition in ⁸⁷Rb [6], [7], $5s\ ^2S_{1/2} - 4d\ ^2D_{5/2}$ optical transition of the ⁸⁸Sr⁺ ion [8], [9], $5d^{10}6s\ ^2S_{1/2}(F = 0) - 5d^96s^2\ ^2D_{5/2}(F = 2)$ optical transition in ¹⁹⁹Hg⁺ ion [10], [11], $6s\ ^2S_{1/2}(F = 0) - 5d\ ^2D_{5/2}(F = 2)$ optical transition in ¹⁷¹Yb⁺ ion [12], [13] and $5s^2\ ^1S_0 - 5s5p\ ^3P_0$ transition in ⁸⁷Sr neutral atom [14], [15], [16]. With better stability and accuracy as well as extremely low systematic perturbations such optical frequency standards can reach a systematic fractional uncertainty of the order of 10^{-18} [9], [17]. The ability to develop more precise optical frequency standards will open ways to improve global positioning systems and tracking of deep-space probes, and perform more accurate measurements of the fundamental constants and testing of physics postulates.

The major contributions to the systematic frequency shifts come from Stark shifts with the blackbody radiation (BBR) being one of the most important contributions at room temperature for many of the frequency standards. Experimental measurements of the BBR shifts are difficult. In this paper, we review the current status of the theoretical calculations of the BBR shifts in various systems of interest to the development of both microwave and optical frequency standards. New preliminary result for the BBR shift of the ground-state hyperfine microwave transition in ⁸⁷Rb is presented [18]. The evaluation of BBR shifts and their uncertainties in optical frequency standards in monovalent ions, such as as Ca⁺ and Sr⁺ [19], [20] is discussed. New method for accurate calculations of the BBR shifts for divalent systems such as Sr is discussed. This approach combines the relativistic all-order method and the configuration interaction (CI) method [21]. This method is generally applicable, i.e. not restricted to the specific type of the system.

II. THEORETICAL CALCULATION OF BBR SHIFTS

The electrical field E radiated by a blackbody at temperature T , as given by Planck's law,

$$E^2(\omega)d\omega = \frac{8\alpha^3}{\pi} \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1}, \quad (1)$$

induces a nonresonant perturbation of the atomic transitions at room temperature [22], [23]. The average electric field radiated by a blackbody at temperature T is

$$\langle E^2 \rangle = (831.9 \text{ V/m})^2 \left(\frac{T(K)}{300} \right)^4. \quad (2)$$

Assuming that the system evolves adiabatically, the frequency shift of an atomic state due to such an electrical field can be related to the static electric-dipole polarizability α_0 by (see Ref. [24])

$$\delta\nu = -\frac{1}{2}(831.9 \text{ V/m})^2 \left(\frac{T(K)}{300} \right)^4 \alpha_0(1 + \eta), \quad (3)$$

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 contributions from M1 and E2 transitions are suppressed by factors of α^2 [24]. The overall BBR shift of the clock frequency is then calculated as the difference between the BBR shifts of the individual levels F and I involved in the transition.

Therefore, theoretical evaluation of the BBR shift requires accurate calculation of static scalar polarizabilities of the relevant states. In the case of the optical transitions, the lowest (second) order polarizabilities of the clock states are different. In the case of the ground-state hyperfine microwave frequency standards, the lowest (second) order polarizabilities of the clock states are the same and the lowest-order BBR shift is zero. To evaluate the BBR shift, the third-order F-dependent polarizabilities have to be calculated. Therefore, we treat these cases separately. We note that from the theoretical standpoint, the number of the valence electrons (and the presence of core holes) defines the type (and final accuracy) of the approach. For example, the calculations of the BBR shift in Ca^+ and Sr^+ are effectively the same, but the treatment of Sr^+ and Sr are completely different. The main sources of uncertainties in these cases are also different for different types of systems and are discussed separately for each distinct case.

III. MICROWAVE FREQUENCY STANDARDS

The third-order F-dependent static polarizability $\alpha_F^{(3)}(0)$ required for the evaluation of the BBR shift for the microwave frequency standards in Rb and Cs can be evaluated as [24]

$$\alpha_F^{(3)}(0) = A g_I \mu_n (2T + C + R), \quad (4)$$

where A is an angular coefficient, g_I is the nuclear gyromagnetic ratio, and μ_n is nuclear magneton. The quantities T , C , and R contain terms with two electric-dipole reduced matrix elements $\langle i || D || j \rangle$ and one matrix element of the magnetic hyperfine operator $\langle i || T^{(1)} || j \rangle$. For example, term T is given by [24]

$$T = \sum_{m \neq v} \sum_{n \neq v} A_1 \delta_{jn, j_v} \frac{\langle v || D || m \rangle \langle m || D || n \rangle \langle n || T^{(1)} || v \rangle}{(E_m - E_v)(E_n - E_v)}, \quad (5)$$

where A_1 is an angular coefficient and sums over m , n run over all possible states allowed by the selection rules. The

sums are made finite with the use of finite B-spline basis set in a spherical cavity. Two other terms, C and R , contain sums of the $DT^{(1)}D$ and $T^{(1)}D^2$ terms. It is practical to separate sum over states to the main contribution calculated using the high-precision all-order (or experimental) matrix elements and experimental energies, and the remainder (“tail”) calculated using either Dirac-Fock or random-phase (RPA) approximation. In Cs calculation [24], the main term contained sum over orbitals with the principal quantum number $n \leq 12$. While tail contributions is small, it is significant (on the order of 7% in Cs [24]).

Therefore, the calculation of the BBR shift reduces to the evaluation of the electric-dipole and magnetic hyperfine matrix elements. Accurate evaluation of these quantities, in particular for heavy systems, requires all-order type approaches where dominant electronic correlation terms are summed to all orders of many-body perturbation theory. Two such approaches implemented in significantly different ways have been used for the calculation of the blackbody radiation shifts: the relativistic all-order method (or linearized coupled-cluster method LCCSD[pT] method) [3], [18], [25], [26], [27] and perturbation theory in the screened Coulomb interaction (PTSCI) [2], [28] (also referred to as the correlation potential method). We describe the LCCSD[pT] method briefly below and summarize PTSCI method in Section III-C.

The relativistic all-order method including single, double, and partial valence triple excitations (or LCCSDpT) was 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 monovalent atoms (Li, Na, Mg II, Al III, Si IV, P V, S VI, K, Ca II, In, In-like ions, Ga, Ga-like ions, Rb, Cs, Ba II, Tl, Fr, Th IV, U V, other Fr-like ions, Ra II) as well as the calculation of parity-violating amplitudes in Cs, Fr, and Ra^+ . We refer the reader to review [29] and references therein for the detail description of this method, its extensions, and applications. The relativistic all-order method is applicable to the calculation of the monovalent systems, i.e. alkali-metal atoms, Ca^+ , Sr^+ , Zn^+ , etc. For example, it can be used to evaluate the properties of the ground or $5d^{10}6p$ excited state of Hg^+ , but not the properties involving $5d^96s^2$ configuration in Hg^+ since it is not a single valence electron state (but two-particle and one-hole state). We discuss an all-order approach capable of treating more complicated systems in Section V.

A. The all-order LCCSD[pT] method

In the linearized LCCSDpT approach, the atomic wave function of a monovalent atom in a state v is given by an expansion

$$|\Psi_v\rangle = \left[1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{mna} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v \right] \quad (6)$$

$$+ \frac{1}{6} \sum_{mnrab} \rho_{mnrwab} a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v \left] a_v^\dagger |\Psi_C\rangle,$$

where $|\Psi_C\rangle$ is the lowest-order frozen-core wave function; a_i^\dagger , a_i are creation and annihilation operators. In Eq. (6), the indices m , n , and r range over all possible virtual states while indices a and b range over all occupied core states. The quantities ρ are excitation coefficients. In single-double (LCCSD) implementation of the all-order method, only single and double excitations are included. In the LCCSDpT variant of the all-order method, valence triple excitations are included perturbatively as described in Ref. [30]. Shorter designation SD and SDpT are used some of the other works on the all-order method, indicating exactly the same quantities.

The equations for the correlation energy and all excitation coefficients are solved iteratively. Every iteration picks up correlation terms that correspond to the next order of perturbation theory until the correlation energy converges to sufficient numerical accuracy. Therefore, the all-order approach includes dominant many-body perturbation theory (MBPT) terms to all orders.

The matrix elements of any one-body operator $Z = \sum_{ij} z_{ij} a_i^\dagger a_j$ are obtained within the framework of the all-order method as

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}, \quad (7)$$

where $|\Psi_v\rangle$ and $|\Psi_w\rangle$ are given by the expansion (6). In the SD approximation, the resulting expression for the numerator of Eq. (7) consists of the sum of the DF matrix element z_{wv} and 20 other terms that are linear or quadratic functions of the excitation coefficients. The advantage of this approach is that the matrix elements of any one-body operators (for example, electric-dipole and magnetic hyperfine ones needed for the evaluation of the BBR shifts) are calculated with the same general code.

B. Evaluation of the uncertainties

There are two distinct sources of uncertainties in the evaluation of the $\alpha_F^{(3)}(0)$ given by Eqs. (4-5):

- (1) uncertainty in the values of the individual matrix elements used in the calculation of the main terms and
- (2) uncertainty of the remaining tail contribution.

Stability checks have to be also carried out to ensure that no significant cancellations are present in the sums that may adversely affect the accuracy. In such tests, sets of completely *ab initio* LCCSD or LCCSDpT values are used in place of the experimental data and the final results are compared [3]. The uncertainty of the experimental energy values [31], [32] is negligible. Where the experimental (electric-dipole or hyperfine) matrix elements were used, the experimental uncertainties were taken. The uncertainty of the theoretical matrix elements were assigned based on comparison of the theoretical and experimental values, estimation of the size of the correlation corrections, and importance of the higher-order terms for the particular matrix elements. The estimation of

the uncertainty of the tail contribution can be either carried out in the same fashion (by assigning the uncertainties to the individual terms) or by estimating the accuracy of the DHF approach for the entire tail.

C. Summary of the results

Following the designations of the Ref. [3], we give the summary of the results for the Stark shift coefficient k in 10^{-10} Hz/(V/m)² and the blackbody radiation shift parameter β . The Stark coefficient k is defined as

$$\delta\nu = kE^2, \quad (8)$$

where $\delta\nu$ is the frequency shift in the static electric field. The Stark coefficient for the transition between states F and I is related to the polarizability as

$$k = -\frac{1}{2}[\alpha_0(F) - \alpha_0(I)]. \quad (9)$$

The parameter β of the relative temperature-dependent BBR shift of the microwave frequency standard is defined as

$$\frac{\delta\nu}{\nu_0} = \beta \left(\frac{T(K)}{T_0} \right)^4 \left(1 + \epsilon \left(\frac{T(K)}{T_0} \right)^2 \right), \quad (10)$$

where T_0 is generally taken to be room temperature, 300K, ϵ parameterizes the lowest-order (in T) contribution to the dynamic correction η in Eq. (3), and ν_0 is clock transition frequency. The parameter β is calculated directly from the Stark-shift coefficient k defined by Eqs. (8-9) as

$$\beta = \frac{k}{\nu_0} (831.9 \text{ V/m})^2. \quad (11)$$

Small parameter ϵ has been calculated in Ref. [28] to be equal to 0.011 for ⁸⁷Rb, 0.013 for ¹³³Cs, 0.004 for ¹³⁷Ba⁺, 0.002 for ¹⁷¹Yb⁺, and 0.0005 for ¹⁹⁹Hg⁺.

Recent high-precision theoretical results [2], [3], [18], [26], [27], [28] for the Stark shift coefficient k in 10^{-10} Hz/(V/m)² and the blackbody radiation shift parameter β are summarized in Table I. We use [pT] designation to indicate that valence triple excitations were taken into account were LCCSDpT data were expected to be more accurate than the LCCSD ones. The result for Yb⁺ from Ref. [25] is obtained using relativistic third-order perturbation theory (RMBPT3). Theoretical results are compared with experimental data from Refs. [33], [4], [34]. The most complete comparison with other theory and experimental results for Cs is given in Ref. [28].

New preliminary *ab initio* β value [18] for the ⁸⁷Rb frequency standards obtained using LCCSD[pT] method is presented. We have also evaluated the Stark shift coefficient k and parameter β for ²³Na to study how these quantities vary among alkali-metal atoms. We find that β for Na is nearly identical to that of Li and is significantly (by a factor of 3.4) smaller than β (Cs).

Theoretical results are in good agreement with each other. We note that both of the approaches contain all-order correlation corrections. However, these methods include somewhat different types of the high-order correlation terms. The implementation of the all-order approaches is quite different. In the

TABLE I

SUMMARY OF THE RECENT THEORETICAL CALCULATIONS OF THE STARK SHIFT COEFFICIENT k IN 10^{-10} Hz/(V/m)² AND THE BLACKBODY RADIATION SHIFT PARAMETER β FOR TRANSITIONS BETWEEN THE GROUND HYPERFINE STATES AND COMPARISON WITH EXPERIMENT.

| Atom | Transition | | Ref. | k | β |
|--------------------------------|------------------------------------|-------------------|---------------|-----------|------------------------------|
| ⁷ Li | $2s (F = 2 \leftrightarrow F = 1)$ | Theory, LCCSD[pT] | [26] | -0.05824 | -0.5017×10^{-14} |
| | | Experiment | [33] | -0.061(2) | |
| ²³ Na | $3s (F = 2 \leftrightarrow F = 1)$ | Theory, LCCSD[pT] | Present | -0.1285 | -0.5019×10^{-14} |
| | | Experiment | [33] | -0.124(3) | |
| ³⁹ K | $4s (F = 2 \leftrightarrow F = 1)$ | Theory, LCCSD[pT] | [27] | -0.0746 | -1.118×10^{-14} |
| | | Experiment | [33] | -0.071(2) | |
| ⁸⁷ Rb | $5s (F = 2 \leftrightarrow F = 1)$ | Theory, LCCSD[pT] | Present, [18] | -1.272* | -1.287×10^{-14} |
| | | Theory, PTSCI | [28] | -1.24(1) | $-1.26(1) \times 10^{-14}$ |
| | | Experiment | [33] | -1.23(3) | |
| ¹³³ Cs | $6s (F = 4 \leftrightarrow F = 3)$ | Theory, LCCSD[pT] | [3] | -2.271(8) | $-1.710(6) \times 10^{-14}$ |
| | | Theory, PTSCI | [2] | -2.26(2) | $-1.70(2) \times 10^{-14}$ |
| | | Experiment | [4] | -2.271(4) | $-1.710(3) \times 10^{-14}$ |
| | | Experiment | [34] | -2.05(5) | $-1.54(4) \times 10^{-14}$ |
| ¹³⁷ Ba ⁺ | $6s (F = 2 \leftrightarrow F = 1)$ | Theory, PTSCI | [28] | -0.284(3) | $-0.245(2) \times 10^{-14}$ |
| ¹⁷¹ Yb ⁺ | $6s (F = 1 \leftrightarrow F = 0)$ | Theory, RMBPT3 | [25] | -0.1796 | -0.0983×10^{-14} |
| | | Theory, PTSCI | [28] | -0.171(9) | $-0.094(5) \times 10^{-14}$ |
| ¹⁹⁹ Hg ⁺ | $6s (F = 1 \leftrightarrow F = 0)$ | Theory, PTSCI | [28] | -0.060(3) | $-0.0102(5) \times 10^{-14}$ |

*Preliminary value

PTSCI (or correlation potential) method used in Refs. [2], [28] the calculations start from the relativistic Hartree-Fock method in the V^{N-1} approximation. The correlations are incorporated by means of the correlation potential Σ . The correlation potential is used to build a new set of single-electron states for subsequent evaluation of the hyperfine and electric-dipole matrix elements using the random-phase approximation. Structure radiation and the normalization corrections are included for hyperfine matrix elements. Hg⁺ and Yb⁺ calculations were carried out with the correlation potential calculated in second-order and rescaled to fit the experimental energies. For the other systems, two classes of terms are included in the correlation potential to all orders: screening of the Coulomb interaction and hole-particle interactions. The resulting correlation potential is scaled to fit the experimental energies. Scaling of the all-order correlation potential leads to only small adjustments and serves as a part of the uncertainty evaluation. For Rb, Cs, and Ba⁺ scaling of both second-order and all-order correlation potential operator was carried out for additional confirmation of the quoted uncertainties. The assignment of the uncertainty values was also based on the comparison of the polarizabilities and hyperfine constants with experimental values.

The agreement of results in Table I obtained with distinct high-precision approaches gives another estimate of the accuracy of the theoretical values. The evaluation of the uncertainty of the Rb LCCSD[pT] result is in progress [18]. Table I also illustrates the relative size of the electrostatic frequency shifts for the ground state hyperfine transitions in various systems. ¹⁹⁹Hg⁺ has both the lowest value of β and the lowest resulting

fractional uncertainty in the frequency standard (5×10^{-18}) due to BBR shift among the systems listed in Table I.

IV. OPTICAL FREQUENCY STANDARDS WITH CA⁺ AND SR⁺ IONS

In this section, we discuss the calculation of the BBR shifts for the optical frequency standards based on the $4s - 3d_{5/2}$ transition in Ca⁺ [19] and the $5s - 4d_{5/2}$ transition in Sr⁺ [20]. We note that while the calculations were conducted for ⁴³Ca⁺ and ⁸⁸Sr⁺ we have verified that the results given in this section do not depend on the particular isotope. Therefore, we will omit the A labels in text and tables below. According to Eq. (3), the calculation of the BBR shift for these transitions requires the calculation of the lowest-order atomic polarizability (unlike the cases of the hyperfine transitions, it does not cancel out for optical frequency standards) and the evaluation of the dynamic correction η . The third-order F-dependent polarizability was verified in Ref. [19] to give negligible contribution to the BBR shift.

Therefore, the evaluation of the BBR shift requires accurate calculation of static scalar polarizabilities of the $ns_{1/2}$ ground and $(n-1)d_{5/2}$ excited states. The effect of the tensor part of the $(n-1)d_{5/2}$ polarizability is averaged out due to the isotropic nature of the electric field radiated by the blackbody.

A. Calculation of the ground state and $nd_{5/2}$ state polarizabilities

The calculation of the scalar polarizability of a monovalent atom can be separated into three parts: the contribution of the electrons in the ionic core, α_{core} ; a small term, α_{vc} , that changes the core polarizability due to the presence of the

TABLE II
CONTRIBUTIONS TO THE GROUND STATE STATIC SCALAR
POLARIZABILITIES IN Ca^+ AND Sr^+ IN UNITS OF a_0^3 .

| Ca^+ | $\alpha(4s)$ | Sr^+ | $\alpha(5s)$ |
|---------------------------|--------------|---------------------------|--------------|
| $4s_{1/2} - 4p_{1/2}$ | 24.4 | $5s_{1/2} - 5p_{1/2}$ | 29.23 |
| $4s_{1/2} - 4p_{3/2}$ | 48.4 | $5s_{1/2} - 5p_{3/2}$ | 56.48 |
| $4s_{1/2} - (5,6)p_{1/2}$ | 0.014 | $5s_{1/2} - (6-8)p_{1/2}$ | 0.008 |
| $4s_{1/2} - (5,6)p_{3/2}$ | 0.022 | $5s_{1/2} - (6-8)p_{3/2}$ | 0.008 |
| α_{tail} | 0.006 | α_{tail} | 0.02 |
| $\alpha_{\text{core+vc}}$ | 3.25 | $\alpha_{\text{core+vc}}$ | 5.55 |
| α_{total} | 76.1 | α_{total} | 91.30 |

TABLE III
CONTRIBUTIONS TO THE $3d_{5/2}$ AND $4d_{5/2}$ STATIC SCALAR
POLARIZABILITIES IN Ca^+ AND Sr^+ , RESPECTIVELY, IN UNITS OF a_0^3 .

| Ca^+ | $\alpha(3d_{5/2})$ | Sr^+ | $\alpha(4d_{5/2})$ |
|----------------------------|--------------------|----------------------------|--------------------|
| $3d_{5/2} - 4p_{3/2}$ | 22.78(25) | $4d_{5/2} - 5p_{3/2}$ | 44.16(29) |
| $3d_{5/2} - 5p_{3/2}$ | 0.011(2) | $4d_{5/2} - 6p_{3/2}$ | 0.012(2) |
| $3d_{5/2} - 6p_{3/2}$ | 0.004 | $4d_{5/2} - 7p_{3/2}$ | 0.003 |
| $3d_{5/2} - 4f_{5/2}$ | 0.120(3) | $4d_{5/2} - 4f_{5/2}$ | 0.329(4) |
| $3d_{5/2} - 5f_{5/2}$ | 0.039(2) | $4d_{5/2} - 5f_{5/2}$ | 0.085(2) |
| $3d_{5/2} - 6f_{5/2}$ | 0.018(1) | $4d_{5/2} - 6f_{5/2}$ | 0.035 |
| $3d_{5/2} - (7-12)f_{5/2}$ | 0.027 | $4d_{5/2} - (7-12)f_{5/2}$ | 0.045 |
| $3d_{5/2} - 4f_{7/2}$ | 2.392(53) | $4d_{5/2} - 4f_{7/2}$ | 6.576(70) |
| $3d_{5/2} - 5f_{7/2}$ | 0.773(33) | $4d_{5/2} - 5f_{7/2}$ | 1.699(30) |
| $3d_{5/2} - 6f_{7/2}$ | 0.350(12) | $4d_{5/2} - 6f_{7/2}$ | 0.698(11) |
| $3d_{5/2} - 7f_{7/2}$ | 0.191(7) | $4d_{5/2} - 7f_{7/2}$ | 0.360(5) |
| $3d_{5/2} - 8f_{7/2}$ | 0.117(4) | $4d_{5/2} - 8f_{7/2}$ | 0.212(4) |
| $3d_{5/2} - 9f_{7/2}$ | 0.077(3) | $4d_{5/2} - 9f_{7/2}$ | 0.136(2) |
| $3d_{5/2} - 10f_{7/2}$ | 0.054(2) | $4d_{5/2} - 10f_{7/2}$ | 0.093(1) |
| $3d_{5/2} - 11f_{7/2}$ | 0.039(1) | $4d_{5/2} - 11f_{7/2}$ | 0.067(1) |
| $3d_{5/2} - 12f_{7/2}$ | 0.029(1) | $4d_{5/2} - 12f_{7/2}$ | 0.050(1) |
| α_{tail} | 1.7(1.1) | α_{tail} | 2.06(20) |
| $\alpha_{\text{core+vc}}$ | 3.25(17) | $\alpha_{\text{core+vc}}$ | 5.41(31) |
| α_{total} | 32.0(1.1) | α_{total} | 62.0(5) |

valence electron; and the dominant contribution, α_v , from the valence electron. The ionic core polarizability used here was calculated using the random-phase approximation (RPA) [35]. We calculate the α_{vc} contribution in the RPA approximation as well for consistency with the ionic core value. The valence scalar polarizability α_0 of an atom in a state v can be expressed as the sum over all excited intermediate states n allowed by the electric-dipole selection rules:

$$\alpha_0 = \frac{2}{3(2j_v + 1)} \sum_n \frac{\langle n || D || v \rangle^2}{E_n - E_v}, \quad (12)$$

where $\langle n || D || v \rangle$ are the reduced electric-dipole matrix elements and E_i is the energy of the i th state. Just as in the case of the third-order sums in the previous section, the valence polarizability is separated into two parts, the main term containing the first few dominant contributions and the

remainder α_{tail} . The matrix elements are calculated using the all-order LCCSD or LCCSDpT approaches described in Section III-A.

Contributions to the ground state static scalar polarizabilities in Ca^+ and Sr^+ in units of a_0^3 are listed in Table II. The tail contributions are grouped together as α_{tail} . For the main contribution, we use our *ab initio* LCCSD all-order values of the matrix elements and experimental energies from Ref. [31]. The first $ns - np$ transitions contribute over 99.9% to the valence polarizability. Contributions to the $3d_{5/2}$ and $4d_{5/2}$ static scalar polarizabilities in Ca^+ and Sr^+ , respectively, are listed in Table III. Unlike the case of the ground state polarizabilities, the contribution from other excited states are significant for the $nd_{5/2} - n'f_{7/2}$ transition contributions that converge very slowly. To improve accuracy, contributions up to $n > 13$ were included in the main term and evaluated using the all-order approach. The evaluation of the uncertainties of the ground state and $nd_{5/2}$ polarizabilities is discussed in the next section.

B. Evaluation of the uncertainties

There are three sources of the uncertainties contributing to the polarizabilities of Ca^+ and Sr^+ in the ground and $nd_{5/2}$ states. The ionic core contribution taken from Ref. [35] is relatively small and is expected to be accurate to better than 5%, based on the comparison of the RPA and experimental polarizability values for noble gases. Its uncertainty is, however, irrelevant to the evaluation of the uncertainty of the BBR shift since the core polarizability is the same for both clock states. The small compensating term α_{vc} is different for the two states, but its entire contribution is below the present uncertainty of the other terms.

(1) Ground state polarizability. The uncertainties in the values of the $4s - 4p_{1/2,3/2}$ and the $5s - 5p_{1/2,3/2}$ matrix elements for Ca^+ and Sr^+ , respectively, completely determine the uncertainty in the valence ground state polarizability values since they contribute over 99.9%. The LCCSD values for the primary $ns - np$ transitions in Li, Na, K, Rb, and Cs agree with various types of high-precision experiments to 0.1% - 0.4% [30]. There is no reason to expect reduced theoretical accuracy in the cases of either Ca^+ or Sr^+ and 0.5% uncertainty was assigned to the $5s - 5p_{1/2}$ and $5s - 5p_{3/2}$ Sr^+ matrix elements [20]. The resulting uncertainty of the $5s$ polarizability is 1%. Our theoretical LCCSD $5p_{1/2,3/2}$ lifetimes [20] are in agreement with 1% experiment conducted in 1995 [36]. The contribution of the $5s - 5p$ transitions to the lifetimes is dominant (94%). However, the theoretical lifetimes of the Ca^+ $4p_{1/2,3/2}$ states calculated by exactly the same approach in [19] are in significant (over 3%) disagreement with 1993 0.3% measurement [37]. This issue is discussed in detail in Ref. [19]. Unfortunately, we know of no way to accurately estimate the missing additional contributions to the dominant correlation correction to these transitions as it can be done for some other transitions (see discussion below). Accurate new measurements of the np lifetimes or $ns - np$ oscillator

TABLE IV

EVALUATION OF THE UNCERTAINTIES OF ELECTRIC-DIPOLE MATRIX ELEMENTS IMPORTANT FOR BBR SHIFT CALCULATION IN Ca^+ AND Sr^+ . ABSOLUTE VALUES IN A.U. ARE GIVEN.

| Atom | Transition | LCCSD | LCCSD _{sc} | LCCSDpT | LCCSDpT _{sc} | Final |
|---------------|-----------------------|-------|---------------------|---------|-----------------------|-----------|
| Ca^+ | $3d_{5/2} - 4p_{3/2}$ | 3.245 | 3.306 | 3.313 | 3.288 | 3.306(18) |
| | $3d_{5/2} - 4f_{5/2}$ | 0.501 | 0.516 | 0.517 | 0.511 | 0.516(6) |
| | $3d_{5/2} - 4f_{7/2}$ | 2.238 | 2.309 | 2.310 | 2.284 | 2.309(25) |
| Sr^+ | $4d_{5/2} - 5p_{3/2}$ | 4.150 | 4.187 | 4.198 | 4.173 | 4.187(14) |
| | $4d_{5/2} - 4f_{5/2}$ | 0.779 | 0.789 | 0.790 | 0.785 | 0.789(4) |
| | $4d_{5/2} - 4f_{7/2}$ | 3.486 | 3.528 | 3.536 | 3.509 | 3.528(19) |
| | $4d_{3/2} - 5p_{1/2}$ | 3.083 | 3.112 | 3.119 | 3.102 | 3.112(10) |
| | $4d_{3/2} - 5p_{3/2}$ | 1.369 | 1.383 | 1.386 | 1.378 | 1.383(5) |

strengths in Ca^+ and Sr^+ are needed to resolve this issue and improve final BBR shift results.

(2) Excited $nd_{5/2}$ state polarizability: the main term.

Uncertainty of the main term of the $nd_{5/2}$ state polarizability is dominated by a very few terms as illustrated by Table III. We obtain accurate values for these matrix elements using a semi-empirical scaling procedure that evaluates some classes of correlation corrections omitted by the current all-order calculations. The scaling procedure is described in Ref. [29]. We conduct the scaling starting from both LCCSD and LCCSDpT approximations. The scaling factors for the LCCSD and LCCSDpT calculations are different, and we take scaled LCCSD values to be the final results based on the comparisons of similar calculations in alkali-metal atoms with experiments [38], [39], [40]. The uncertainty evaluation of the reduced matrix elements that give significant contributions to the polarizabilities is illustrated in Table IV, scaled values are listed with subscript “sc”. The uncertainties are determined as the maximum difference between the scaled LCCSD values and the *ab initio* LCCSDpT and scaled LCCSDpT values. A notable feature of this table is close agreement of the scaled LCCSD and LCCSDpT results.

(3) Excited $nd_{5/2}$ state polarizability: the tail term.

The tail contribution of the $nd_{5/2} - n'f_{7/2}$ terms is particularly large; its DF value (3.5 a.u.) is 5% of the total polarizability for Sr^+ . The uncertainty in the tail dominated the uncertainty of the Ca^+ BBR shift value calculated in Ref. [19]. In a later work on Sr^+ , this issue was resolved by performing additional RPA calculations of the tail and carrying out the rescaling procedures starting from both DF and RPA approximations. Since the largest part of the correlation correction for the $4d_{5/2} - nf_{7/2}$ transitions with $n > 9$ comes from RPA-like terms, the RPA approximation is expected to produce a better result than the DF one. We carried out the RPA calculation of the tail and obtained a lower value of 2.9 a.u. We also calculated the main terms using the DF and RPA approximations and compared the results with our all-order values. The contributions to scalar polarizability of the $4d_{5/2}$ state in Sr^+ from terms involving $4d_{5/2} - nf_{7/2}$ transitions with $n = 4 - 12$ calculated in the DF, RPA, and all-order approximations are listed in Table V. The relative differences

TABLE V

CONTRIBUTIONS TO THE $4d_{5/2}$ STATIC SCALAR POLARIZABILITIES IN Sr^+ FROM $nf_{7/2}$ STATES IN DF, RPA, AND ALL-ORDER APPROXIMATIONS IN UNITS OF a_0^3 . THE RELATIVE DIFFERENCES BETWEEN DF AND ALL-ORDER RESULTS AND BETWEEN RPA AND ALL-ORDER RESULTS ARE LISTED IN % IN THE LAST TWO COLUMNS.

| | DF | RPA | All-order | $\Delta(\text{DF})$ | $\Delta(\text{RPA})$ |
|------------------------|--------|--------|-----------|---------------------|----------------------|
| $4d_{5/2} - 4f_{7/2}$ | 11.427 | 10.903 | 6.576 | 42.46 | 39.69 |
| $4d_{5/2} - 5f_{7/2}$ | 2.725 | 2.545 | 1.698 | 37.66 | 33.26 |
| $4d_{5/2} - 6f_{7/2}$ | 1.089 | 1.004 | 0.698 | 35.91 | 30.51 |
| $4d_{5/2} - 7f_{7/2}$ | 0.556 | 0.509 | 0.359 | 35.33 | 29.32 |
| $4d_{5/2} - 8f_{7/2}$ | 0.327 | 0.297 | 0.212 | 35.10 | 28.70 |
| $4d_{5/2} - 9f_{7/2}$ | 0.210 | 0.191 | 0.136 | 35.08 | 28.43 |
| $4d_{5/2} - 10f_{7/2}$ | 0.144 | 0.130 | 0.093 | 35.09 | 28.25 |
| $4d_{5/2} - 11f_{7/2}$ | 0.103 | 0.093 | 0.067 | 35.10 | 28.14 |
| $4d_{5/2} - 12f_{7/2}$ | 0.077 | 0.069 | 0.050 | 35.15 | 28.03 |
| Tail | 3.48 | 2.86 | | | |
| Adjusted tail | 2.26 | 2.06 | | | |

between DF and all-order results and between RPA and all-order results are listed in % in columns labeled $\Delta(\text{DF})$ and $\Delta(\text{RPA})$, respectively. The DF and RPA approximations overestimate the polarizability contributions by 35% and 28%, respectively. To improve our accuracy, we scale both DF and RPA results for the tail by these respective amounts to obtain a DF-scaled value of 2.26 a.u. and RPA-scaled value of 2.06 a.u. We take RPA-scaled value as the final one and the difference of these two values as its uncertainty.

C. Results for the BBR shifts

The scalar polarizability values are used to evaluate the BBR shifts in the Ca^+ and Sr^+ clock transitions at $T = 300$ K using Eq. (3) [19], [20]. The dynamic correction was estimated for Sr^+ to be $\eta = 0.0013$ and $\eta = 0.0064$ for the $5s$ and $4d_{3/2}$ states, respectively using the formulas from [24]. The resulting correction to Sr^+ BBR shift is -0.002 Hz and the final value for the BBR shift is $0.250(9)$ Hz [20]. The M1 and E2 contributions to the Sr^+ BBR shift were evaluated in [20] using the approach described in Ref. [24] and found to be

TABLE VI

THE BBR SHIFT $\delta\nu$ AT $T = 300K$, CLOCK TRANSITION FREQUENCY ν_0 , FRACTIONAL UNCERTAINTIES $\delta\nu/\nu_0$ DUE TO BBR SHIFT, AND THE FRACTIONAL ERROR IN THE ABSOLUTE TRANSITION FREQUENCY INDUCED BY THE BBR SHIFT UNCERTAINTY.

| Ion | $\delta\nu$ (Hz) | ν_0 (Hz) | $\delta\nu/\nu_0$ | Uncertainty |
|-----------------|------------------|-----------------------|------------------------|-----------------------|
| Ca ⁺ | 0.38(1) [19] | 4.11×10^{14} | 9.24×10^{-16} | 2.4×10^{-17} |
| Sr ⁺ | 0.250(9) [20] | 4.45×10^{14} | 5.62×10^{-16} | 2.0×10^{-17} |

negligible (below 0.01%). The comparisons of the LCCSD[pT] BBR shift values with other theoretical results are given in Ref. [19] and Ref. [20], for Ca⁺ and Sr⁺, respectively.

The results for the BBR shift $\delta\nu$ at $T = 300K$, the corresponding fractional uncertainties $\delta\nu/\nu_0$, and the fractional error in the absolute transition frequency induced by the BBR shift uncertainties are listed in Table VI. We note that relative uncertainty in the BBR shift is significantly larger than the polarizability uncertainties owing to the cancellation between the values of the polarizabilities of the clock states.

Further improvement in the BBR shift values will require settling the issue of the accuracy of the primary $ns - np$ matrix elements as well as experimental determination of the $np_{3/2} - (n-1)d_{5/2}$ matrix elements, where ns is the ground state. The types of experiments that can provide better understanding of the theoretical uncertainties or extraction of the specific matrix elements for more accurate evaluation of the BBR shifts include np lifetime (or $ns - np$ oscillator strength) measurements, light shift ratio measurements [41], or ac or dc Stark shift measurements on the any of the lines involving ns , np , or $(n-1)d$ states. We estimated that the experimental determination of the $ns - np_{1/2,3/2}$ matrix elements, where ns is a ground state accurate to 0.15% (or 0.3% $np_{1/2,3/2}$ lifetime measurement) would reduce fractional error in the absolute transition frequency induced by the BBR shift uncertainty by a factor of 2.

V. OPTICAL FREQUENCY STANDARDS WITH DIVALENT ATOMS

BBR shifts for optical lattice clocks based on the $ns^2 \ ^1S_0 - nsnp \ ^3P_0$ transitions in divalent atoms were calculated for Mg, Ca, Sr, and Yb in Ref. [24] and for Hg in Ref. [42]. The evaluation of the BBR shift in these systems requires evaluation of the ground and $nsnp \ ^3P_0$ state polarizabilities. Different theoretical methods have to be used for the evaluation of these polarizabilities in comparison with the monovalent systems discussed in the previous sections. The CI + MBPT approach initially developed in Ref. [43] that combines the configuration-interaction (CI) method and perturbation theory was used in Refs. [24], [42]. Experimental data were used where available for dominant contributions. Sr BBR shift was later investigated in more detail in Ref. [44] using the same approach.

In the CI method, the many-electron wave function is obtained as a linear combination of all distinct states of a

given angular momentum J and parity:

$$\Psi_J = \sum_i c_i \Phi_i, \quad (13)$$

in other words, a linear combination of Slater determinants of a proper symmetry from a model subspace [43].

Energies and wave functions of low-lying states are determined by diagonalizing the effective Hamiltonian:

$$H^{\text{eff}} = H_1 + H_2, \quad (14)$$

where H_1 represents the one-body part of the Hamiltonian, and two-body part H_2 contains the Coulomb (or Coulomb + Breit) matrix elements v_{ijkl} . The resulting wave functions are used to calculate matrix elements and other properties.

The CI + MBPT approach allows one to incorporate core excitations in the CI method by including certain perturbation theory terms into an effective Hamiltonian (14). The one-body part H_1 is modified to include the correlation potential Σ_1 that accounts for part of the core-valence correlations,

$$H_1 \rightarrow H_1 + \Sigma_1. \quad (15)$$

Either the second-order expression, $\Sigma_1^{(2)}$, or all-order chains of such terms can be used (see, for example, Ref. [45]). The two-body Coulomb interaction term H_2 is modified by including the two-body part of core-valence interaction that represents screening of the Coulomb interaction by valence electrons;

$$H_2 \rightarrow H_2 + \Sigma_2, \quad (16)$$

where Σ_2 is calculated in second-order MBPT in CI+MBPT approach. The CI method is then applied as usual with the modified H^{eff} to obtain improved energies and wave functions. Estimated accuracy of BBR values calculated by this approach was 2.7% for Mg, 1.4% for Ca and Sr, and 10% for Yb [24]. The resulting fractional uncertainties in the clock transition frequencies ranged from 1×10^{-17} for Mg to 3×10^{-16} for Yb. The development of more accurate approach is needed for further improvement of the BBR values for the optical lattice clocks.

A. CI+ all-order method

MBPT corrections associated with terms Σ_1 in Eq. (15) and Σ_2 in Eq. (16) typically grow with nuclear charge Z . This leads to deterioration of the accuracy of the CI + second order MBPT results for heavier, more complicated systems (as illustrated by significantly reduced accuracy of the Yb BBR in Ref. [24]).

In the CI + all-order approach, introduced in Ref. [21], the corrections to the effective Hamiltonian Σ_1 and Σ_2 are calculated using a modified version of the LCCSD all-order method described in Section III-A. Therefore, the effective Hamiltonian contains dominant core and core-valence correlation corrections to all orders. The core-core and core-valence sectors of the correlation corrections for systems with few valence electrons are treated in the all-order method with the same accuracy as in the all-order approach for the monovalent

TABLE VII

COMPARISON OF THE CI + ALL-ORDER RESULTS FOR THE ENERGY LEVELS IN cm^{-1} OF SR WITH EXPERIMENT. TWO-ELECTRON BINDING ENERGY IS GIVEN IN THE FIRST ROW, THE OTHER VALUES ARE COUNTED FROM THE GROUND STATE.

| Level | Expt. | Present | $\Delta(\%)$ |
|-------------------------|--------|---------|--------------|
| $5s^2\ ^1S_0$ | 134896 | 134894 | 0.001 |
| $5s5p\ ^3P_0$ | 14318 | 14301 | 0.11 |
| $5s5p\ ^3P_1$ | 14504 | 14487 | 0.12 |
| $5s5p\ ^3P_2$ | 14899 | 14892 | 0.04 |
| $5s4d\ ^3D_1$ | 18159 | 18148 | 0.06 |
| $5s4d\ ^3D_2$ | 18219 | 18218 | 0.01 |
| $5s4d\ ^3D_3$ | 18319 | 18335 | -0.09 |
| $5s4d\ ^1D_2$ | 20150 | 20222 | -0.36 |
| $5s5p\ ^1P_1$ | 21698 | 21746 | -0.22 |
| $5s6s\ ^3S_1$ | 29039 | 29090 | -0.18 |
| $5s6s\ ^1S_0$ | 30592 | 30656 | -0.21 |
| $\Delta(^3D_1 - ^3P_0)$ | 3842 | 3847 | 0.14 |

systems. The CI method is then used to treat valence-valence correlations.

This approach has been tested on the calculation of energy levels of Mg, Ca, Sr, Zn, Cd, Ba, and Hg in Ref. [21]. The CI+all-order method described above treats electronic correlation in systems with several valence electrons in a significantly more complete way than the CI + MBPT approach owing to the inclusion of the additional classes of MBPT terms in Σ_1 and addition of all-order (rather than second-order) correction in Σ_2 . We also find almost no deterioration in accuracy of the two-electron binding energies from Ca to Hg with CI+all-order method. At least factor of three improvement in agreement with experimental values for the two-electron binding energies and most excited state energies in comparison with the CI + MBPT method was found even when completely *ab initio* version of the method was used. The results are brought to very close agreement with experiment when the energy dependence of $\Sigma(\tilde{\epsilon}_v)$ is used to further improve the wave functions for subsequent use in the polarizability calculations. The results for Sr energy levels calculated by the CI + all-order method with adjusted $\tilde{\epsilon}_v$ are listed in Table VII for illustration of the CI + all-order approach. Two-electron binding energy is given in the first row, the other values are counted from the ground state. The energies are given in cm^{-1} . The relative difference with experimental values is given in the last column in %. Our preliminary calculations of the 3P_0 polarizability values in Ca and Sr indicate better agreement of the CI+all-order *ab initio* results with recommended values from Ref. [24] in comparison with the CI+MBPT approach.

Our further development of this method will include addition of the all-order terms beyond RPA to the treatment of the transition matrix elements for precision calculation of BBR shifts in divalent systems.

TABLE VIII

SUMMARY OF THE FRACTIONAL UNCERTAINTIES $\delta\nu/\nu_0$ DUE TO BBR SHIFT AND THE FRACTIONAL ERROR IN THE ABSOLUTE TRANSITION FREQUENCY INDUCED BY THE BBR SHIFT UNCERTAINTY IN VARIOUS FREQUENCY STANDARDS.

| Atom | Clock transition | Ref. | $\delta\nu/\nu_0$ | Uncertainty |
|---------------------|-----------------------------|------|--------------------------|---------------------|
| ^{87}Rb | $5s\ (F=2 - F=1)$ | [28] | -1.25×10^{-14} | 1×10^{-16} |
| ^{133}Cs | $6s\ (F=4 - F=3)$ | [3] | -1.732×10^{-14} | 6×10^{-17} |
| | | [2] | -1.72×10^{-14} | 2×10^{-16} |
| | | [4] | -1.732×10^{-14} | 3×10^{-17} |
| | | [28] | -2.46×10^{-15} | 2×10^{-17} |
| $^{137}\text{Ba}^+$ | $6s\ (F=2 - F=1)$ | [28] | -2.46×10^{-15} | 2×10^{-17} |
| $^{171}\text{Yb}^+$ | $6s\ (F=1 - F=0)$ | [28] | -9.4×10^{-16} | 5×10^{-17} |
| $^{199}\text{Hg}^+$ | $6s\ (F=1 - F=0)$ | [28] | -1.02×10^{-16} | 5×10^{-18} |
| Ca^+ | $4s - 3d_{5/2}$ | [19] | 9.24×10^{-16} | 2×10^{-17} |
| Sr^+ | $5s - 4d_{5/2}$ | [20] | 5.62×10^{-16} | 2×10^{-17} |
| Mg | $3s^2\ ^1S_0 - 3s3p^3\ P_0$ | [24] | -3.9×10^{-16} | 1×10^{-17} |
| Ca | $4s^2\ ^1S_0 - 4s4p^3\ P_0$ | [24] | -2.6×10^{-15} | 4×10^{-17} |
| Sr | $5s^2\ ^1S_0 - 5s5p^3\ P_0$ | [24] | -5.5×10^{-15} | 7×10^{-17} |
| Yb | $6s^2\ ^1S_0 - 6s6p^3\ P_0$ | [24] | -2.6×10^{-15} | 3×10^{-16} |
| Hg | $6s^2\ ^1S_0 - 6s6p^3\ P_0$ | [42] | -1.6×10^{-16} | |

VI. SUMMARY AND CONCLUSION

In this work, we presented a review of the most recent high-precision *ab initio* theoretical calculations of the black-body radiation (BBR) shifts in various systems of interest to the atomic clock research. New method that combines the relativistic all-order method and the configuration interaction method for accurate calculations of BBR shifts for divalent systems such as Sr is discussed. The high-precision methods used in the recent calculations of the BBR shifts are described. The evaluation of the uncertainties of the BBR shift values is discussed in detail. The results for fractional uncertainties $\delta\nu/\nu_0$ due to BBR shift and the fractional error in the absolute transition frequencies induced by the BBR shift uncertainty in various frequency standards are summarized in Table VIII. As illustrated by Table VIII, the fractional errors in the absolute transition frequency induced by the BBR shift uncertainty are still quite large for most of the optical frequency standards. Both new experiments and improvement in theory accuracy will be needed for further improvement.

ACKNOWLEDGMENT

Part of this research was performed under the sponsorship of the US Department of Commerce, National Institute of Standards and Technology. This work was supported in part by US National Science Foundation Grant No. PHY-07-58088 and by the RFBR grant No. 08-02-00460. MGK thanks University of Delaware for hospitality.

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