Blackbody radiation shift in $^{87}$Rb frequency standard

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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 for the effect of finite temperature of which the leading contributor is the blackbody radiation (BBR) shift. Experimental measurements of the BBR shifts are difficult. In this work, we have calculated the blackbody radiation shift of the ground-state hyperfine microwave transition in $^{87}$Rb using the relativistic all-order method and carried out detailed evaluation of the accuracy of our final value. Particular care is taken to accurately account for the contributions from highly-excited states. Our predicted value for the Stark coefficient, \( k_S = -1.240(4) \times 10^{-16} \text{Hz}/(\text{V/m})^2 \) is three times more accurate than the previous calculation \[1\].

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I. INTRODUCTION

The present definition of the 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 $^{133}$Cs ground state and refers to the clock transition in an atom at absolute zero. The relative standard uncertainty of the Cs microwave frequency standard is $4 \times 10^{-16}$ \[2\] at the present time. In 2006, the International Committee for Weights and Measures (CIPM) recommended \[3\] that the ground-state hyperfine microwave transition in $^{87}$Rb \[4, 5\] be used as secondary representation of the second, along with four optical transition frequencies.

The operation of atomic clocks is generally carried out at room temperature implying that the clock transition frequency should be corrected for effects of finite temperature, of which the leading contributor is the blackbody radiation (BBR) shift. The BBR shift at room temperature effecting the Cs microwave frequency standard has been calculated to high accuracy (0.35\% and 1\%, respectively) in Refs. \[4, 7\] implying a $6 \times 10^{-17}$ fractional uncertainty. These calculations are in agreement with a 0.2\% measurement \[8\].

The BBR shift contributes to Rb frequency standard at $10^{-14}$ level (see \[9\] for the review of the present status of BBR shift uncertainties for all atomic clocks). The most recent value of the BBR shift in Rb microwave frequency standard is accurate to 1\% \[1\]. As a result, ultimate relative uncertainty induced by the BBR shift in $^{87}$Rb frequency standard was significantly larger than that of the $^{133}$Cs frequency standard. We note that we refer to uncertainty of the scalar Stark coefficient. Actual experimental uncertainty will also include error due to temperature stabilization. The calculation of Ref. \[1\] also disagreed with the old 1975 theoretical calculation of Ref. \[10\] by 2.5\%. As a result, more accurate calculation of Rb BBR shift is in order.

In this work, we calculated the blackbody radiation shift of the ground-state hyperfine microwave transition in $^{87}$Rb using the relativistic all-order method and evaluated the accuracy of our final value. Our predicted value of the scalar Stark coefficient, \( k_S = -1.240(4) \times 10^{-16} \text{Hz}/(\text{V/m})^2 \) is accurate to 0.3\%. Our calculation reduced the uncertainty in Rb frequency standard due to BBR shift to the level of accuracy similar to that of the Cs case.

Another motivation for the present work was to provide a systematic approach to evaluation of theoretical uncertainty using the calculation of BBR shift in Rb as an example. Modern applications of theoretical atomic calculations frequently require some knowledge of the accuracy of theoretical numbers. With new advances in theoretical methods and in computational power, it is essential to develop consistent strategies to evaluate the accuracy of theoretical data. Such evaluations are difficult but very beneficial both to specific applications and benchmark comparisons of theory and experiment. In this work, we described the evaluation of uncertainties of the electric-dipole matrix elements, hyperfine matrix elements, and remainders of various sums in sufficient detail.

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was found to be small, $\varepsilon$ polarizability electrical field can be related to the static electric-dipole moment. In the case of the ground-state hyperfine microwave frequency standard. Therefore, we do not recalculate it in this work.

II. METHOD

The electrical field $E$ radiated by a blackbody at temperature $T$ and described by Planck’s law induces a non-resonant perturbation of atomic transitions at room temperature $[11]$. The average electric field radiated by a blackbody at temperature $T$ is

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

(1)

The frequency shift of an atomic state due to such an electrical field can be related to the static electric-dipole polarizability $\alpha(0)$ by $[12]$

$$\delta \nu = -\frac{1}{2} (831.9 \text{ V/m})^2 \left(\frac{T}{T_0}\right)^4 \alpha(0) \left(1 + \varepsilon \left(\frac{T}{T_0}\right)^2\right),$$  

(2)

where $\varepsilon$ is a small dynamic correction due to the frequency distribution, and $T_0$ is usually taken to be 300 K. The dynamic correction $\varepsilon$ was evaluated in Ref. $[11]$ and was found to be small, $\varepsilon = 0.011$, for Rb microwave frequency standard. Therefore, we do not recalculate it in this work.

In the case of the optical transitions, the lowest (second) order polarizabilities of the clock states are identical and the lowest-order BBR shift vanishes. Therefore, the Stark shift of the ground state $^{87}$Rb hyperfine interval $(F = 2 - F' = 1)$ is governed by the static third-order $F$-dependent polarizability $\alpha_F^{(3)}(0)$.

In this work, we evaluate the scalar Stark coefficient $k_S$,

$$k_S = -\frac{1}{2} (\alpha_F^{(3)}(0) - \alpha_F^{(3)}(1)).$$  

(3)

The expression for the $\alpha_F^{(3)}(0)$ is given by $[12]$:

$$\alpha_F^{(3)}(0) = \frac{1}{3} \sqrt{(2I)(2I+1)(2I+2)} \left\{ j_v \begin{pmatrix} 1 & 1 \\ F & 1 \end{pmatrix} x \right\} g_I \mu_n (-1)^{F+1+j_v} (2T + C + R),$$  

(4)

where $g_I$ is the nuclear gyromagnetic ratio, $\mu_n$ is the nuclear magneton, $I = 3/2$ is the nuclear spin, and $j_v = 1/2$ is the total angular momentum of the atomic ground state. The $F$-independent sums $T$, $C$, and $R$ for the ground state of Rb, $|v\rangle \equiv |5s\rangle$, are given by $[12]$:

$$T = \sum_{m,n \neq 5s} A_T \frac{\langle 5s||D||m\rangle\langle m||D||n\rangle\langle n||T^{(1)}||5s\rangle}{(E_m - E_{5s})(E_n - E_{5s})},$$  

(5)

$$C = \sum_{m,n \neq 5s} A_C \frac{\langle 5s||D||m\rangle\langle m||T^{(1)}||n\rangle\langle n||D||5s\rangle}{(E_m - E_{5s})(E_n - E_{5s})},$$  

$$R = \frac{1}{2} \langle 5s||T^{(1)}||5s\rangle \left(\sum_{m \in \text{val}} - \sum_{m \in \text{core}}\right) \frac{|\langle 5s||D||n\rangle|^2}{(E_m - E_{5s})^2}.$$  

(6)
where \( \langle i | D | j \rangle \) are electric-dipole reduced matrix elements and \( \langle i | T^{(1)} | j \rangle \) are the matrix elements of the magnetic hyperfine operator \( T^{(1)} \). The quantities \( A_T \) and \( A_C \) are the angular coefficients given in our case by

\[
A_T = \frac{(-1)^{j_{m+1/2}}}{2}
\]

\[
A_C = (-1)^{j_m-j_n} \left\{ \begin{array}{c}
1/2 \\
1/2 \\
1/2
\end{array} \right\}
\]

The sums are made finite with the use of finite B-spline basis set in a spherical cavity. The sum over the complete finite basis set is equivalent to the sum over the bound states and integration over the continuum. We use a complete set of DHF wave functions on a nonlinear grid generated using B-splines constrained to a spherical cavity. A cavity radius of 220 \( a_0 \) is chosen to accommodate all \( ns \) and \( np \) valence orbitals up to \( n = 12 \). The basis set consists of 70 splines of order 11 for each value of the relativistic angular quantum number \( \kappa \).

Sums over \( m \) and \( n \) run over all possible states allowed by the selection rules and limits of the sums. Therefore, three distinct sets of matrix elements are needed for the present calculations: electric-dipole matrix elements between \( ns \) and \( mp \) states, \( \langle mp || D || ns \rangle \), and diagonal and off-diagonal matrix elements of the magnetic hyperfine operator for both \( ns \) and \( np \) states: \( \langle ns || T^{(1)} || 5s \rangle \), \( \langle mp || T^{(1)} || np \rangle \). Therefore, the calculation of the BBR shift reduces to the evaluation of the electric-dipole and magnetic hyperfine matrix elements.

In this work, we use atomic units, in which, \( c, m_e, 4\pi\epsilon_0 \) and the reduced Planck constant \( \hbar \) have the numerical value 1. Polarizability in a.u. has the dimension of \( \alpha \) in the units of \( a_0^{-3} \), where \( a_0 \approx 0.052918 \) nm is the Bohr radius. The atomic units for \( \alpha \) can be converted to SI units via \( \alpha/[Hz/(V/m)^2] = 2.48832 \times 10^{-8} \alpha_{[a.u.]} \), where the conversion coefficient is \( 4\pi\epsilon_0\alpha_0^3/\hbar \) and Planck constant \( \hbar \) is factored out.

We start our calculation by evaluating all three terms in Dirac-Hartree-Fock (DHF) approximation. The resulting DHF values for the \( T, C, \) and \( R \) terms in atomic units are

\[
2T_{DHF} = 2.376 \times 10^{-3}, \quad C_{DHF} = 6.111 \times 10^{-6}, \quad R_{DHF} = 3.199 \times 10^{-3}
\]

Then, we replace all dominant matrix elements by the “best set” values that have been evaluated for their accuracy and replace corresponding energies by their experimental values [13, 14]. We refer to the terms where such replacements have been made as “main” terms, and refer to the remaining terms calculated in the DHF approximation as remainders.

We note that it is essential not to mix DHF and high-precision data within a single contribution. For example, experimental energies should not be combined with DHF matrix elements in any of the terms. In the present calculations, all data in main terms are high-precision theory or experiment values and all data in the remainders and in core terms are taken to be DHF values. Mixing values of significantly different accuracy leads to fictitious changes in the final results, in particularly in Term T. We carried out numerical tests that support this statement, and we attribute this issue to the violation of the finite basis set completeness.

We note that while we use the experimental values of the energies in the main terms, the accuracy of our all-order theoretical energy values is very high. We made extensive comparison of removal energies calculated using the SD all-order method and experimental values [13, 14] for the \( (5 - 11)s, (5 - 10)p_j, (4 - 10)d_j, \) and \( (4 - 7)f_j \)
TABLE III: Absolute values of the electric-dipole reduced matrix elements used in the calculation of the BBR shift and their uncertainties in atomic units ($e\alpha_0^2$).

| Transition | $n = 5$ | $n = 6$ | $n = 7$ | $n = 8$ | $n = 9$ | $n = 10$ | $n = 11$ |
|------------|---------|---------|---------|---------|---------|---------|---------|
| $5s - np_{1/2}$ | 4.231(3) | 0.325(9) | 0.115(3) | 0.060(2) | 0.037(1) | 0.026(1) | 0.020(1) |
| $6s - np_{1/2}$ | 4.146(27) | 9.75(6) | 0.993(7) | 0.388(5) | 0.222(3) | 0.148(2) | 0.109(2) |
| $7s - np_{1/2}$ | 0.953(2) | 9.21(2) | 16.93(9) | 1.856(9) | 0.751(8) | 0.430(6) | 0.289(4) |
| $8s - np_{1/2}$ | 0.502(2) | 1.862(8) | 16.00(2) | 25.9(2) | 2.95(2) | 1.20(1) | 0.69(1) |
| $9s - np_{1/2}$ | 0.331(1) | 0.936(5) | 3.00(2) | 24.5(1) | 36.7(2) | 4.25(2) | 1.73(2) |
| $10s - np_{1/2}$ | 0.243(1) | 0.607(3) | 1.474(7) | 4.40(2) | 34.8(2) | 49.4(2) | 5.78(3) |
| $11s - np_{1/2}$ | 0.189(1) | 0.442(2) | 0.942(5) | 2.12(1) | 6.05(3) | 46.8(2) | 63.9(3) |
| $5s - np_{3/2}$ | 5.978(5) | 0.528(13) | 0.202(4) | 0.111(3) | 0.073(2) | 0.053(2) | 0.040(2) |
| $6s - np_{3/2}$ | 6.047(34) | 13.68(9) | 1.53(1) | 0.621(7) | 0.363(5) | 0.246(4) | 0.182(3) |
| $7s - np_{3/2}$ | 1.350(2) | 13.38(2) | 23.7(1) | 2.82(2) | 11.1(1) | 0.68(1) | 0.405(7) |
| $8s - np_{3/2}$ | 0.708(2) | 2.61(1) | 23.19(2) | 36.3(2) | 44.5(2) | 1.85(2) | 1.08(2) |
| $9s - np_{3/2}$ | 0.466(2) | 1.306(7) | 4.19(2) | 35.5(2) | 51.2(3) | 6.39(3) | 2.66(3) |
| $10s - np_{3/2}$ | 0.341(1) | 0.845(4) | 2.04(1) | 6.13(3) | 50.3(3) | 68.9(3) | 8.65(4) |
| $11s - np_{3/2}$ | 0.266(1) | 0.614(3) | 1.302(7) | 2.92(2) | 8.40(4) | 67.7(3) | 89.2(4) |

states. Additional first and second-order Breit contributions, Lamb shift, and third-order Coulomb correlation correction not accounted for by the SD approximations were also included into the calculation. Our values agree to better than 10 cm$^{-1}$ for all levels with exception of the 5s, 6s, 7s, 4d$_{3/2}$, and 4d$_{5/2}$ levels, where the differences are 27, 25, 12, 32, and 29 cm$^{-1}$, respectively. We note that the ground state energy is -33691 cm$^{-1}$, making the agreement better than 0.1%.

III. "BEST SET" MATRIX ELEMENTS AND THEIR UNCERTAINTIES

The "best set" consists of our all-order high-precision results and several experimental values. The following 128 matrix elements have been replaced by the all-order or experimental values:

- $\langle mp_j | D | ns \rangle$, $m = 5 - 12$, $n = 5 - 12$;
- $\langle ns | T^{(1)} | 5s \rangle$, $n = 5 - 12$;
- $\langle mp_j | T^{(1)} | np_{1/2} \rangle$, $m = 5 - 7$, $n = 5 - 7$.

The all-order calculation of Rb matrix elements has been described in detail in Ref. [13].

We illustrate the selection of the “best set” values of the electric-dipole matrix elements and determination of their uncertainties in Table III where we list a few examples. The complete table is given in Ref. [16]. The absolute values in atomic units ($e\alpha_0^2$) are given in all cases. We list the lowest-order DHF results, all-order SD values, and their relative differences in percent in columns 2-4 of Table III. The relative differences of DHF and single-double (SD) all-order numbers give a good estimate of the size of the correlation correction. In general, the smaller the correlation correction, the more precise our theoretical values are. The final values used in our “best set” are listed in column 5. The next column identifies the source of these values for each of the matrix elements. The $5s - 5p_j$ matrix elements are experimental values from [17]. All other E1 matrix elements are from all-order calculation that included SD, SDpT, or SD$_{ac}$ values. The SD$_{ac}$ values include additional corrections added to SD $ab\ initial$ results by means of the scaling procedure described in Ref. [18] and references therein. The SDpT label refers to $ab\ initial$ all-order calculations that include single, double, and partial triple excitations. The selection of the particular value as final is determined by the study of the dominant correlation correction terms (because the scaling procedure is only applicable for certain classes of terms) and accuracy requirements. In the present calculation, very high accuracy is not needed for matrix elements with high values of principal quantum numbers. In such cases, SD values are sufficiently accurate for E1 matrix elements.

Evaluation of theoretical uncertainties is a very difficult problem since it essentially involves evaluation of the quantity that is not known beforehand. Several strategies can be used in evaluating the uncertainties of the all-order results, including the study of the breakdown of the various all-order contributions, identification of the most important terms, and semi-empirical determination of important missing contributions. Our uncertainty estimates are listed in percent in column labeled “Unc.”. The method for determining uncertainty is noted in the next column labeled “Unc. source”. Where the scaling was performed, it is expected to estimate the dominant missing correlation correction (see Ref. [18] and references therein for explanation). Therefore, it is reasonable to take the difference of the $ab\ initial$ and scaled results as the uncertainty. This is indicated by SDsc-SD note in the “Unc. source” column. We note that this procedure is expected to somewhat overestimate the uncertainty.

In some cases, where such high accuracy was not required but the same correlation terms were dominant, we carried out $ab\ initial$ SDpT calculation (i.e. partially included triples) instead and took these values as final.
The uncertainties were estimated at the stages of the SD and SDpT numbers in those cases. We note that numerous tests were conducted in the past that demonstrated that the above-mentioned procedures of the uncertainty estimates are valid (see Ref. [18] for review of the all-order method and its applications). In the cases of transitions with high values of the principal quantum numbers (for example, np − 10s transitions) where only rough estimates of uncertainties were needed, we used uncertainty estimate from the previous transition. For example, we use 0.5% as uncertainty estimate for the 6p_j − 9s transitions since the uncertainty for the 6p_j − 8s ones was 0.5%. Since relative correction correlation generally decreases with n, such procedure can overestimate the uncertainty, but should not underestimate it. The final results and their uncertainties are summarized in the last columns of Table III.

The best set values for the electric-dipole matrix elements and their uncertainties are summarized in Table III.

Selection of the “best set” values for diagonal and off-diagonal matrix elements of the magnetic hyperfine operator T(1) in 10^{-8} a.u. is illustrated in Table III. The complete table is given in Ref. [16]. To convert the diagonal matrix element in atomic units to hyperfine constants in MHz, one multiplies the values in Table III by

\[ 6.5797 \times 10^9 g_i \sqrt{j_i (j_i + 1)(2j_i + 1)}, \]

where the nuclear gyromagnetic ratio \( g_i = 1.83416 \) for \(^{87}\)Rb and \( j_i \) is total angular momentum of the electronic state. Triple corrections are large for hyperfine matrix elements and have to be included. Scaling procedure can not be applied here since the terms that it corrects are generally not dominant unlike the cases of the \( ns - n'p \) matrix elements above. The remaining columns in Table III are the same as in the E1 matrix element tables.

Most of the diagonal hyperfine matrix elements are taken from the experiment. Experimental uncertainties are listed where experimental data are used. Off-diagonal hyperfine matrix elements between the \( s \)-states \( \langle ns|T^{(1)}|n's\rangle \) can be also evaluated from experimental hyperfine constants using the formula

\[ \langle ns|T^{(1)}|n's\rangle = \sqrt{\langle ns|T^{(1)}|ns\rangle \langle n's|T^{(1)}|n's\rangle}, \]

that is useful for the cases where accurate values of the hyperfine constants \( A \) are available. We list such values for the off-diagonal matrix elements as experimental. Since a large number of high-precision experimental values is available for matrix elements in Table III the remaining uncertainties for off-diagonal matrix elements are assigned based on the differences of the theory values for the most relevant diagonal matrix elements with experiment. For example, the entry “from 5p1/2” in the “Unc. source” column indicates that the difference of the theoretical 5p1/2 hyperfine constant with the experimental value was used to assign the uncertainty of the

| Matrix element Value | Matrix element Value |
|----------------------|----------------------|
| 5s − 5s | 34.681 | 5p1/2 − 5p1/2 | 4.122(8) |
| 5s − 6s | 16.861 | 5p1/2 − 5p3/2 | 0.327(3) |
| 5s − 7s | 10.609(2) | 5p1/2 − 6p1/2 | 2.36(1) |
| 5s − 8s | 7.479(7) | 5p1/2 − 6p3/2 | 0.189(2) |
| 5s − 9s | 5.64(2) | 5p1/2 − 7p1/2 | 1.59(1) |
| 5s − 10s | 4.45(1) | 5p1/2 − 7p3/2 | 0.127(1) |
| 5s − 11s | 3.63(1) | | |

TABLE IV: Absolute values of the diagonal and off-diagonal matrix elements of the magnetic hyperfine operator \( T^{(1)} \) in 10^{-8} a.u. See text for conversion of diagonal matrix elements in atomic units to hyperfine constants in MHz.

| n | DHF | Final | Dif. |
|---|-----|-------|------|
| 6 | 0.0016114 | 0.0015159(83) | -6.3% |
| 7 | 0.0002277 | 0.0002156(18) | -5.6% |
| 8 | 0.0000787 | 0.0000756(7) | -4.1% |
| 9 | 0.0000378 | 0.0000365(5) | -3.7% |
| 10 | 0.0000217 | 0.0000209(4) | -3.7% |
| 11 | 0.0000141 | 0.0000135(4) | -3.9% |
| 12 | 0.0000104 | 0.0000099(4) | -5.0% |

TABLE V: Comparison of the DHF values for the main contributions (\( \sum_{m=0}^{12} \)) to term T with the final “best set” values. \( n \) refers to terms of the \( ns \) sum. The relative difference between the two values is given in the last column.

IV. BBR SHIFT UNCERTAINTY

The total uncertainty of the main terms of the static Stark coefficient \( k_s \) is very small, and approximate estimate of uncertainties is sufficient.

The best set values for the hyperfine matrix elements and their uncertainties are summarized in Table IV.

off-diagonal matrix element. We note that contributions of the \( np - np' \) matrix elements to total uncertainty of the static Stark coefficient \( k_s \) is very small, and approximate estimate of uncertainties is sufficient.
There is no 5s term according to Eq. (5). For 6s, 7s, and 8s terms, the \( m > 12 \) tail accounts for only 0.05\%, 0.3\%, and 0.9\%, respectively. As expected, the relative tail contribution increases with \( n \) since the contributions from higher \( m \) states become relatively more important. However, the contribution of the \( mp_j \) tail is so small for the most important terms that its uncertainty is negligible. The sum over \( ns \) converges much slower, with \( n > 12 \) terms contributing 17\%. Therefore, we had to evaluate the accuracy of the DHF approximation for the term \( T \). To do so, we used DHF approximation for main \( ns \) terms, and compared the results with our final “best set” values.

The comparison is illustrated in Table VI. The columns 2 and 3 contain main \( T \) terms given by Eq. (5) for each \( ns \), \( n = 6 - 12 \):

\[
\sum_{m=5}^{12} A_{m} \frac{\langle 5s\|D\|mp_j\rangle\langle mp_j\|D\|ns\rangle\langle ns\|T^{(1)}\|5s\rangle}{(E_{mp_j} - E_{5s})(E_{ns} - E_{5s})}. \tag{7}
\]

Column 4 gives the relative differences between DHF and final results. We expect slightly larger differences for \( n = 6 \) and \( n = 7 \) owing to larger relative correlation corrections for lower \( n \). Then, the ratio is stable and on the order of 4\%. Slightly larger ratio for \( n = 12 \) is due to cavity size, i.e. \( n = 12 \) basis set orbitals already slightly differ from true DHF orbitals. We conclude that the accuracy of the DHF approximation for term \( T \) is very high, about 4\%. Therefore, we adjusted DHF tail for the term \( T \) by 4\%. We took 100\% of the adjustment to be the uncertainty of the term \( T \) remainder.

The DHF value for term \( C \) is three orders of magnitude smaller than other terms. However, it is necessary to evaluate this term accurately as its final contribution to the total is 0.5\%. Term \( C \) also contains two sums, but terms with \( m, n = 5 - 7 \) account for 97\% of the total making the uncertainty in the remainder negligible. In fact, \( \{m, n\} = 5 \) term contributes 89\%. The interesting feature of term \( C \) is a very strong cancellations between individual contributions leading to change of sign between DHF and final values. We list DHF and “best set” values for individual contributions to term \( C \) in Table VI to illustrate this cancellation. The terms with \( m \leftrightarrow n \) are the same and are added together.

Term \( R \) is essentially defined by the \( n = 5 \) term, that contributes 99.8\% of the total. Therefore, its uncertainty is dominated by the experimental uncertainty of the \( 5s - 5p_j \) matrix elements [15]. The contribution of the remainder and its uncertainty is negligible.

The resulting final values for the \( T, C, \) and \( R \) terms in atomic units are

\[
2T = 2.247(17) \times 10^{-3}, \quad C = -2.385(20) \times 10^{-5}, \quad R = 2.769(2) \times 10^{-3}.
\]

We substitute these values into the Eqs. (3,4) and multiply the total by \( 2.48832 \times 10^{-8} \) conversion factor (see paragraph on atomic units above) to obtain our predicted value of the Stark coefficient, \( k_S = \frac{-1.240(4) \times 10^{-10}}{2} \text{ Hz/(V/m)}^2 \). It is in agreement with the value \( -1.24 \times 10^{-10} \text{ Hz/(V/m)}^2 \) of Ref. [1] that was estimated to be accurate to 1\%. It is also in agreement with measurement \( k_S = -1.23(3) \times 10^{-10} \text{ Hz/(V/m)}^2 \) by Mowat [13].

We use our value of the scalar Stark shift coefficient to calculate the quantity \( \beta \) defined as

\[
\beta = \frac{k_S}{\nu_0} (831.9 \text{ V/m})^2. \tag{8}
\]

to be \( -1.256(4) \times 10^{-14} \).

V. CONCLUSION

We calculated the scalar Stark coefficient \( k_S \) for the \(^{87}\text{Rb} \) microwave frequency standard and carried out detailed evaluation of the uncertainties of all its contributions. Our calculation reduced ultimate limit to the uncertainty of \(^{87}\text{Rb} \) frequency standard due to BBR shift to \( 4 \times 10^{-17} \).

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