

Blackbody radiation shifts and magic wavelengths for atomic clock research

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Abstract—We developed a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with few valence electrons. Preliminary results for systems of interest to atomic clock development are reported. We also 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. The uncertainty estimate is discussed in detail.

I. INTRODUCTION

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. Experimental measurements of the BBR shifts are difficult.

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, $k_s = -1.240(4) \times 10^{-10} \text{ Hz}/(\text{V/m})^2$ is three times more accurate than the previous calculation.

We have developed a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with few valence electrons [1]. This method combines the all-order approach currently used in precision calculations of properties of monovalent atoms with the configuration-interaction approach that is applicable for many-electron systems. In the present work, we have extended CI+all-order method to the calculation of the transition properties and polarizabilities of divalent systems. Preliminary results are reported.

II. BBR SHIFT IN ^{87}Rb FREQUENCY STANDARD

The electrical field E radiated by a blackbody at temperature T and described by Planck's law induces a nonresonant perturbation of atomic transitions at room temperature [2]. The average electric field radiated by a blackbody at temperature T is

$$\langle E^2 \rangle = (831.9 \text{ V/m})^2 \left(\frac{T(K)}{300} \right)^4. \quad (1)$$

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. [3])

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

where ϵ is a small dynamic correction due to the frequency distribution.

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 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 third-order F -dependent polarizability $\alpha_F^{(3)}(0)$.

In this work, we evaluate the scalar Stark coefficient k_s ,

$$k_s = -\frac{1}{2} \left(\alpha_{F=2}^{(3)}(0) - \alpha_{F=1}^{(3)}(0) \right). \quad (3)$$

The dynamic correction ϵ (see Eq. 2) was evaluated in Ref. [4] and was found to be small, $\epsilon = 0.011$, for Rb. Therefore, we do not re-evaluate it in this work.

The expression for the $\alpha_F^{(3)}(0)$ is [5]:

$$\alpha_F^{(3)}(0) = \frac{1}{3} \sqrt{(2I)(2I+1)(2I+2)} \left\{ \begin{array}{ccc} j_v & I & F \\ I & j_v & 1 \end{array} \right\} \times g_I \mu_n (-1)^{F+I+j_v} (2T + C + R), \quad (4)$$

where g_I is the nuclear gyromagnetic ratio, μ_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 [5]:

$$\begin{aligned} T &= \sum_{\{m,n\} \neq 5s} A_T \frac{\langle 5s || D || m \rangle \langle m || D || n \rangle \langle n || T^{(1)} || 5s \rangle}{(E_m - E_{5s})(E_n - E_{5s})}, \quad (5) \\ C &= \sum_{\{m,n\} \neq 5s} A_C \frac{\langle 5s || D || m \rangle \langle m || T^{(1)} || n \rangle \langle n || D || 5s \rangle}{(E_m - E_{5s})(E_n - E_{5s})}, \\ R &= \frac{1}{2} \langle 5s || T^{(1)} || 5s \rangle \left(\sum_{m \in \text{val}} - \sum_{m \in \text{core}} \right) \frac{|\langle 5s || D || m \rangle|^2}{(E_m - E_{5s})^2}, \end{aligned}$$

TABLE I

SELECTION OF THE “BEST SET” VALUES FOR THE $5p_j - ns$, $6p_j - ns$, AND $7p_j - ns$ ELECTRIC-DIPOLE REDUCED MATRIX ELEMENTS. SEE TEXT FOR DETAILS. ABSOLUTE VALUES OF THE LOWEST ORDER DHF AND SD ALL-ORDER VALUES IN A.U. AND THEIR RELATIVE DIFFERENCE IN % ARE GIVEN IN COLUMNS 2-4.

Transition	DHF	SD	$\Delta(\text{SD-DHF})$	Final	Source	Unc. (%)	Unc. source	“Best set”
$5p_{1/2} - 5s$	4.8189	4.2199	14.2%	4.2310	Expt	0.07%	Expt.	4.231(3)
$5p_{1/2} - 6s$	4.2564	4.1187	3.3%	4.1458	SDsc	0.66%	SDsc-SD	4.146(27)
$5p_{1/2} - 7s$	0.9809	0.9543	2.8%	0.9527	SDsc	0.17%	SDsc-SD	0.953(2)
$5p_{1/2} - 8s$	0.5139	0.5037	2.0%	0.5022	SDsc	0.30%	SDsc-SD	0.502(2)
$5p_{1/2} - 9s$	0.3380	0.3326	1.6%	0.3314	SDsc	0.36%	SDsc-SD	0.331(1)
$5p_{1/2} - 10s$	0.2472	0.2438	1.4%	0.2429	SDsc	0.38%	SDsc-SD	0.243(1)
$5p_{1/2} - 11s$	0.1924	0.1899	1.3%	0.1892	SDsc	0.40%	SDsc-SD	0.189(1)
$5p_{1/2} - 12s$	0.1562	0.1543	1.3%	0.1537	SDsc*	0.40%	0.4%	0.154(1)
$5p_{3/2} - 5s$	6.8017	5.9551	14.2%	5.9780	Expt	0.08%	Expt	5.978(5)
$5p_{3/2} - 6s$	6.1865	6.0135	2.9%	6.0472	SDsc	0.56%	SDsc-SD	6.047(34)
$5p_{3/2} - 7s$	1.3925	1.3521	3.0%	1.3497	SDsc	0.18%	SDsc-SD	1.350(2)
$5p_{3/2} - 8s$	0.7265	0.7098	2.4%	0.7077	SDsc	0.29%	SDsc-SD	0.708(2)
$5p_{3/2} - 9s$	0.4771	0.4677	2.0%	0.4662	SDsc	0.34%	SDsc-SD	0.466(20)
$5p_{3/2} - 10s$	0.3487	0.3425	1.8%	0.3413	SDsc	0.36%	SDsc-SD	0.341(1)
$5p_{3/2} - 11s$	0.2712	0.2667	1.7%	0.2656	SDsc*	0.40%	0.4%	0.266(1)
$5p_{3/2} - 12s$	0.2202	0.2165	1.7%	0.2156	SDsc*	0.40%	0.4%	0.216(1)
$6p_{1/2} - 5s$	0.3825	0.3335	14.7%	0.3248	SDsc	2.69%	SDsc-SD	0.325(9)
$6p_{1/2} - 6s$	10.2856	9.6839	6.2%	9.7450	SDpT	0.63%	SD-SDpT	9.745(61)
$6p_{1/2} - 7s$	9.3594	9.1896	1.8%	9.2092	SDpT	0.21%	SD-SDpT	9.209(20)
$6p_{1/2} - 8s$	1.9219	1.8532	3.7%	1.8616	SDpT	0.45%	SD-SDpT	1.862(8)
$6p_{1/2} - 9s$	0.9702	0.9364	3.6%	0.9364	SD	0.50%	0.5%	0.936(5)
$6p_{1/2} - 10s$	0.6281	0.6071	3.5%	0.6071	SD	0.50%	0.5%	0.607(3)
$6p_{1/2} - 11s$	0.4563	0.4416	3.3%	0.4416	SD	0.50%	0.5%	0.442(2)
$6p_{1/2} - 12s$	0.3550	0.3436	3.3%	0.3436	SD	0.50%	0.5%	0.344(2)
$6p_{3/2} - 5s$	0.6055	0.5409	11.9%	0.5276	SDsc	2.51%	SDsc-SD	0.528(13)
$6p_{3/2} - 6s$	14.4575	13.5918	6.4%	13.6804	SDpT	0.65%	SD-SDpT	13.680(89)
$6p_{3/2} - 7s$	13.5514	13.3529	1.5%	13.3755	SDpT	0.17%	SD-SDpT	13.376(23)
$6p_{3/2} - 8s$	2.7047	2.6001	4.0%	2.6129	SDpT	0.49%	SD-SDpT	2.613(13)
$6p_{3/2} - 9s$	1.3583	1.3056	4.0%	1.3056	SD	0.50%	0.5%	1.306(7)
$6p_{3/2} - 10s$	0.8776	0.8446	3.9%	0.8446	SD	0.50%	0.5%	0.845(4)
$6p_{3/2} - 11s$	0.6370	0.6135	3.8%	0.6135	SD	0.50%	0.5%	0.614(3)
$6p_{3/2} - 12s$	0.4952	0.4770	3.8%	0.4770	SD	0.50%	0.5%	0.477(2)
$7p_{1/2} - 5s$	0.1418	0.1150	23.3%	0.1150	SD	2.32%	SD-SDpT	0.115(3)
$7p_{1/2} - 6s$	0.9763	0.9996	2.3%	0.9931	SDpT	-0.66%	SD-SDpT	0.993(7)
$7p_{1/2} - 7s$	17.6123	16.8435	4.6%	16.9282	SDpT	0.50%	SD-SDpT	16.928(85)
$7p_{1/2} - 8s$	16.1513	15.9838	1.0%	16.0016	SDpT	0.11%	SD-SDpT	16.002(18)
$7p_{1/2} - 9s$	3.1130	3.0018	3.7%	3.0018	SD	0.50%	0.5%	3.002(15)
$7p_{1/2} - 10s$	1.5317	1.4738	3.9%	1.4738	SD	0.50%	0.5%	1.474(7)
$7p_{1/2} - 11s$	0.9787	0.9418	3.9%	0.9418	SD	0.50%	0.5%	0.942(5)
$7p_{1/2} - 12s$	0.7076	0.6808	3.9%	0.6808	SD	0.50%	0.5%	0.681(3)
$7p_{3/2} - 5s$	0.2373	0.2024	17.2%	0.2024	SD	2.07%	SD-SDpT	0.202(4)
$7p_{3/2} - 6s$	1.4975	1.5399	2.8%	1.5297	SDpT	0.67%	SD-SDpT	1.530(10)
$7p_{3/2} - 7s$	24.7076	23.5865	4.8%	23.7106	SDpT	0.52%	SD-SDpT	23.71(12)
$7p_{3/2} - 8s$	23.3428	23.1723	0.7%	23.1893	SDpT	0.07%	SD-SDpT	23.189(17)
$7p_{3/2} - 9s$	4.3619	4.1902	4.1%	4.1902	SD	0.50%	0.5%	4.190(21)
$7p_{3/2} - 10s$	2.1337	2.0430	4.4%	2.0430	SD	0.50%	0.5%	2.043(10)
$7p_{3/2} - 11s$	1.3602	1.3020	4.5%	1.3020	SD	0.50%	0.5%	1.302(7)
$7p_{3/2} - 12s$	0.9824	0.9399	4.5%	0.9399	SD	0.50%	0.5%	0.940(5)

TABLE II

SELECTION OF THE “BEST SET” VALUES FOR THE $8p_j - ns$, $9p_j - ns$, AND $10p_j - ns$ ELECTRIC-DIPOLE REDUCED MATRIX ELEMENTS.

Transition	DHF	SD	$\Delta(\text{SD-DHF})$	Final	Source	Unc. (%)	Unc. source	“Best set”
$8p_{1/2} - 5s$	0.0783	0.0596	31.5%	0.0596	SD	3.30%	SD-SDpT	0.060(2)
$8p_{1/2} - 6s$	0.3745	0.3927	4.6%	0.3880	SDpT	1.22%	SD-SDpT	0.388(5)
$8p_{1/2} - 7s$	1.8006	1.8653	3.5%	1.8560	SDpT	0.50%	SD-SDpT	1.856(9)
$8p_{1/2} - 8s$	26.8165	25.8296	3.8%	25.9417	SDpT	0.43%	SD-SDpT	25.94(11)
$8p_{1/2} - 9s$	24.6543	24.5174	0.6%	24.5174	SD	0.50%	0.5%	24.52(12)
$8p_{1/2} - 10s$	4.5584	4.4017	3.6%	4.4017	SD	0.50%	0.5%	4.402(22)
$8p_{1/2} - 11s$	2.1997	2.1160	4.0%	2.1160	SD	0.50%	0.5%	2.116(11)
$8p_{1/2} - 12s$	1.3929	1.3381	4.1%	1.3381	SD	0.50%	0.5%	1.338(7)
$8p_{3/2} - 5s$	0.1355	0.1110	22.0%	0.1110	SD	2.68%	SD-SDpT	0.111(3)
$8p_{3/2} - 6s$	0.5963	0.6286	5.1%	0.6212	SDpT	1.18%	SD-SDpT	0.621(7)
$8p_{3/2} - 7s$	2.7269	2.8330	3.7%	2.8183	SDpT	0.52%	SD-SDpT	2.818(15)
$8p_{3/2} - 8s$	37.5758	36.1213	4.0%	36.2874	SDpT	0.46%	SD-SDpT	36.29(17)
$8p_{3/2} - 9s$	35.5931	35.4959	0.3%	35.4959	SD	0.50%	0.5%	35.50(18)
$8p_{3/2} - 10s$	6.3702	6.1248	4.0%	6.1248	SD	0.50%	0.5%	6.125(31)
$8p_{3/2} - 11s$	3.0547	2.9223	4.5%	2.9223	SD	0.50%	0.5%	2.922(15)
$8p_{3/2} - 12s$	1.9296	1.8426	4.7%	1.8426	SD	0.50%	0.5%	1.843(9)
$9p_{1/2} - 5s$	0.0517	0.0374	38.2%	0.0374	SD	3.00%	3%	0.037(1)
$9p_{1/2} - 6s$	0.2093	0.2219	5.7%	0.2219	SD	1.50%	1.5%	0.222(3)
$9p_{1/2} - 7s$	0.7050	0.7509	6.1%	0.7509	SD	1.00%	1%	0.751(8)
$9p_{1/2} - 8s$	2.8443	2.9492	3.6%	2.9492	SD	0.50%	0.5%	2.949(15)
$9p_{1/2} - 9s$	37.9027	36.6646	3.4%	36.6646	SD	0.50%	0.5%	36.67(18)
$9p_{1/2} - 10s$	34.8746	34.7962	0.2%	34.7962	SD	0.50%	0.5%	34.80(17)
$9p_{1/2} - 11s$	6.2590	6.0524	3.4%	6.0524	SD	0.50%	0.5%	6.052(30)
$9p_{1/2} - 12s$	2.9803	2.8666	4.0%	2.8666	SD	0.50%	0.5%	2.867(14)
$9p_{3/2} - 5s$	0.0914	0.0727	25.7%	0.0727	SD	3.00%	3%	0.073(2)
$9p_{3/2} - 6s$	0.3409	0.3633	6.2%	0.3633	SD	1.50%	1.5%	0.363(5)
$9p_{3/2} - 7s$	1.0997	1.1747	6.4%	1.1747	SD	1.00%	1%	1.175(12)
$9p_{3/2} - 8s$	4.2781	4.4472	3.8%	4.4472	SD	0.50%	0.5%	4.447(22)
$9p_{3/2} - 9s$	53.0686	51.2278	3.6%	51.2278	SD	0.50%	0.5%	51.23(26)
$9p_{3/2} - 10s$	50.3114	50.3324	0.0%	50.3324	SD	0.50%	0.5%	50.33(25)
$9p_{3/2} - 11s$	8.7311	8.4034	3.9%	8.4034	SD	0.50%	0.5%	8.403(42)
$9p_{3/2} - 12s$	4.1299	3.9487	4.6%	3.9487	SD	0.50%	0.5%	3.949(20)
$10p_{1/2} - 5s$	0.0376	0.0262	43.5%	0.0262	SD	4.00%	4%	0.026(1)
$10p_{1/2} - 6s$	0.1389	0.1481	6.2%	0.1481	SD	1.50%	1.5%	0.148(2)
$10p_{1/2} - 7s$	0.3973	0.4297	7.5%	0.4297	SD	1.50%	1.5%	0.430(6)
$10p_{1/2} - 8s$	1.1250	1.1969	6.0%	1.1969	SD	1.00%	1%	1.197(12)
$10p_{1/2} - 9s$	4.1037	4.2539	3.5%	4.2539	SD	0.50%	0.5%	4.254(21)
$10p_{1/2} - 10s$	50.8726	49.3551	3.1%	49.3551	SD	0.50%	0.5%	49.36(25)
$10p_{1/2} - 11s$	46.8146	46.8223	0.0%	46.8223	SD	0.50%	0.5%	46.82(23)
$10p_{1/2} - 12s$	8.2275	7.9625	3.3%	7.9625	SD	0.50%	0.5%	7.963(40)
$10p_{3/2} - 5s$	0.0675	0.0525	28.4%	0.0525	SD	4.00%	4%	0.053(2)
$10p_{3/2} - 6s$	0.2297	0.2462	6.7%	0.2462	SD	1.50%	1.5%	0.246(4)
$10p_{3/2} - 7s$	0.6307	0.6838	7.8%	0.6838	SD	1.50%	1.5%	0.684(10)
$10p_{3/2} - 8s$	1.7358	1.8518	6.3%	1.8518	SD	1.00%	1%	1.852(19)
$10p_{3/2} - 9s$	6.1461	6.3867	3.8%	6.3867	SD	0.50%	0.5%	6.387(32)
$10p_{3/2} - 10s$	71.1883	68.9149	3.3%	68.9149	SD	0.50%	0.5%	68.92(35)
$10p_{3/2} - 11s$	67.5015	67.6853	0.3%	67.6853	SD	0.50%	0.5%	67.69(34)
$10p_{3/2} - 12s$	11.4620	11.0380	3.8%	11.0380	SD	0.50%	0.5%	11.04(6)

TABLE III

SELECTION OF THE “BEST SET” VALUES FOR DIAGONAL AND OFF-DIAGONAL MATRIX ELEMENTS OF THE MAGNETIC HYPERFINE OPERATOR $\mathcal{T}^{(1)}$ IN 10^{-8} A.U. ABSOLUTE VALUES OF THE LOWEST ORDER DHF, ALL-ORDER SD, AND ALL-ORDER SDpT VALUES ARE GIVEN IN COLUMNS 2-4.

	DHF	SD	SDpT	Expt.	Final	Source	Unc. (%)	Unc. source	“Best set”
$5s - 5s$	22.0830	36.1633	34.6801	34.6810	34.6810	Expt.	0.00%	Expt.	34.681
$5s - 6s$	11.4126	17.4008	16.8497	16.8602	16.8602	Expt.	0.06%	Expt-SDpT	16.860(10)
$5s - 7s$	7.3042	10.9262	10.6061	10.6086	10.6086	Expt.	0.02%	Expt-SDpT	10.609(2)
$5s - 8s$	5.1907	7.6957	7.4786	7.4855	7.4786	SDpT	0.09%	Expt-SDpT	7.479(7)
$5s - 9s$	3.9328	5.8004	5.6404	5.6563	5.6404	SDpT	0.28%	Expt-SDpT	5.640(16)
$5s - 10s$	3.1127	4.5748	4.4505		4.4505	SDpT	0.3%	0.3%	4.451(13)
$5s - 11s$	2.5429	3.7281	3.6279		3.6279	SDpT	0.3%	0.3%	3.628(11)
$5s - 12s$	2.1332	3.1194			3.0333	SD adj. -3%	0.3%	0.3%	3.033(9)
$5p_{1/2} - 5p_{1/2}$	2.4023	4.3197	4.1460	4.1223	4.1223	Expt.	0.2%	Expt.	4.122(8)
$5p_{1/2} - 6p_{1/2}$	1.4218	2.4431	2.3582		2.3582	SDpT	0.6%	from $5p_{1/2}$	2.358(14)
$5p_{1/2} - 7p_{1/2}$	0.9681	1.6390	1.5853		1.5853	SDpT	0.6%	from $5p_{1/2}$	1.585(10)
$5p_{1/2} - 5p_{3/2}$	0.3835	0.3396	0.3274		0.3274	SDpT	1%	from $5p_{3/2}$	0.327(3)
$5p_{1/2} - 6p_{3/2}$	0.2273	0.1946	0.1886		0.1886	SDpT	1%	from $5p_{3/2}$	0.189(2)
$5p_{1/2} - 7p_{3/2}$	0.1550	0.1312	0.1272		0.1272	SDpT	1%	from $5p_{3/2}$	0.127(1)
$5p_{3/2} - 5p_{3/2}$	1.3496	2.7786	2.6682	2.7229	2.7229	Expt.	0.065%	Expt.	2.723(2)
$5p_{3/2} - 6p_{3/2}$	0.8000	1.5755	1.5212		1.5483	av. SD, SDpT	1%	from $5p_{3/2}$	1.548(15)
$5p_{3/2} - 7p_{3/2}$	0.5453	1.0583	1.0241		1.0412	av. SD, SDpT	1%	from $5p_{3/2}$	1.041(10)
$5p_{3/2} - 6p_{1/2}$	0.2269	0.1905	0.1845		0.1845	SDpT	1%	from $5p_{3/2}$	0.185(2)
$5p_{3/2} - 7p_{1/2}$	0.1545	0.1275	0.1236		0.1236	SDpT	1%	from $5p_{3/2}$	0.124(1)
$6p_{1/2} - 6p_{1/2}$	0.8443		1.3431	1.3453	1.3453	Expt.	0.02%	Expt.	1.3453(3)
$6p_{1/2} - 7p_{1/2}$	0.5747		0.9024		0.9024	SDpT	0.2%	from $6p_{1/2}$	0.902(2)
$6p_{1/2} - 6p_{3/2}$	0.1350		0.1076		0.1076	SDpT	2%	from $6p_{3/2}$	0.108(2)
$6p_{1/2} - 7p_{3/2}$	0.0919		0.0727		0.0727	SDpT	2%	from $6p_{3/2}$	0.073(1)
$6p_{3/2} - 7p_{1/2}$	0.0918		0.0722		0.0722	SDpT	2%	from $6p_{3/2}$	0.072(1)
$6p_{3/2} - 6p_{3/2}$	0.4759		0.8675	0.8890	0.8890	Expt.	0.06%	Expt.	0.889(1)
$6p_{3/2} - 7p_{3/2}$	0.3241		0.5834		0.5834	SDpT	2%	from $6p_{3/2}$	0.583(12)
$7p_{1/2} - 7p_{1/2}$	0.3916		0.6067	0.6020	0.6020	Expt.	0.05%	Expt.	0.6020(3)
$7p_{1/2} - 7p_{3/2}$	0.0627		0.0488		0.0488	SDpT	3%	from $7p_{3/2}$	0.049(1)
$7p_{3/2} - 7p_{3/2}$	0.2211		0.3925	0.4034	0.4034	Expt.	0.08%	Expt.	0.4034(3)

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

$$A_T = \frac{(-1)^{j_m+1/2}}{2}$$

$$A_C = (-1)^{j_m-j_n} \begin{Bmatrix} 1 & 1/2 & 1/2 \\ 1 & j_m & j_n \end{Bmatrix}.$$

Sums over m and n run over all possible states allowed by the selection rules. Therefore, three distinct sets of matrix elements are needed for the present calculations: electric-dipole matrix elements between ns and mp_j states, $\langle mp_j||D||ns\rangle$, and diagonal and off-diagonal matrix elements of the magnetic hyperfine operator for both ns and np states: $\langle ns||\mathcal{T}^{(1)}||5s\rangle$, $\langle mp_{j_1}||\mathcal{T}^{(1)}||np_{j_2}\rangle$. Therefore, the calculation of the BBR shift reduces to the evaluation of the electric-dipole and magnetic hyperfine matrix elements.

We start our calculation by evaluating all three terms in

Dirac-Hartree-Fock approximation. The resulting DF values for the T , C , and R terms in atomic units are

$$2T^{\text{DF}} = 2.376 \times 10^{-3}, \quad C^{\text{DF}} = 6.111 \times 10^{-6},$$

$$R^{\text{DF}} = 3.199 \times 10^{-3}.$$

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 [6], [7]. 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. The “best set” consists of our all-order high-precision values and several experimental values. The following 128 matrix elements have been replaced by the all-order or experimental values:

$$\langle mp_j||D||ns\rangle, m = 5 - 12, n = 5 - 12$$

$$\langle ns||\mathcal{T}^{(1)}||5s\rangle, n = 5 - 12$$

$$\langle mp_{j_1}||\mathcal{T}^{(1)}||np_{j_2}\rangle, m = 5 - 7, n = 5 - 7.$$

The all-order calculation Rb matrix elements has been described in detail in [8].

We illustrate the selection of the “best set” values of the electric-dipole matrix elements and determination of their uncertainties in Tables I and II. The absolute values in atomic units (a_0e) 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 Tables I and II. The relative differences of DHF and 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 [9]. All other E1 matrix elements are from all-order calculation that included SD, SDpT, or SD_{sc} values. The SD_{sc} values include additional corrections added to SD *ab initio* results by means of the scaling procedure described in Ref. [10] and references therein. The SDpT label refers to *ab initio* 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 (as scaling procedure is only applicable for certain classes of terms) and accuracy requirements. In the present calculation, extremely 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. [10] and references therein for explanation). Therefore, it is reasonable to take the difference of *ab initio* and scaled results as the uncertainty. This is indicated by SD_{sc}-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 initio* SDpT calculation (i.e. partially included triples) instead and took these values as final. The uncertainties were estimated at the differences 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. [10] 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 correlation correction 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 Tables I and II.

Selection of the “best set” values for diagonal and off-diagonal matrix elements of the magnetic hyperfine operator $\mathcal{T}^{(1)}$ in 10^{-8} a.u is illustrated in Table III. 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 $\langle ns || \mathcal{T}^{(1)} || n's \rangle$ can be also evaluated from experimental hyperfine constants using the formula

$$|\langle ns || \mathcal{T}^{(1)} || n's \rangle| = \sqrt{\langle ns || \mathcal{T}^{(1)} || ns \rangle \langle n's || \mathcal{T}^{(1)} || n's \rangle}, \quad (6)$$

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 large number of experimental values are available for data 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. We note that contributions of $np - np'$ matrix elements to total uncertainty of the static Stark coefficient k_S is very small, and approximate estimate of uncertainties is sufficient.

The total uncertainty of the main terms of the static Stark coefficient is obtained by adding uncertainties from all terms in quadrature. The uncertainties in the remainders are evaluated separately for each term. They are found to be very small for terms C and R. The remainder (over ns sum) in term T is large, about 15% of the total term T, and was considered in detail. We found that the accuracy of the DHF approximation for the remainder of term T is about 4%, bases on the comparison of the DHF and final results for the main terms. Therefore, we adjusted DHF tail for the term T by 4%. We took 100% of the adjustment to be the uncertainty of the T term remainder.

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

$$\begin{aligned} 2T &= 2.247(17) \times 10^{-3}, & C &= -2.385(20) \times 10^{-5}, \\ R &= 2.769(2) \times 10^{-3}. \end{aligned}$$

Using these values, we obtain our predicted value of the Stark coefficient, $k_s = -1.240(4) \times 10^{-10}$ Hz/(V/m)². It is in

agreement with the value -1.24×10^{-10} Hz/(V/m)² of Ref. [4] that was estimated to be accurate to about 1% based on the uncertainty estimate done for Cs atom.

III. DEVELOPMENT OF CI + ALL-ORDER METHOD

The all-order method use to evaluate Rb matrix elements above is designed to treat core-core and core-valence correlations with high accuracy. It is not directly applicable to evaluate properties of divalent systems used in many optical atomic clock schemes (Ca, Sr, Yb, etc.) Precision calculations for atoms with several valence electrons require an accurate treatment of the very strong valence-valence correlation. A perturbative approach leads to significant difficulties.

A combination of the configuration-interaction method and perturbation theory was developed in Ref. [11] and later applied to the calculation of atomic properties of various systems in a number of works. The CI + MBPT approach allows one to incorporate core excitations in the CI method by constructing an effective Hamiltonian that incorporates certain perturbation theory terms. The CI method is then applied to the modified H^{eff} to obtain improved energies and wave functions. The CI+MBPT approach includes only a limited number of the core-valence excitation terms (mostly in second order) and deteriorates in accuracy for heavier, more complicated systems.

TABLE IV

COMPARISON OF THE CI, CI+MBPT, AND OUR FINAL *ab initio* CI+ALL-ORDER RESULTS WITH RECOMMENDED VALUES FROM REF. [12] THAT INCORPORATE HIGH-PRECISION EXPERIMENTAL RESULTS.

Atom	State	CI	CI+MBPT	CI+all	Ref. [12]
Mg	$3s^2 \ ^1S_0$	73.56	71.20	71.19	71.3(7)
	$3s3p \ ^3P_0$	101.97	100.76	100.81	101.2(3)
Ca	$4s^2 \ ^1S_0$	168.66	156.58	157.64	157.1(1.3)
	$4s4p \ ^3P_0$	236.09	300.83	288.69	290.3(1.5)
Sr	$5s^2 \ ^1S_0$	219.34	195.60	198.01	197.2(2)
	$5s5p \ ^3P_0$	341.29	483.64	459.39	458.3(3.6)

In the CI+all-order approach, the effective Hamiltonian is constructed using fully converged all-order excitations coefficients. Therefore, the core-core and core-valence sectors of the correlation corrections for systems with few valence electrons will be treated with the same accuracy as in the all-order approach for the monovalent systems. The CI method is then used to treat valence-valence correlations. This approach has been tested on the calculation of energy levels of divalent systems from Mg to Ra. We have demonstrated an improvement of at least a factor of 3 in agreement with experimental values for the two-electron binding energies and most excited-state energies in comparison with the CI+MBPT (many-body perturbation theory) method [1]. In the present work, we have extended CI+all-order method to the calculation of the transition properties and polarizabilities of divalent systems. Preliminary results for polarizabilities are listed in

Table IV. The CI, CI+MBPT, and CI + all-order values for the polarizabilities of Mg, Ca, and Sr in the ground 1S_0 and excited 3P_0 states are given. The BBR shift for optical atomic clocks is closely related to the difference of static polarizabilities of these states (up to relatively small dynamic correction) [3], [13]. We observe that while CI+MBPT and CI+all order results are nearly the same for Mg, the difference is large for Sr. Our CI+all-order results are in very good agreement with recommended values from [12], where experimental values for transition matrix elements were used where available.

IV. CONCLUSION

We had carried out accurate evaluation of the blackbody radiation shift for the ^{87}Rb microwave frequency standard. Progress on the development of the CI+all-order method for calculation of properties of divalent atoms relevant to the atomic clock research is reported. Our preliminary *ab initio* values for atomic polarizabilities of Mg, Ca, and Sr are in very good agreement with the present recommended values that incorporate experimental results for transition properties.

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