Investigating ground-state fine-structure properties to explore suitability of boronlike S^{11+}-K^{14+} and galliumlike Nb^{10+}-Ru^{13+} ions as possible atomic clocks

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We study various properties of the $2p\,^2P_{1/2}-2p\,^2P_{3/2}$ fine-structure splittings in the boronlike S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions and the $4p\,^2P_{1/2}-4p\,^2P_{3/2}$ fine-structure splittings in the galliumlike Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions to find out the feasibility of using these highly charged ions as suitable optical atomic clocks. The roles of the electron correlations due to the Dirac-Coulomb-Breit Hamiltonian and accounting for lower-order quantum electrodynamics effects are shown explicitly in the calculations of electron affinities, excitation energies, transition-matrix elements, lifetimes, hyperfine-structure constants, and electric quadrupole moments of the states involved with clock transitions using a relativistic couple-cluster method. We also estimate the most commonly appearing systematic effects in the atomic clock experiments due to the electric quadrupole, the second-order Zeeman, both the dc and ac Stark, and the black-body radiation shifts in the aforementioned fine-structure splittings to demonstrate typical orders of magnitude of fractional frequency shifts.

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I. INTRODUCTION

The atomic data of highly charged ions (HCIs) are of immense interest in many areas of physics since they are useful for studying plasmas, astrophysics, nuclear fusion processes, etc. [1]. Also, they are used to test the quantum electrodynamics (QED) corrections comparing with high-precision measurements and to infer the ratio between proton and electron masses [2]. Since these days HCIs are realized to be potential candidates for making ultrahigh-precision atomic clocks with projected uncertainties below the 10^{-19} level, investigating more of such ions is of particular interest to consider for the experiments. In contrast to the singly charged atomic clocks, principles to make HCI clocks can be very different, owing to the fact that there are no suitable optical transitions that have been realized yet to apply laser cooling and trapping techniques to perform the clock frequency measurements [3]. Recently, we found few HCIs which can offer a quality factor for making optical clocks about 10^{15} [4] and had suggested possible schemes for carrying out the measurements. However, some of the systematics in these HCIs are still significantly large to achieve very-high-precision frequency measurements. It was argued earlier that the magnetic dipole ($M1$) transitions between the fine-structure splittings from the ground configuration of several HCIs can be better suitable for developing very precise clocks [5]. In this context, the HCIs of the $4f$-shelled configurations such as Nd-like Ir^{17+}, Pm-like Ir^{16+}, I-like Ho^{14+}, etc., were investigated, owing to their advantages of having highly forbidden transitions, having large relativistic sensitivity to probe possible variations of the fine-structure constant (α_e), and possessing several intercombination lines among the low-lying states [6–9]. However, these HCIs have limitations as they do not possess simple atomic structures, so performing accurate atomic calculations is challenging and identifying energy levels is difficult [10,11]. Therefore, we intend to find other suitable HCIs having simpler structures in which $M1$ transitions can be used as clock transitions. From this point of view, considering atomic systems with one outer valence electron can be a better choice for the HCI clock candidates. Earlier, we had analyzed the aluminumlike HCIs for such a purpose [12]. In the present work, we study various spectroscopic properties of the $M1$ transitions between the $2p\,^2P_{1/2}-2p\,^2P_{3/2}$ fine-structure splittings of the boronlike (B-like) S^{11+}-K^{14+} ions and the $4p\,^2P_{1/2}-4p\,^2P_{3/2}$ fine-structure splittings of the galliumlike (Ga-like) $Nb^{10+}-Ru^{13+}$ ions. Using these spectroscopic properties, we estimate many of the systematic effects to comprehend these ions as the probable candidates for the optical atomic clocks.

A number of studies have already been reported previously to understand the roles of electron correlation and relativistic effects in the determination of energies, line strengths, transition rates, lifetimes, and hyperfine-structure constants of the B and B-like systems by employing a number of relativistic many-body methods such as the relativistic many-body perturbation theory (MBPT) [13–15], the multiconfiguration Hartree-Fock (MCHF) method [16–23], and the relativistic coupled-cluster (RCC) theory [24–26]. These calculations demonstrate strong electron correlation effects and large contributions from the Breit interaction [18] in order to achieve high-accuracy values of energies. Since the B-like systems have only five electrons, *ab initio* calculations using QED

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theory have also been performed in such systems in the determination of electron affinities (EAs), excitation energies (EEs), oscillator strengths, transition probabilities, lifetimes, and hyperfine structures of the fine-structure levels of the ground state in the B-like HCIs [27–35]. However, similar accurate calculations cannot be performed in the Ga-like ions because of the presence of 31 electrons in these ions. Previously, EEs and transition probabilities of the $4p\,^2P_{1/2}$–$4p\,^2P_{3/2}$ fine-structure splittings of some of the Ga-like ions were reported using the Dirac-Hartree-Fock (DHF) methods [36,37] and finite-order MBPT method [38]. In some other works, the roles of the electron correlation effects in the Ga isoelectronic sequences have been investigated using the multiconfiguration Dirac-Fock (MCDF) method [39,40].

In this paper, we intend to analyze various properties like EAs, EEs, hyperfine-structure constants, transition probabilities, lifetimes, etc. of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states of the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} HCIs and of the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} HCIs by using the RCC theory in order to scrutinize frequencies of the $M1$ transitions between these fine-structure states for making atomic clocks. We also show contributions from the electronic correlation effects by considering the Dirac-Coulomb (DC) Hamiltonian, the Breit interaction, and the lower-order QED effects explicitly for the above properties. Using some of these properties we also estimate various shifts such as the electric quadrupole, the second-order Zeeman, the dc and ac Stark, and the blackbody radiation (BBR) shifts of the aforementioned possible clock transitions in order to learn about their typical orders of magnitude. We also determine the relativistic sensitivity coefficients of these transitions to make a case to probe possible temporal variation of α_e using these clocks when undertaken experimentally.

II. METHODS OF CALCULATIONS

We start the calculations with the DC Hamiltonian given by

$$H^{DC} = \sum_i [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_n(r_i)] + \sum_{i,j>i} \frac{1}{r_{ij}}, \quad (1)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β are the usual Dirac matrices, $\mathbf{p}_i$ is the single-particle momentum operator, $V_n(r)$ denotes the nuclear potential, and $\frac{1}{r_{ij}}$ represents the Coulomb potential between the electrons located at the i and j positions. Then, we investigate the Breit interaction contribution by including the following potential in the atomic Hamiltonian:

$$V^B = -\sum_{j>i} \frac{[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \hat{\mathbf{r}}_{\mathbf{ij}})(\boldsymbol{\alpha}_j \cdot \hat{\mathbf{r}}_{\mathbf{ij}})]}{2r_{ij}}, \quad (2)$$

where $\hat{\mathbf{r}}_{\mathbf{ij}}$ is the unit vector along $\mathbf{r}_{\mathbf{ij}}$.

Similarly, contributions from the QED effects are estimated by considering the lower-order vacuum polarization (VP) interaction ($V_{\rm VP}$) and the self-energy (SE) interactions ($V_{\rm SE}$). We account for $V_{\rm VP}$ through the Uehling [41] and Wichmann-Kroll potentials ($V_{\rm VP} = V^{Uehl} + V^{WK}$) given by

$$V^{Uehl} = -\frac{2}{3}\sum_i \frac{\alpha_e^2}{r_i}\int_0^\infty dx\, x\, \rho_n(x) \int_1^\infty dt \sqrt{t^2-1} \times \left(\frac{1}{t^3} + \frac{1}{2t^5}\right)[e^{-2ct|r_i - x|} - e^{-2ct(r_i+x)}] \quad (3)$$

and

$$V^{WK} = \sum_i \frac{0.368Z^2}{9\pi c^3(1 + (1.62cr_i)^4)}\rho_n(r_i), \quad (4)$$

respectively, with the electron density over the nucleus, $\rho_n(r)$, and the atomic number of the system, Z.

The SE contribution $V_{\rm SE}$ is estimated by including two parts:

$$V_{\rm SE}^{ef} = -A_l \sum_i \frac{2\pi Z\alpha_e^3}{r_i} I_1^{ef}(r_i) + B_l \sum_i \frac{\alpha_e}{r_i} I_2^{ef}(r_i), \quad (5)$$

known as the effective electric form factor part, and

$$V_{\rm SE}^{mg} = \sum_k \frac{i\alpha_e^3}{4}\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}_k \frac{1}{r_k}\int_0^\infty dx\, x\, \rho_n(x)\int_1^\infty dt \frac{1}{t^3\sqrt{t^2-1}} \times [e^{-2ct|r_k - x|} - e^{-2ct(r_k+x)} - 2ct(r_k + x - |r_k - x|)], \quad (6)$$

known as the effective magnetic form factor part. In the above expressions [42],

$$A_l = \begin{cases} 0.074 + 0.35Z\alpha_e & \text{for } l = 0, 1 \\ 0.056 + 0.05Z\alpha_e + 0.195Z^2\alpha_e^2 & \text{for } l = 2, \end{cases} \quad (7)$$

$$B_l = \begin{cases} 1.071 - 1.97x^2 - 2.128x^3 + 0.169x^4 & \text{for } l = 0, 1 \\ 0 & \text{for } l \geqslant 2, \end{cases} \quad (8)$$

$$I_1^{ef}(r) = \int_0^\infty dx\, x\, \rho_n(x)[(Z|r - x + 1)|e^{-Z|r-x|} - (Z(r + x) + 1)e^{-2ct(r+x)}], \quad (9)$$

and

$$I_2^{ef}(r) = \int_0^\infty dx\, x\, \rho_n(x)\int_1^\infty dt \frac{1}{\sqrt{t^2-1}}\left\{\left(1 - \frac{1}{2t^2}\right) \times \left[\ln(t^2-1) + 4\ln\left(\frac{1}{Z\alpha_e} + \frac{1}{2}\right)\right] - \frac{3}{2} + \frac{1}{t^2}\right\} \times \left\{\frac{\alpha_e}{t}[e^{-2ct|r-x|} - e^{-2ct(r+x)}] + 2r_A e^{2r_A ct} \times [E_1(2ct(|r - x| + r_A)) - E_1(2ct(r + x + r_A))]\right\}, \quad (10)$$

with the orbital quantum number l of the system, $x = (Z - 80)\alpha_e$, $r_A = 0.07Z^2\alpha_e^3$, and the exponential integral $E_1(r) = \int_r^\infty ds(e^{-s}/s)$. We have used the Fermi nuclear charge distribution in our calculations by defining

$$\rho_n(r) = \frac{\rho_0}{1 + e^{\frac{r-b}{a}}} \quad (11)$$

for the normalization factor ρ_0, the half-charge radius b, and $a = 2.3/4(\ln 3)$, which is related to the skin thickness. We have determined b using the relation

$$b = \sqrt{\frac{5}{3}r_{\rm rms}^2 - \frac{7}{3}a^2\pi^2}, \tag{12}$$

with the root-mean-square (rms) charge radius of the nucleus evaluated by using the formula

$$r_{\rm rms} = 0.836A^{1/3} + 0.570, \tag{13}$$

in femtometers for the atomic mass A.

We adopt two procedures to estimate the QED corrections. In one of the approaches, we include the QED interaction potentials with the DC Hamiltonian and solve the energies and wave functions self-consistently. Corrections to energies and properties are estimated through comparing results obtained by the DC Hamiltonian. In another procedure, we treat QED interaction potentials as perturbative operators and determine the first-order energy corrections with respect to the DC Hamiltonian.

The exact states of the fine-structure splittings in the considered systems are expressed in the RCC theory as [43,44]

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle, \tag{14}$$

where $|\Phi_v\rangle = a_v^\dagger|\Phi_0\rangle$ is the working reference state with valence orbital v for the DHF wave function of the $[2s^2]$ and $[4s^2]$ closed-shell configurations in the B-like and Ga-like HCIs, respectively. The RCC excitation operators T and S_v are responsible for exciting electrons from $|\Phi_0\rangle$ and $|\Phi_v\rangle$, respectively. We consider all possible single and double excitations and perturbative triple excitation approximation in the RCC theory (CCSDpT method) in a sufficiently large configuration space by defining

$$T = T_1 + T_2 + T_3^{\rm pert} \quad \text{and} \quad S_v = S_{1v} + S_{2v} + S_{3v}^{\rm pert}, \tag{15}$$

where subscripts 1, 2, and 3 represent the level of excitations and the superscript "pert" denotes the perturbative approach. The amplitudes of these RCC operators are evaluated using the following equations:

$$\langle\Phi_0^*|\overline{H}_N|\Phi_0\rangle = 0 \tag{16}$$

and

$$\langle\Phi_v^*|(\overline{H}_N - \Delta E_v)S_v|\Phi_v\rangle = -\langle\Phi_v^*|\overline{H}_N|\Phi_v\rangle, \tag{17}$$

where $|\Phi_0^*\rangle$ and $|\Phi_v^*\rangle$ are the singly and doubly excited state configurations with respect to the respective DHF states $|\Phi_0\rangle$ and $|\Phi_v\rangle$, respectively. The notation $\overline{H}_N$ is defined as $\overline{H}_N = (He^{T_1+T_2+T_3^{\rm pert}})_l$, where the subscript N denotes the normal order form of the operator with respect $|\Phi_0\rangle$ and l means that all terms are linked. The quantity ΔE_v corresponds to the EAs of the state with the valence electron v. We evaluate ΔE_v by

$$\Delta E_v = \langle\Phi_v|\overline{H}_N\{1 + S_v\}|\Phi_v\rangle - \langle\Phi_0|\overline{H}_N|\Phi_0\rangle. \tag{18}$$

It has to be noted that Eqs. (17) and (18) are coupled and the $T_3^{\rm pert}$ and $S_{3v}^{\rm pert}$ operators are included in all the above equations. The EEs between the fine-structure splittings are determined by taking differences between their EAs.

The transition-matrix element and the expectation value of any operator O between the fine-structure states $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are calculated in terms of the expression

$$\frac{\langle\Psi_f|O|\Psi_i\rangle}{\sqrt{\langle\Psi_i|\Psi_i\rangle\langle\Psi_f|\Psi_f\rangle}} = \frac{\langle\Phi_f|\tilde{O}_{fi}|\Phi_i\rangle}{\sqrt{\langle\Phi_i|\tilde{N}_i|\Phi_i\rangle\langle\Phi_f|\tilde{N}_f|\Phi_f\rangle}}, \tag{19}$$

where $\tilde{O}_{fi} = \{1 + S_f^\dagger\}e^{T^\dagger}Oe^T\{1 + S_i\}$ and $\tilde{N}_{k=f,i} = \{1 + S_k^\dagger\}e^{T^\dagger}e^T\{1 + S_k\}$. In the expectation value evaluation, it turns out to be $|\Psi_i\rangle = |\Psi_f\rangle$. We adopt the iterative procedures [43–45] to account for contributions from both nonterminating series $e^{T^\dagger}Oe^T$ and $e^{T^\dagger}e^T$ that appear in Eq. (19). We, however, consider only single and double excitation RCC operators to determine the final results while perturbative valence triple excitation operators are used to estimate the uncertainties.

In order to determine the static dipole polarizability (α^{E1}) we use the Fock-space-based relativistic coupled-cluster method of the DIRAC [46] package. The static values of α^{E1} are inferred from the energies that are determined after including the interaction Hamiltonian due to an arbitrary electric field into the atomic Hamiltonian and then adopting the finite-field procedure. We have used Dyall's uncontracted correlation-consistent double-, triple-, and quadrupole-X_ζ basis functions [47] (denoted by $X = 2$, 3, and 4, respectively) to verify convergence in the results. The exact procedure of evaluating the scalar (α_0^{E1}) and tensor (α_2^{E1}) components of α^{E1} is discussed elsewhere [12,48].

III. RESULTS AND DISCUSSION

We present the EAs and EEs of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states of the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions in Table I. The energy values obtained by the DHF method ($E_{\rm DHF}$) and the CCSD and CCSDpT correlation contributions to the energies ($\Delta^{\rm (CCSD)}$ and $\Delta^{\rm (CCSDpT)}$) are given in Table I. Moreover, the relativistic corrections from the Breit and the lower-order QED interactions, $\Delta^{\rm (Breit)}$ and $\Delta^{\rm (QED)}$, that are estimated using our CCSD method are given explicitly in the same table. Our final results of the EAs, adding all the above contributions, are compared with the values reported using rigorous treatment of QED effects (denoted as the RQED method) [34] and the recommended data from the NIST database [49]. This comparison shows excellent agreement between our calculations with the previous theoretical results. We also compare the EEs inferred from the EA values with the earlier calculations [13,21,33] and the experimental values [50–53] in the above table. Similarly, the breakdown of the contributions to these values from various sources is mentioned explicitly. As can be seen from Table I, the correlation contributions through the CCSD method and triple excitations are about to be similar orders of magnitude but with opposite sign in the evaluation of EAs. The Breit contribution plays the decisive role in attaining the final results. The QED contribution is found to be quite small compared with the other contributions. In the case of the EEs, both the Breit interaction and the electron correlation effects contribute significantly; the former gives slightly larger contributions than the latter. The contributions due to the triple excitations to the EAs of both states cancel out strongly and then give rise to small contributions to the EEs. The QED corrections

TABLE I. The electron affinities (EAs) in cm^{-1} of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states and the excitation energies (EEs) in cm^{-1} of the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions. The total value is determined by summing the results from the DHF method (E_{DHF}), and corrections from the CCSD ($\Delta^{(CCSD)}$) and CCSDpT ($\Delta^{(CCSDpT)}$) methods, Breit interaction ($\Delta^{(Breit)}$), and QED effects ($\Delta^{(QED)}$). Our final values are compared with the other available results. The numbers in parentheses are the given uncertainties. The uncertainties to our final results are estimated by adding $\Delta^{(CCSDpT)}$ and $\Delta^{(QED)}$ contributions.

	S^{11+}	Cl^{12+}	Ar^{13+}	K^{14+}
		EAs of the $2p\,^2P_{1/2}$ state		
From DC Hamiltonian				
E_{DHF}	−4553784	−5296263	−6094819	−6949617
$\Delta^{(CCSD)}$	−952	−117	736	1607
$\Delta^{(CCSDpT)}$	837	902	960	1005
Relativistic corrections				
$\Delta^{(Breit)}$	1514	1882	2305	2788
$\Delta^{(QED)}$	−79	−79	−94	−130
Total	−4552464(758)	−5293676(823)	−6090912(866)	−6944346(875)
NIST [49]	−4552250(440)	−5293400(1000)	−6090500(1800)	−6943800(2000)
RQED [34]	−4552259(34)	−5293519(36)	−6090805(37)	−6944277(39)
		EAs of the $2p\,^2P_{3/2}$ state		
From DC Hamiltonian				
E_{DHF}	−4539589	−5277514	−6070500	−6918568
$\Delta^{(CCSD)}$	−1540	−899	−277	320
$\Delta^{(CCSDpT)}$	1024	1142	1262	1380
Relativistic corrections				
$\Delta^{(Breit)}$	801	1001	1231	1493
$\Delta^{(QED)}$	−47	−37	−40	−68
Total	−4539351(977)	−5276307(1105)	−6068324(1222)	−6915443(1312)
		EEs of the $2p\,^2P_{1/2} - 2p\,^2P_{3/2}$ splitting		
From DC Hamiltonian				
ΔE_{DHF}	14196	18749	24319	31049
$\Delta^{(CCSD)}$	−589	−782	−1013	−1287
$\Delta^{(CCSDpT)}$	187	240	302	375
Relativistic corrections				
$\Delta^{(Breit)}$	−713	−881	−1075	−1295
$\Delta^{(QED)}$	32	42	54	62
Total	13113(219)	17369(282)	22587(356)	28903(437)
Experiment	13153.3(7) [50]	17410 [51]	22656.220(10) [52]	29016(22) [53]
MBPT [13]	13149	17425	22670	29022
MCDHF [21]	13149	17424	22668	29020
RQED [33]	13135	17416(3)	22657(3)	29017(4)

to these quantities are also quite small. Our results agree with the other calculations reported using the RQED, MCDF, and MBPT methods. Consideration of triple excitations exactly or inclusion of correlation effects from the quadrupole and pentaple excitations in these B-like ions may improve both our EA and EE calculated values further. Nevertheless, the analysis given in Table I would be useful to understand accuracies of the EAs in the undertaken Ga-like HCIs, where such precise results are not available from the experiments or by means of any other theoretical studies.

In Table II, we give results for both EAs and EEs of the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions. Similar to the B-like ions, we also find that the electron correlation effects and the Breit interaction contribute to the EAs and EEs quite significantly in these ions. The QED corrections to the EAs and EEs are also observed to be of similar orders of magnitude like in the B-like ions. However, the triple contributions to the EEs and EAs in these ions are much smaller than in the B-like ions even though the Ga-like systems have more electrons. It implies that the electrons in the B-like systems are more correlated than in the Ga-like ions. We also compare our values of the EAs for the ground states with the NIST data [49] and our values of the EEs with the available experimental results [54] and another calculation from the MBPT method [38]. While there exist a few-thousand cm^{-1} discrepancies between ours and the NIST data for the EAs of the ground state, our calculations for the EEs show good agreement with the experimental and the MBPT results for the Ga-like ions in Table II.

In order to understand the role of the correlation effects in evaluation of the QED corrections to the EAs and the EEs of our interested states, we compare the values of the QED

TABLE II. The EAs in cm^{-1} of the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states and the EEs in cm^{-1} of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions. The total value is determined by summing the results from the DHF method ($E_{\rm DHF}$), and corrections from the CCSD ($\Delta^{(\rm CCSD)}$) and CCSDpT ($\Delta^{(\rm CCSDpT)}$) methods, Breit interaction ($\Delta^{(\rm Breit)}$), and QED effects ($\Delta^{(\rm QED)}$). Our final values are compared with the other available results. The numbers in parentheses are the given uncertainties. The uncertainties of our final values are estimated as described in the previous table.

	Nb^{10+}	Mo^{11+}	Tc^{12+}	Ru^{13+}
		EAs of the $4p\,^2P_{1/2}$ state		
From DC Hamiltonian				
$E_{\rm DHF}$	−1609692	−1852373	−2110059	−2382738
$\Delta^{(\rm CCSD)}$	−10513	−10769	−11018	−11245
$\Delta^{(\rm CCSDpT)}$	40	41	42	42
Relativistic corrections				
$\Delta^{(\rm Breit)}$	1015	1205	1404	1626
$\Delta^{(\rm QED)}$	−91	−105	−132	−112
Total	−1619242(51)	−1862000(64)	−2119763(89)	−2392428(70)
NIST [49]	−1615400(500)	−1857300(500)	−2113800(1000)	−2386600(700)
		EAs of the $4p\,^2P_{3/2}$ state		
From DC Hamiltonian				
$E_{\rm DHF}$	−1585377	−1823428	−2075926	−2342813
$\Delta^{(\rm CCSD)}$	−10594	−10840	−11118	−11384
$\Delta^{(\rm CCSDpT)}$	99	97	102	106
Relativistic corrections				
$\Delta^{(\rm Breit)}$	628	796	927	1070
$\Delta^{(\rm QED)}$	−39	−44	−61	−37
Total	−1595283(60)	−1833418(53)	−2086075(41)	−2353059(69)
		EEs of the $4p\,^2P_{1/2}$−$4p\,^2P_{3/2}$ splitting		
From DC Hamiltonian				
$\Delta E_{\rm DHF}$	24315	28944	34134	39925
$\Delta^{(\rm CCSD)}$	−81	−71	−100	−139
$\Delta^{(\rm CCSDpT)}$	59	56	60	64
Relativistic corrections				
$\Delta^{(\rm Breit)}$	−386	−409	−477	−556
$\Delta^{(\rm QED)}$	52	61	71	75
Total	23959(111)	28582(117)	33687(131)	39369(139)
Experiment [54]	23928(6)	28467(4)		39240(15)
MBPT [38]	23862	28403	33496	39181

corrections estimated in different ways. First, $\delta\epsilon^{(1)}_{\rm QED}$ and $\delta\epsilon^{\rm DF}_{\rm QED}$ represent the QED correction in the DHF method approximation obtained by the first-order perturbation calculation and the self-consistent approach, as listed in Table III. We have also quoted contributions from both the VP and SE effects independently to $\delta\epsilon^{(1)}_{\rm QED}$ as $\delta\epsilon^{(1)}_{\rm VP}$ and $\delta\epsilon^{(1)}_{\rm SE}$ in Table III. We can find that the SE contributions are much larger than the VP contributions and they are in opposite signs. The differences between the $\delta\epsilon^{(1)}_{\rm QED}$ and $\delta\epsilon^{\rm DHF}_{\rm QED}$ values are found to be quite significant in both the B-like and Ga-like HCIs. This implies that it is necessary to estimate QED corrections by adopting the self-consistent procedure. In our final determination of the EAs and EEs, we estimate the QED corrections using the self-consistent approach in the CCSD method and they are quoted as $\delta\epsilon^{\rm RCC}_{\rm QED}$ in Table III. The correlation effects reduce QED corrections to EAs compared to the corrections obtained by the DHF method, while the QED corrections to EEs are almost comparable in both the DHF and CCSD methods due to large cancellation among the correlation corrections. The fractional differences $(\delta\epsilon^{(1)}_{\rm QED} - \delta\epsilon^{\rm RCC}_{\rm QED})/\delta\epsilon^{\rm RCC}_{\rm QED}$ for the EEs in Table III are found to be about 10–20% in both groups of undertaken HCIs. Therefore, rigorous treatment of SE effects may improve our results for the EAs and EEs. We consider the $\delta\epsilon^{\rm RCC}_{\rm QED}$ values as the final QED contributions to both EAs and EEs in our calculations.

After analyzing energies, we now turn to determine the lifetimes of the upper fine-structure levels of the ground states in the respective undertaken B-like and Ga-like ions. In Table IV, we give the amplitude of the $M1$ transition-matrix elements (O^{M1}) between these fine-structure splittings of the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions and those of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions. Likewise for the energies, we also give contributions from the electron correlation effects from the CCSD and CCSDpT methods as well as the corrections from the Breit interaction and the QED effects. The relativistic corrections are estimated using the CCSD method. The lifetimes (τ) of the upper $^2P_{3/2}$ states in the respective ions are determined using the

TABLE III. Investigation of QED corrections to the EAs (in a.u.) and EEs (in a.u.) of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states in the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions and of the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states in the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions. Contributions through the first-order perturbative approach ($\epsilon^{(1)}_{\rm QED}$) and self-consistent procedure ($\delta\epsilon^{\rm (DF)}_{\rm QED}$) from the DHF method are given. Individual VP ($\delta\epsilon^{(1)}_{\rm VP}$) and SE ($\delta\epsilon^{(1)}_{\rm SE}$) contributions to $\epsilon^{(1)}_{\rm QED}$ are also given explicitly. Finally, QED corrections using the RCC theory ($\delta\epsilon^{\rm (RCC)}_{\rm QED}$) at the CCSD method approximation are quoted.

	$\delta\epsilon^{(1)}_{\rm VP}$	$\delta\epsilon^{(1)}_{\rm SE}$	$\delta\epsilon^{(1)}_{\rm QED}$	$\delta\epsilon^{\rm (DF)}_{\rm QED}$	$\delta\epsilon^{\rm (RCC)}_{\rm QED}$
S^{11+}					
$2p\,^2P_{1/2}$	−0.0000005	−0.000041	−0.000042	−0.000468	−0.000360
$2p\,^2P_{3/2}$	−0.0000001	0.000121	0.000121	−0.000301	−0.000215
$2p\,^2P_{1/2} - 2p\,^2P_{3/2}$	−0.0000004	−0.000162	−0.000163	−0.000167	−0.000145
Cl^{12+}					
$2p\,^2P_{1/2}$	−0.0000008	−0.000055	−0.000056	−0.000482	−0.000362
$2p\,^2P_{3/2}$	−0.0000001	0.000159	0.000159	−0.000261	−0.000170
$2p\,^2P_{1/2} - 2p\,^2P_{3/2}$	−0.0000006	−0.000214	−0.000215	−0.000220	−0.000192
Ar^{13+}					
$2p\,^2P_{1/2}$	−0.0000011	−0.000070	−0.000071	−0.000583	−0.000429
$2p\,^2P_{3/2}$	−0.0000002	0.000208	0.000207	−0.000297	−0.000184
$2p\,^2P_{1/2} - 2p\,^2P_{3/2}$	−0.0000009	−0.000278	−0.000279	−0.000286	−0.000245
K^{14+}					
$2p\,^2P_{1/2}$	−0.0000016	−0.000067	−0.000068	−0.000835	−0.000591
$2p\,^2P_{3/2}$	−0.0000003	0.000269	0.000269	−0.000485	−0.000309
$2p\,^2P_{1/2} - 2p\,^2P_{3/2}$	−0.0000013	−0.000336	−0.000337	−0.000349	−0.000282
Nb^{10+}					
$4p\,^2P_{1/2}$	−0.0000069	0.000013	0.000006	−0.000420	−0.000415
$4p\,^2P_{3/2}$	−0.0000010	0.000222	0.000221	−0.000175	−0.000179
$4p\,^2P_{1/2} - 4p\,^2P_{3/2}$	−0.0000059	−0.000209	−0.000215	−0.000245	−0.000236
Mo^{11+}					
$4p\,^2P_{1/2}$	−0.0000088	0.000022	0.000013	−0.000485	−0.000479
$4p\,^2P_{3/2}$	−0.0000012	0.000268	0.000267	−0.000196	−0.000201
$4p\,^2P_{1/2} - 4p\,^2P_{3/2}$	−0.0000075	−0.000246	−0.000253	−0.000289	−0.000278
Tc^{12+}					
$4p\,^2P_{1/2}$	−0.0000110	0.000039	0.000028	−0.000609	−0.000600
$4p\,^2P_{3/2}$	−0.0000015	0.000324	0.000322	−0.000271	−0.000278
$4p\,^2P_{1/2} - 4p\,^2P_{3/2}$	−0.0000094	−0.000285	−0.000294	−0.000338	−0.000322
Ru^{13+}					
$4p\,^2P_{1/2}$	−0.0000136	0.000077	0.000064	−0.000519	−0.000510
$4p\,^2P_{3/2}$	−0.0000019	0.000376	0.000374	−0.000164	−0.000169
$4p\,^2P_{1/2} - 4p\,^2P_{3/2}$	−0.0000117	−0.000299	−0.000311	−0.000355	−0.000341

formula

$$\tau = \frac{1}{A^{M1}}, \tag{20}$$

where A^{M1} represents the $M1$ transition probability. We have also verified the roles of transition probabilities due to the electric quadrupole transitions in the determination of τ values and found that they are negligibly small. The A^{M1} values are evaluated as

$$A^{M1} = \frac{2.69735 \times 10^{13}}{3\lambda^3} S^{M1}, \tag{21}$$

where the line strength $S^{M1} = |O^{M1}|^2$, the $M1$ operator $O^{M1} = \frac{1}{2\mu_B}(\mathbf{L} + 2\mathbf{S})$, and λ (in Å) is the wavelength of the transition in the corresponding ion. To reduce the uncertainties in the determination of τ values, we have used available experimental EE values quoted in Tables I and II for the B-like and Ga-like HCIs, respectively. It has been suggested earlier that there are the lowest-order QED corrections to the $M1$ transition amplitudes due to the electron anomalous magnetic moment (EAMM) effect [27]. We have also taken into account the EAMM effect by redefining the modified $M1$ line strength as $S^{M1}_{\rm new} = S^{M1} + 4\mu_B^2\kappa_e^2|\mathbf{L} + 2\mathbf{S}|^2$, where $\kappa_e \approx \alpha/2\pi$ [27]. The revised lifetimes considering the modified line strengths are mentioned as τ' in Table IV. We find a considerable amount of differences between the τ and τ' values. We also compare our results with the other available theoretical and experimental results of the B-like ions in Table IV. Tupitsyn *et al.* had calculated the lifetimes of the $2p\,^2P_{3/2}$ states without and with the EAMM correction [27]. Among the other theoretical works, Fisher *et al.* and Bilal *et al.* had reported these values using a variety of many-body methods after including the EAMM effect [23,35]. For the proper comparison purpose, we have labeled lifetimes deduced by Tupitsyn *et al.* as "*a*" and "*b*" for the values without and with the EAMM correction taken into account, respectively. We find that our τ values

TABLE IV. The reduced O^{M1} matrix elements (in a.u.) of the $2p\,^2P_{1/2}-2p\,^2P_{3/2}$ $M1$ transition in the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions and of the $4p\,^2P_{1/2}-4p\,^2P_{3/2}$ $M1$ transition of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions. Contributions from various sources are defined in a similar way as in the previous two tables. The estimated lifetimes of the upper $^2P_{3/2}$ states in the respective ions using the $M1$ matrix elements are given as τ (in ms), while the modified values after including the EAMM effect are mentioned as τ' (in ms). Our results are also compared with previously reported experimental and other theoretical values. The numbers in parentheses are the given uncertainties. The uncertainties to our $O^{M1}_{\rm Total}$ values are estimated using the perturbative valence triple excitation operator and including QED contributions. Numbers in the square brackets represent powers of 10.

	S^{11+}	Cl^{12+}	Ar^{13+}	K^{14+}	Nb^{10+}	Mo^{11+}	Tc^{12+}	Ru^{13+}
From DC Hamiltonian								
$O^{M1}_{\rm DHF}$	1.15395	1.15383	1.15371	1.15357	1.15359	1.15346	1.15332	1.15316
$\Delta^{\rm (CCSD)}$	8.33[−4]	7.06[−4]	5.96[−4]	4.97[−4]	1.11[−3]	1.00[−3]	9.03[−4]	8.16[−4]
$\Delta^{\rm (CCSDpT)}$	3.01[−6]	2.50[−6]	2.46[−6]	1.97[−6]	1.5[−6]	1.3[−6]	1.0[−6]	1.0[−6]
Relativistic corrections								
$\Delta^{\rm (Breit)}$	−5.34[−5]	−5.66[−5]	−5.79[−5]	−5.85[−5]	−1.42[−5]	−1.17[−5]	−1.08[−5]	−9.73[−6]
$\Delta^{\rm (QED)}$	−4.60[−7]	−6.29[−7]	−8.97[−7]	−1.01[−6]	6.12[−6]	6.35[−6]	6.78[−6]	7.24[−6]
$O^{M1}_{\rm Total}$	1.154729(3)	1.154482(2)	1.154245(1)	1.154012(1)	1.15470(1)	1.15446(1)	1.15422(1)	1.15399(1)
τ	48.871	21.083	9.571	4.558	8.098	4.809	2.901	1.830
τ'	48.645(1)	20.986(1)	9.527(1)	4.537(1)	8.061(1)	4.787(1)	2.888(1)	1.825(1)
	49.16[a]	21.12[a]	9.582[a]	4.567[a]	8.15[b]	4.83[b]	2.94[b]	1.84[b]
	48.93(1)[c]	21.02(7)[c]	9.538(2)[c]	4.546(12)[c]				
	48.913[d]	21.011[d]	9.5361[d]	4.5403[d]				
			9.5354(20)[e]					
		21.2(0.6)[f]	9.573(4)(5)[g]	4.47(0.10)[h]				

[a]QED [27].
[b]MBPT [38].
[c]QED+EAMM [27].
[d]Gordon-EAMM [23].
[e]MCDHF+EAMM [35].
[f]Experiment [55].
[g]Experiment [28].
[h]Experiment [56].

are closer to the central values of the experimental results than the τ' values. The lifetime of the $2p\,^2P_{3/2}$ state of the Ar^{13+} ion has been measured with very small error bars in Ref. [28]. Comparison between this measured value with all the theoretical values of the lifetime of the above state demonstrates that consideration of the EAMM correction leads to obvious discrepancies between them. The reasons could be the higher-order relativistic and electron correlation effects or some unidentified systematic effects in the measurement that have not been taken into account so far. Therefore, more rigorous theoretical and experimental studies in this direction are strongly needed to address to this ambiguity. For the Ga-like ions there are very limited data available for the lifetime of the $4p\,^2P_{3/2}$ state. In contrast to the B-like ions, only one more theoretical work reported lifetimes of the $4p\,^2P_{3/2}$ states in the considered Ga-like ions [38]. As can be seen from the above table, both our τ and τ' values show good agreement with these theoretical results.

We consider here to discuss the magnetic dipole (A_{hf}) and electric quadrupole (B_{hf}) hyperfine-structure constant results for both the B-like and Ga-like ions. We present these results in Table V. The nuclear spin (I), magnetic dipole moment (μ_I in μ_N), and electric quadrupole moment (Q_I) used from Ref. [57] to obtain these constants by combining with our calculated A_{hf}/g_I and B_{hf}/Q_I values, with $g_I = \mu_I/I$, are mentioned in the same table. The correlation contributions from the CCSD and CCSDpT methods and the relativistic correlations to these effects are mentioned explicitly. We have also taken into account the Bohr-Weisskopf (BW) corrections stemming from the nuclear magnetization distribution inside the atomic nucleus to A_{hf} adopting the formulas defined in Ref. [32]. Unlike energies, we observe negligible correlation contributions to the A_{hf} values through the triple excitations in both the B-like and Ga-like ions. The QED corrections are also found to be quite small in the B-like ions, but they are significant in the $4p\,^2P_{1/2}$ states of the Ga-like ions. The BW corrections are seen to be relatively small. However, corrections from the Breit interaction are a little prominent in both types of ions. These trends are almost similar in the determination of B_{hf} values. There are no experimental values of these quantities available, but we compare our calculations with the other theoretical results. For the case of the B-like HCIs, Volotka *et al.* [32] have calculated the A_{hf} values of the $2p\,^2P_{1/2}$ state by using the RQED method, Dutta *et al.* [25] have calculated the A_{hf} values of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states by employing an RCC theory but considering the DC Hamiltonian and only the Gaunt term of the Breit interaction, and Verdebout *et al.* [58] have carried out the MCDF calculations of the A_{hf} and B_{hf} values. The RCC method employed by Dutta *et al.* and ours are almost similar except for the fact that we treat the nonterminating series appearing in Eq. (19) self-consistently in an iterative procedure while Dutta *et al.*

TABLE V. Demonstration of various contributions to the magnetic dipole (A_{hf}) and electric quadrupole (B_{hf}) hyperfine-structure constants (in MHz), by defining sources in a similar way as in the previous tables, of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states of the B-like S^{11+}, Cl^{12+}, and K^{14+} ions and of the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states of the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions using the mentioned values of nuclear spin I, magnetic moment μ_I (in μ_N), and electric quadrupole moment Q_I (in b) taken from Ref. [57]. Additionally, Bohr-Weisskopf corrections to A_{hf} values are quoted as $\Delta^{(BW)}$. There is no experimental result available, but we have compared our calculations with the other theoretical results. The numbers in parentheses are the given uncertainties. The uncertainties are estimated using the perturbative valence triple excitation operator and including QED contributions.

	$^{33}S^{11+}$	$^{35}Cl^{12+}$	$^{39}K^{14+}$	$^{93}Nb^{10+}$	$^{95}Mo^{11+}$	$^{99}Tc^{12+}$	$^{99}Ru^{13+}$
I	3/2	3/2	3/2	9/2	5/2	9/2	5/2
μ_I	0.6438212	0.8218743	0.39147	6.1705	−0.9142	5.6847	−0.641
Q_I	−0.064	0.085	0.585	−0.32	−0.022	−0.129	0.0790
				A_{hf} of $^2P_{1/2}$			
From DC Hamiltonian							
A_{hf}^{DHF}	12657.74	19977.16	13989.92	26743.75	−8344.12	33497.30	−7833.52
$\Delta^{(CCSD)}$	208.77	305.56	186.67	1978.58	−582.60	2215.12	−491.77
$\Delta^{(CCSDpT)}$	75.6	111.2	457.1	124.8	45.0	334.8	113.2
$\Delta^{(BW)}$	0.06	0.34	0.30	−3.98	1.87	−6.38	2.24
Relativistic corrections							
$\Delta^{(Breit)}$	−18.32	−30.75	−24.11	−92.08	29.41	−120.79	28.89
$\Delta^{(QED)}$	−0.61	−1.15	−1.10	−23.81	8.04	−34.81	8.78
Total	12847(75)	20251(110)	14151(456)	28602(101)	−8887(53)	35550(300)	−8285(122)
RCC [25]	12854	20266	14169				
RQED [32]	12794(2)	20174(4)	14109(2)				
MCDHF[a] [58]	12786	20163	14100				
				A_{hf} of $^2P_{3/2}$			
From DC Hamiltonian							
A_{hf}^{DHF}	2479.10	3901.48	2715.06	4601.29	−1424.63	5673.88	−1316.02
$\Delta^{(CCSD)}$	−47.44	−69.38	−41.40	584.00	−174.20	669.63	−150.17
$\Delta^{(CCSDpT)}$	38.9	79.9	62.9	184.4	53.8	413.7	47.8
$\Delta^{(BW)}$	−0.16	−0.28	−0.17	−1.29	0.45	−1.49	0.41
Relativistic corrections							
$\Delta^{(Breit)}$	−2.15	−3.62	−2.83	−10.41	3.31	−13.55	3.22
$\Delta^{(QED)}$	0.10	0.15	0.09	−0.35	0.17	−0.72	0.17
Total	2430(39)	3829(80)	2671(63)	5174(184)	−1595(54)	6328(413)	−1462(48)
RCC [25]	2586	4064	2824				
MCDHF[a] [58]	2470	3886	2704				
				B_{hf} of $^2P_{3/2}$			
From DC Hamiltonian							
B_{hf}^{DHF}	−684.73	1121.57	11287.81	−2035.20	−162.84	−1101.36	771.95
$\Delta^{(CCSD)}$	32.56	−51.25	−473.34	−190.45	−14.30	−91.12	60.44
$\Delta^{(CCSDpT)}$	35.0	48.0	228.6	51.3	4.0	8.1	7.9
Relativistic corrections							
$\Delta^{(Breit)}$	0.63	−1.11	−12.52	5.30	0.44	3.03	−2.18
$\Delta^{(QED)}$	0.02	−0.04	−0.59	−0.31	−0.02	−0.13	0.09
Total	−652(35)	1069(48)	10801(228)	−2221(51)	−177(4)	−1190(8)	830(8)
MCDHF[a] [58]	−660	1083	10922				

[a]The data are recompiled using data in Ref. [58] multiplied by μ_I/I and Q_I quoted here.

have approximated these terms considering only a few nonlinear terms. Nonetheless, agreement between both of the RCC calculations implies that higher-order nonlinear terms from these nonterminating series do not contribute much to the A_{hf} values in the B-like ions significantly. However, our results differ from the RQED and MCDF calculations by about 1–2% in the B-like ions. To our knowledge, no study has been performed on B_{hf} of the Ga-like ions earlier, so we anticipate that our calculations are of similar accuracies as in the B-like ions.

One of the main motivations to investigate these ions is to find out their suitability as plausible HCI clock candidates. In this context, we quote the wavelength (λ), natural linewidth (Γ), and quality factors (Q) of the ground-state fine-structure splittings of the undertaken B-like and Ga-like HCIs in Table VI. Since Tc does not have a stable isotope, we do not analyze its ion for a possible atomic clock. As can be seen from the above table, the Γ values are found to be quite small in the B-like ions apart from $^{39}K^{14+}$ but they

TABLE VI. Clock-related properties of the representative stable isotopes of the B-like and Ga-like ions, where λ is the wavelength, Γ is the natural linewidth, Q is the quality factor, Θ is the electric quadrupole moment, α_0^{E1} and α_2^{E1} are the scalar and tensor components of the electric dipole polarizability and α^{M1} is the magnetic dipole polarizability are given. The uncertainties are quoted in parentheses. Typical orders of fractional frequency shifts with respect to the frequencies υ in the proposed HCI clocks caused by the dc Stark shifts ($\delta E_{\text{dc Stark}}$), the ac Stark shift ($\delta E_{\text{ac Stark}}$) due to the probe light, the second-order Zeeman shifts ($\delta E^{(2)}_{\text{Zeem}}$), and the BBR shifts ($\delta E^{\text{E1}}_{\text{BBR}}$ and $\delta E^{\text{M1}}_{\text{BBR}}$) due to the $E1$ and $M1$ channels, and the relativistic sensitive coefficient q are also mentioned. Numbers in the square brackets represent powers of 10.

Items	$^{33}S^{11+}$	$^{35}Cl^{12+}$	$^{40}Ar^{13+}$	$^{39}K^{14+}$	$^{93}Nb^{10+}$	$^{96}Mo^{11+}$	$^{102}Ru^{13+}$
λ (nm)	760.265(81)	574.38	441.3799(1)	344.63(13)	417.92(21)	351.28(10)	254.71(13)
Γ (Hz)	3.27	7.59	16.71	35.07	19.76	55.10	87.01
$Q \times 10^{14}$	1.2	0.69	0.41	0.25	0.36	0.13	0.13
$\Theta(^2P_{3/2})$ ($\times 10^{-11}$Hz/(V/m^2))	−0.2087(2)	−0.1813(2)	−0.1589(1)	−0.1405(1)	−1.8262(1)	−1.6441(1)	−1.3568(1)
$\alpha_0^{E1}(^2P_{1/2})$ ($\times 10^{-8}$Hz/(V/m)^2)	0.1863(4)	0.1492(3)	0.1205(2)	0.0989(3)	2.740(5)	2.296(5)	1.659(3)
$\alpha_0^{E1}(^2P_{3/2})$ ($\times 10^{-8}$Hz/(V/m)^2)	0.1855(4)	0.1487(4)	0.1200(2)	0.0986(1)	2.803(6)	2.352(5)	1.706(3)
$\alpha_2^{E1}(^2P_{3/2})$ ($\times 10^{-8}$Hz/(V/m)^2)	0.0129(1)	0.0107(1)	0.0095(1)	0.0050(1)	0.213(2)	0.184(2)	0.140(1)
$\alpha^{M1}(^2P_{1/2})$($\times 10^{8}$Hz/T^2)	4.2331(1)	2.6856(1)	0.0013(1)	3.8431(1)	0.2534(1)	0.0010(1)	0.0007(1)
$\alpha^{M1}(^2P_{3/2})$($\times 10^{8}$Hz/T^2)	521(10)	591(12)	−0.0006(1)	−200(4)	7.7(2)	−0.0005(1)	−0.0004(1)
$\delta E_{\text{dc Stark}}/\upsilon$ ($E = 10$ V/m)	9.5[−25]	4.8[−25]	3.7[−25]	1.4[−25]	−4.4[−23]	−3.3[−23]	−2.0[−23]
$\delta E_{\text{ac Stark}}/\upsilon$ ($E = 8$ V/m)	7.0[−25]	3.5[−25]	2.7[−25]	1.1[−25]	−3.3[−23]	−2.4[−23]	−1.5[−23]
$\delta E^{(2)}_{\text{Zeem}}/\upsilon$ ($B = 10^{-8}$ T)	−6.6[−21]	−5.6[−21]	1.4[−26]	1.2[−21]	−5.2[−23]	8.9[−27]	4.7[−27]
$\delta E^{E1}_{\text{BBR}}/\upsilon$ ($T = 300$ K)	6.6[−21]	3.3[−21]	2.5[−21]	9.0[−22]	−3.0[−19]	−2.3[−19]	−1.4[−19]
$\delta E^{M1}_{\text{BBR}}/\upsilon$ ($T = 300$ K)	2.5[−22]	5.1[−22]	−1.1[−21]	8.4[−22]	4.3[−22]	−7.0[−22]	−3.7[−22]
q (cm^{-1})	12795	16960	22137	28424	23928	29895	41741

are one order larger in the B-like $^{39}K^{14+}$ and Ga-like ions. Consequently, the Q values range from 10^{13} to 10^{14} in the aforementioned fine-structure splitting. The wavelengths of these transitions are also either within or in the border lines of the optical region. Values of these quantities along with the lifetimes of the excited states discussed earlier suggest that the investigated B-like and Ga-like ions mostly satisfy the primary conditions to be undertaken as atomic clocks. The next step is to verify typical orders of major systematic shifts that these ions could undergo when subjected to the clock experiments. From this point of view, we have determined the electric quadrupole moments (Θ), the scalar component (α_0^{E1}) and tensor component (α_2^{E1}) of α^{E1}, and the magnetic dipole polarizabilities (α^{M1}) of the relevant states and given them in Table VI. The Θ values are estimated by evaluating the expectation value of the electric quadrupole operator using our CCSD method. The uncertainty in Θ is estimated to be less than 0.1%, mainly caused by the truncation of higher-order electronic excitation and the empirical parameters in the QED model potential. The α_0^{E1} and α_2^{E1} values for the total angular momentum J with its component M states are determined using the DIRAC packages. The uncertainty in our polarizability data is mainly due to the finite basis set adopted in our calculations and neglected higher-order excited configurations in the FSCCSD method. The error bars in α_0^{E1} and α_2^{E1} are less than 1%. Then, these values for the relevant hyperfine levels are evaluated by multiplying the corresponding angular factors as given in Ref. [59]. Similarly, we estimate the α^{M1} values using the expression

$$\alpha^{M1}(J) = -\frac{2}{3(2J+1)} \sum_{J'} \frac{|\langle J||O^{M1}||J'\rangle|^2}{E_J - E_{J'}}, \qquad (22)$$

where E_J and $E_{J'}$ are the energies of the corresponding J and J' states and matrix elements with double bars mean reduced matrix elements. Contributions to α^{M1} for each state come mostly from the fine-structure splittings in the respective ions. Again, the α^{M1} values of the hyperfine states are estimated using the hyperfine energy levels. It is to be noted that most of the contributions to α^{M1} in a hyperfine level come from the hyperfine manifolds of the respective state. Small changes in the $M1$ dipole polarizabilities will not affect our estimates of typical orders of systematics to the clock frequencies in the considered ions. Since EAMM effects will only introduce small corrections to the $M1$ amplitudes and then to the $M1$ dipole polarizabilities (less than 0.5% in our cases), the EAMM corrections are not taken into account in the α^{M1} values. We consider the uncertainty in our adopted values of the reduced matrix elements $|\langle J||O^{M1}||J'\rangle|$ and the hyperfine constants and estimated the error bar of α^{M1} being around 2%.

Now using the Θ values, we find typical orders of magnitude of the quadrupole shifts in the clock transitions would be around ∼0.1 and ∼10 Hz in the undertaken B-like and Ga-like HCIs, respectively, if the residual electric field gradient is assumed to be about 10^8 V/m^2. These shifts are estimated to be of the order of $10^{-13} \sim 10^{-15}$ in both types of ions. Though these shifts look to be quite large, they can be nullified by carrying out the measurements in all the azimuthal components (M sublevels) of the states and then averaging out. Otherwise, they can be suppressed by choosing a transition like $^2P_{1/2}, F = 0, M_F = 0$ to $^2P_{3/2}, F = 1, M_F = 0$ for the isotopes with nuclear spin $I = 3/2$ like in the $^{33}S^{11+}$, $^{35}Cl^{12+}$, and $^{39}K^{14+}$ ions. Similarly, the first-order Zeeman shift can be canceled out by choosing $M_F = 0$ to $M_F = 0$ clock transitions among the hyperfine levels or averaging over two clock transitions with opposite magnetic quantum numbers M_F. However,

the second-order Zeeman shift can be finite, as formulated by the relation $\delta E^{(2)}_{\rm Zeem} = -\frac{1}{2}\delta\alpha^{M1}B^2$ for the external magnetic field B. By assuming a typical value of $B = 10^{-8}$ T, the fractional differential second-order Zeeman shift, $\delta E^{(2)}_{\rm Zeem}/\nu$, is estimated to be below 10^{-20} in all the proposed clock transitions with the respective frequency ν.

Similarly, another important systematic effect that arises in clock experiments is due to the quadratic Stark shift. This shift for a state $|\gamma, K, M_K\rangle$ can be evaluated by

$$E_{\rm Stark}(\gamma, K, M_K) = -\frac{1}{2}\alpha^{E1}(\gamma, K, M_K)\mathcal{E}^2 = -\frac{1}{2}\alpha_0^{E1}(\gamma, K)\mathcal{E}_z^2 - \frac{1}{4}\alpha_2^{E1}(\gamma, K) \times \frac{\left[3M_K^2 - K(K+1)\right]}{K(2K-1)}\left(3\mathcal{E}_z^2 - \mathcal{E}^2\right), \quad (23)$$

where $\mathcal{E}$ and $\mathcal{E}_z$ are the total electric field strength and the z-directional electric field strength, respectively, and K and M_K denote the angular momentum of either a fine-structure or hyperfine state and its component, respectively. As seen from Table VI, both the scalar and tensor components of α^{E1} in the states associated with the clock transitions in the respective HCIs are quite small, resulting in smaller differential polarizabilities ($\delta\alpha^{E1}$). Using these $\delta\alpha^{E1}$ values and considering a typical value of the electric field strength $\mathcal{E} = 10$ V/m, we estimate the fractional frequency shift due to the dc Stark shifts ($\delta E_{\rm dc\ Stark}/\nu$) to be about $10^{-23} \sim 10^{-25}$ in both the B-like and Ga-like ions. Usually, the clock transitions are probed by locking a laser which can also shift the clock transitions. Such Stark shifts depend on the frequency of the probing laser that can be estimated with the knowledge of dynamic α^{E1} of the states involved. Since $E1$ transitions from the ground state to most of the low-lying excited states are in the XUV range, the dynamic α^{E1} values of the above states can be similar to their static values. Thus, considering the static values of α^{E1} and typical power of a probe laser as 0.1W/m^2 that corresponds to an electric field of 8.0 V/m, we estimate the fractional ac Stark shift of the clock transitions due to the probe light to be about $10^{-23} \sim 10^{-25}$.

Using the differential scalar $E1$ polarizabilities ($\delta\alpha_0^{E1}$), we also estimate the BBR shifts of the clock transitions with respect to the room temperature as [60,61]

$$\delta E^{E1}_{\rm BBR} = -\frac{1}{2}(831.9\ \text{V/m})^2\left[\frac{T(\text{K})}{300}\right]^4\delta\alpha_0^{E1}, \quad (24)$$

where T(K) denotes the temperature at which clocks can operate. This also shows that the fractional frequency shift due to the BBR shifts ($\delta E^{E1}_{\rm BBR}/\nu$) will be around $10^{-21} \sim 10^{-22}$ in the clock transitions of the B-like $^{33}S^{11+}$, $^{35}Cl^{12+}$, $^{40}Ar^{13+}$, and $^{39}K^{14+}$ ions, while they will be of the order of 10^{-19} in the clock transitions of the Ga-like Nb^{10+}, Mo^{11+}, and Ru^{13+} HCIs. Since the actual experiments are carried out at lower temperatures than the room temperature, the fractional frequency shifts ($\delta E^{E1}_{\rm BBR}/\nu$) due to the BBR shift can also be below the 10^{-19} level even in the above Ga-like ions. Similarly, the BBR shift due to the $M1$ channel of the $|\eta\rangle$ state, say, can be estimated using the formula [62]

$$\Delta E^{M1}_{\rm BBR} = -\frac{\mu_0(K_BT)^2}{\pi^2(c\hbar)^3}\sum_\beta\left[|\langle\eta||O^{M1}||\beta\rangle|^2\omega_{\eta\beta} \times \int_0^\infty d\omega\frac{\omega^3}{\left(\omega_{\eta\beta}^2 - \omega^2\right)(\exp^{\hbar\omega/K_BT} - 1)}\right], \quad (25)$$

where μ_0, K_B, $\hbar$, and c are the magnetic permeability, Boltzmann's constant, Plank's constant, and the speed of light, respectively. The respective expressions of $\langle\eta||O^{M1}||\beta\rangle$ for the fine-structure and hyperfine levels are calculated to estimate the $M1$ BBR shifts of the states involved with the clock transitions. This also gives the fractional clock frequency shifts of about $10^{-21} \sim 10^{-22}$ in both the B-like and Ga-like HCIs at the room temperature.

We calculate the relativistic α_e variation-sensitive coefficient q by defining

$$\omega_t = \omega_0 + qx, \quad (26)$$

where ω_0 is the angular frequency of the transition for the present-day value of the fine-structure constant $\alpha_e(0)$ and ω_t is the angular frequency of the transition corresponding to another value of $\alpha_e(t)$ at time t such that $x = [\alpha_e(t)/\alpha_e(0)]^2 - 1 \approx 2[\alpha_e(t) - \alpha_e(0)]/\alpha_e(0)$. We have given values q for the clock transitions using our CCSDpT method in Table VI and found they are quite large. This suggests that if the investigated B-like and Ga-like HCIs are undertaken for the clock experiments in the future then it is possible to probe on the possible temporal variation of α_e.

IV. CONCLUSION

We have investigated energies, magnetic dipole transition-matrix elements, hyperfine-structure constants, electric quadrupole moments, and dipole polarizabilities of the $2p\,^2P_{1/2}$ and $2p\,^2P_{3/2}$ states in the B-like S^{11+}, Cl^{12+}, Ar^{13+}, and K^{14+} ions and the $4p\,^2P_{1/2}$ and $4p\,^2P_{3/2}$ states in the Ga-like Nb^{10+}, Mo^{11+}, Tc^{12+}, and Ru^{13+} ions by employing the relativistic coupled-cluster methods. We have analyzed contributions to these quantities from the Dirac-Coulomb Hamiltonian, Breit interaction, and lower-order QED effects. Corrections from the QED effects are estimated using the first-order perturbation approach and using the self-consistent procedure. We find apparent changes in the results from both the procedures. It is also seen that correlation effects reduce the QED corrections in the estimation of energies. Lifetimes of the upper states are estimated using the calculated magnetic dipole matrix elements. They are found to be in good agreement with the other available calculations and experimental values. A breakdown of various contributions to hyperfine-structure constants is also given. Using the aforementioned properties, we have estimated the electric quadrupole shifts, the second-order Zeeman shifts, the dc Stark shifts, the ac Stark shifts due to the probe laser, and the BBR shift of the $M1$ transition between the fine-structure splittings in the ground configurations of the above HCIs. This

shows that typical orders of magnitude of these systematic shifts can be suppressed below the 10^{-19} level. Since the wavelengths and quality factors of these transitions already meet the criteria to undertake for clock frequency measurements, realization of the low systematic shifts now boosts such chances further. In fact, these clock transitions can be used for probing possible temporal variation of the fine-structure constant because their relativistic sensitivity coefficients are found to be large.

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