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# Scrutinizing Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions for atomic clocks with uncertainties below the $10^{-19}$ level

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We investigate the transition between the fine structure levels of the ground state, $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$, of the highly charged Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions for frequency standards. To comprehend them as prospective atomic clocks, we determine their transition wavelengths, quality factors, and various plausible systematics during the measurements. Since most of these ions have nuclear spin $I = 3/2$, uncertainties due to dominant quadrupole shifts can be evaded in the $F = 0$ hyperfine level of the $3p\,^2P_{3/2}$ state. Other dominant systematics such as quadratic Stark and black-body radiation shifts have been evaluated precisely demonstrating the feasibility of achieving high accuracy, below $10^{-19}$ fractional uncertainty, atomic clocks using the above transitions. Moreover, relativistic sensitivity coefficients are determined to find out the aptness of these proposed clocks to investigate possible temporal variation of the fine structure constant. To carry out these analysis, a relativistic coupled-cluster method considering Dirac-Coulomb-Breit Hamiltonian along with lower-order quantum electrodynamics interactions is employed and many spectroscopic properties are evaluated. These properties are also of immense interest for astrophysical studies.

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## I. INTRODUCTION

It is truly impressive to achieve today's high-precision optical frequency standards with uncertainties about $10^{-18}$. This milestone has been reached in a single Al$^+$ ion in 2010 [1], optical lattice clock using Yb atoms in 2013 [2], and optical lattice clock using Sr atoms in 2014 [3]. It is, however, imperative to further improve uncertainties of frequency standards by at least two orders as demanded in several areas of science and technology such as navigation systems [4,5], telecommunications [6], telescopes [7], testing fundamental physics [8,9], etc.; especially operating in the optical regime. Intending to attain accuracy below $10^{-19}$, many alternatives have been proposed, which include considering a nuclear transition between the isomeric states of $^{229}$Th resonating with an atomic transition having similar energy range [10], rovibrational transitions in the one-electron molecular H$_2{}^+$ and HD$^+$ ions [11,12]. The recent suggestions are to consider highly charged ions (HCIs) for building atomic clocks with unprecedented uncertainties [13,14]. HCIs generally have greatly reduced sizes, which minimizes environmental perturbations in order to realize the least systematics compared to neutral atoms and singly charged ions. Laser trapped and cooled ions are advantageous for precision measurements as they provide longer interrogation time and less Doppler shifts. In addition, the electronic orbitals in HCIs are shrunk typically by a factor $Z_i$, wherein $Z_i$ is the residual charge of the ion related to the nuclear charge $Z$ and the total number of electrons $N_e$ as $Z_i = Z - N_e$. Another key advantage of HCI clocks is the high sensitivity of these ions to probe time and space variation of the fine structure constant $\alpha_e$, which has important applications in testing new physics.

Forbidden transitions are usually suitable for consideration as frequency standards. Among the forbidden channels, electric quadrupole (E2) and electric octupole (E3) transitions are preferable as degree of forbiddeness in these transitions are more owing to the requirement of higher powers in wavelength in the denominator for evaluating transition probabilities of the respective channel. This may be advantageous for attaining narrow linewidth of the clock transition, but sometime it may not be very useful. For example, the octupole forbidden $[4f^{14}6s]\,^2S_{1/2} \rightarrow [4f^{13}6s^2]\,^2F_{7/2}$ transition in Yb$^+$ has very narrow linewidth but owing to very long lifetime of its $[4f^{13}6s^2]\,^2F_{7/2}$ state (lifetime $\gtrsim$6 yrs), it is unsuitable to be considered for the interrogation time. Thus, its probe interaction time ($\sim$10 s) instead has been used [15] during the clock frequency measurement. In this view, consideration of magnetic dipole (M1) forbidden transitions could be more pertinent for the clock transitions. In fact, Yudin *et al.* have also demonstrated the aptness of M1 transitions in the H-like and alkali atomlike HCIs for atomic clocks [16]. Laser trapping of HCIs have already been demonstrated in Refs. [17,18]; but one of the imminent problems with these ions is absence of a suitable allowed electric-dipole (E1) low-lying transition to the excited states of the clock transitions in the optical range that can be used for cooling and detection of the ions. Alternately, recently developed techniques to cool HCIs would be very useful in these clocks [19].

In the past few years, various HCIs have been proposed for the development of atomic clocks and the search for $\alpha$ variation. Derevianko *et al.*, have also identified many HCIs with the $4f^{12}$ ground-state configuration to be especially promising for precision timekeeping [13,14]. They have recommended isoelectronic ions having electronic configurations

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of palladium and cadmium plus twelve $4f$ electrons starting from $\mathrm{Re}^{17+}$ for atomic clocks. Berengut *et al.*, Safronova *et al.*, and Nandy and Sahoo have identified more than twenty states involving core $s$ and $f$ orbitals in the Ag-like, In-like, Cd-like, Sn-like, and Sm-like ions for this purpose [20–24]. Transitions involving electron holes were shown to have frequencies within the range of optical atomic clocks due to the energy level crossing, indicating small systematic errors in the frequency measurements, and highly sensitive to temporal variation of $\alpha_e$. One good example is the Nd-like $\mathrm{Ir}^{17+}$ [25], which offers narrow lines between three electronic configurations $4f^{14}$, $4f^{13}5s$, and $4f^{12}5s^2$ with the highest ever predicted relativistic sensitive coefficients in a stable atomic system. Other ions such as In-like $\mathrm{Sm}^{13+}$ ions, Sn-like $\mathrm{Pr}^{9+}$, and Sm-like $\mathrm{Pt}^{17+}$ ions are found to be particularly attractive in the above studies, because the selected transitions in these ions are within the optical range. Owing to crossings in the $5s$ and $4f$ levels of the Nd-like $\mathrm{W}^{14+}$, $\mathrm{Re}^{15+}$, $\mathrm{Os}^{16+}$, $\mathrm{Ir}^{17+}$, and $\mathrm{Pt}^{18+}$ ions are demonstrated as sensitive to probe variation in $\alpha_e$ and possible optical frequency standards [26]. Following this work, energy level crossings for the first six row elements in the period table have been systematically analyzed very recently by Yu *et al.* suggesting longer lifetimes of the excited states and most of the transitions among low-lying states are lying in the optical range [27]. These candidates are suitable for carrying out high-precision experiments. It is also argued that transitions between the interconfigurations of the $4f^65s$ and $4f^55s^2$ states of the $\mathrm{Ho}^{14+}$ ion would be the most suitable for atomic clocks [28]. Since both the states have strongly interacting open-shell configurations and near degeneracy, the transition among these states gives a very narrow linewidth. Moreover, this ion seems to be advantageous for trapping, cooling, and detection. However, it is strenuous to perform precise calculations in such an open-shell system.

In this paper, we carry out a detailed high-precision study of various spectroscopic properties of many low-lying states of the Al-like $^{51}\mathrm{V}^{10+}$, $^{53}\mathrm{Cr}^{11+}$, $^{55}\mathrm{Mn}^{12+}$, $^{57}\mathrm{Fe}^{13+}$, $^{59}\mathrm{Co}^{14+}$, $^{61}\mathrm{Ni}^{15+}$, and $^{63}\mathrm{Cu}^{16+}$ ions. Calculations have been performed using a relativistic coupled-cluster (RCC) method in the Fock-space framework by considering Dirac-Coulomb-Breit (DCB) Hamiltonian along with lower order corrections due to quantum electrodynamics (QED) effects. We present excitation energies, transition wavelengths, reduced E1, M1, and E2 matrix elements transitions, lifetimes, hyperfine structure constants, and Lande $g_J$ factors of many low-lying states using this method in these ions. Relativistic sensitivity coefficients are also estimated by evaluating excitation energies using two arbitrary values of $\alpha_e$. We have also used another RCC method in the equation-of-motion framework (EOMCC method) to determine differential static polarizabilities of the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition in the finite-gradient approach. Using these properties we demonstrate that most of these M1 transitions are in the optical region, lifetimes of the $3p\,^2P_{3/2}$ state in the respective ions are sufficiently longer for performing high-precision measurements and many dominant systematic shifts are suppressed paving the way for suitable optical frequency standards with unprecedented uncertainty below $10^{-19}$. Many of the above-mentioned properties also have implications in astrophysics and plasma diagnostic processes [29–32].

## II. METHODS OF CALCULATIONS

To account both the relativistic and electron correlation effects accurately in the considered HCIs, we use the DCB Hamiltonian along with the lower order quantum electrodynamics (QED) corrections, which in atomic unit (a.u.) is given by

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

with $\boldsymbol{\alpha}$ and $\beta$ are the usual Dirac matrices, $V_n(r)$ represents for the nuclear potential and $V_{QED}(r) = V_U(r) + V_{WK}(r) + V_{SE}^{ef} + V_{SE}^{mg}$ corresponds to the QED interaction potentials. We account the QED corrections approximately as described by Flambaum and Ginges [33] considering the Fermi nuclear charge distributions as demonstrated in our previous work [34]. In this formalism, the lower-order vacuum polarization (VP) effects are included using the Uehling [$V_U(r)$] and Wichmann-Kroll [$V_{WK}(r)$] potentials, which are given by

$$V_U(r) = -\frac{2\alpha^2}{3r}\int_0^\infty dx\; x\; \rho_n(x)\int_1^\infty dt\sqrt{t^2-1} \times \left(\frac{1}{t^3} + \frac{1}{2t^5}\right)[e^{-2ct|r-x|} - e^{-2ct(r+x)}] \quad (2)$$

and

$$\begin{aligned} V_{WK}(r) = &-\frac{8Z^2\alpha^4}{9r}(0.092)\int_0^\infty dx\; x\; \rho_n(x) \\ &\times (0.22\{\arctan[1.15(-0.87 + 2c|r-x|)] \\ &- \arctan[1.15(-0.87 + 2c(r+x))]\} \\ &+ 0.22\{\arctan[1.15(0.87 + 2c|r-x|)] \\ &- \arctan[1.15(0.87 + 2c(r+x))]\} \\ &- 0.11\{\ln[0.38 - 0.87c|r-x| + c^2(r-x)^2] \\ &- \ln[0.38 - 0.87c(r+x) + c^2(r+x)^2]\} \\ &+ 0.11\{\ln[0.38 + 0.87c|r-x| + c^2(r-x)^2] \\ &- \ln[0.38 + 0.87c(r+x) + c^2(r+x)^2]\}), \quad (3) \end{aligned}$$

with the atomic number of the system $Z$. Similarly, contribution from the self-energy (SE) interaction is accounted by including interaction potentials in two parts. First as contribution coming from the electric form factor and given by

$$\begin{aligned} V_{SE}^{ef}(r) = &-A(Z)(Z\alpha)^4 e^{-Zr} + \frac{B(Z,r)\alpha^2}{r}\int_0^\infty dx x\rho_n(x) \\ &\times \int_1^\infty dt\frac{1}{\sqrt{t^2-1}}\left\{\left(\frac{1}{t} - \frac{1}{2t^3}\right)\right. \\ &\times \left.\left[\ln(t^2-1) + 4\ln\left(\frac{1}{Z\alpha} + \frac{1}{2}\right)\right] - \frac{3}{2} + \frac{1}{t^2}\right\} \\ &\times [e^{-2ct|r-x|} - e^{-2ct(r+x)}]. \quad (4) \end{aligned}$$

The other contribution is coming from the magnetic form factor and given by

$$V_{SE}^{mg}(r) = \frac{i\alpha}{4\pi c}\boldsymbol{\gamma}\cdot\nabla_r \int_0^\infty d^3x\; \rho_n(x) \times \left[\left(\int_1^\infty dt\, \frac{e^{-2tcR}}{Rt^2\sqrt{t^2-1}}\right) - \frac{1}{R}\right]. \tag{5}$$

Here, $A(Z) = 0.074 + 0.35Z\alpha$, $B(Z,r) = \{1.071 - 1.97[(Z-80)\alpha]^2 - 2.128[(Z-80)\alpha]^3 + 0.169[(Z-80)\alpha]^4\}cr/[cr + 0.07(Z\alpha)^2]$ and $R = |\mathbf{r} - \mathbf{x}|$.

For evaluating both the nuclear potential and QED corrections, we consider the Fermi-charge distribution defined by

$$\rho_n(r) = \frac{\rho_0}{1 + e^{(r-b)/a}}, \tag{6}$$

for the normalization factor $\rho_0$, the half-charge radius $b$ and $a = 2.3/4(\ln 3)$ is related to the skin thickness. We have determined $b$ using the relation

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

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

$$r_{rms} = 0.836A^{1/3} + 0.570 \tag{8}$$

in $fm$ for the atomic mass $A$.

In the RCC theory ansatz, the wave functions of the considered states are expressed as

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle, \tag{9}$$

where $T$ and $S_v$ are the RCC excitation operators that excite electrons from $|\Phi_0\rangle$ and $|\Phi_v\rangle$, that are the Dirac-Hartree-Fock (DHF) wave functions of the core $[2p^6 3s^2]$ and of this core along with a valence orbital $v$, respectively, to the virtual space. We consider here the Hamiltonian given in Eq. (1) for the self-consistent calculations. For computational simplicity, we define $|\Phi_v\rangle$ by appending the respective valence orbital with $|\Phi_0\rangle$ as $|\Phi_v\rangle = a_v^\dagger|\Phi_0\rangle$ for carrying out calculations. In this work, we have considered only the single and double excitations in the RCC theory (CCSD method approximation) by defining

$$T = T_1 + T_2 \quad \text{and} \quad S_v = S_{1v} + S_{2v}. \tag{10}$$

The amplitudes of these RCC operators are evaluated using the following equations

$$\langle\Phi_0^*|\overline{H}|\Phi_0\rangle = 0 \tag{11}$$

and

$$\langle\Phi_v^*|(\overline{H} - \Delta E_v)S_v|\Phi_v\rangle = -\langle\Phi_v^*|\overline{H}_N|\Phi_v\rangle, \tag{12}$$

where $|\Phi_0^*\rangle$ and $|\Phi_v^*\rangle$ are the excited-state configurations, here up to doubles, with respect to the DHF states $|\Phi_0\rangle$ and $|\Phi_v\rangle$, respectively, and $\overline{H} = (He^T)_l$ with subscript $l$ represents for the linked terms only. Here $\Delta E_v$ is the attachment energy of the electron of the valence orbital $v$. We evaluate $\Delta E_v$ by

$$\Delta E_v = \langle\Phi_v|\overline{H}\{1 + S_v\}|\Phi_v\rangle - \langle\Phi_0|\overline{H}|\Phi_0\rangle. \tag{13}$$

After obtaining attachment energies of electrons for different states, excitation energy (EE) between two given states is evaluated by taking difference between their respective attachment energies.

It can be noted that the nonlinear terms containing RCC operators in Eqs. (11), (12), and (13) account some contributions from the triples and quadrupoles excitations even in the CCSD method approximation. In order to estimate contributions from the neglected triple excitations in the CCSD method, we construct triple excitation operator perturbatively involving the valence orbital as

$$S_{3v}^{\text{pert}} = \sum_{ab,pqr} \frac{HT_2 + HS_{2v}}{\epsilon_v + \epsilon_a + \epsilon_b - \epsilon_p - \epsilon_b - \epsilon_r}, \tag{14}$$

where $a,b$ and $p,q,r$ represent indices for the occupied and unoccupied orbitals, respectively, and $\epsilon$s are their corresponding single-particle orbital energies. We consider this as part of the $S_v$ operator in Eq. (13) to estimate the leading-order neglected triple excitation contributions and give them as the possible sources of uncertainties to the energies.

After obtaining amplitudes of the RCC operators using the above described equations,, the transition matrix element of an operator $O$ between the states $|\Psi_i\rangle$ and $|\Psi_f\rangle$ is evaluated using the expression

$$\langle\Psi_f|O|\Psi_i\rangle = \frac{\langle\Phi_f|\tilde{O}_{fi}|\Phi_i\rangle}{\sqrt{\langle\Phi_f|\{1 + \tilde{N}_f\}|\Phi_f\rangle\langle\Phi_i|\{1 + \tilde{N}_i\}|\Phi_{\rangle}}}, \tag{15}$$

where $\tilde{O}_{fi} = \{1 + S_f^\dagger\}e^{T^\dagger}Oe^T\{1 + S_i\}$ and $\tilde{N}_{k=f,i} = \{1 + S_k^\dagger\}e^{T^\dagger}e^T\{1 + S_k\}$. For determining expectation value of an operator $O$, the same expression is calculated considering $|\Psi_i\rangle = |\Psi_f\rangle$. As can be seen, it involves two nonterminating series in the numerator and denominator in the above expression, which are $e^{T^\dagger}Oe^T$ and $e^{T^\dagger}e^T$, respectively. As described in our previous works [35–37], we adopt iterative procedures to account contributions from these nontruncative series.

Since Al-like ions have open-shell configurations with three electrons in the outermost orbitals, contributions not only the singly excited states but also from the doubly and higher excited states and core correlation will be important for accurate calculations of dipole polarizabilities ($\alpha$) of the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states of the considered ions. Thus, a sum-over-states approach, in which the E1 matrix elements of only the dominant contributing singly excited states are accounted rigorously and other contributions are included employing only lower-order many-body methods, is not suitable here. Instead, we have applied an EOMCC method with singles and doubles excitation approximation (EOMCCSD method) in the finite gradient approach that has been reported in Ref. [38] using the DIRAC program and Dyall's relativistic basis functions [39,40].

The energy of the $|\gamma,J,M_J\rangle$ state of an atom placed in an isotropic electric field with strength in the $z$ direction $\mathcal{E}_z$ changes as

$$E_{\gamma,J,M_J}(\mathcal{E}_z) = E_{\gamma,J,M_J}(0) - \frac{\alpha_{zz}(\gamma,J,M_J)}{2}\mathcal{E}_z^2 - \ldots, \tag{16}$$

where $E_{\gamma,J,M_J}(\mathcal{E}_z)$ and $E_{\gamma,J,M_J}(0)$ are the total energies of the state in the absence and the presence of the field, respectively, and $\alpha_{zz}(\gamma,J,M_J)$ is its $z$ component of $\alpha$. It is obvious from the above expression that the static polarizability can be evaluated as the second derivative of $E_{\gamma,J,M_J}(\mathcal{E}_z)$ with respect to $\mathcal{E}_z$. Following this approach, we evaluate $\alpha_{zz}(\gamma,J,M_J)$ of the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states of the Al-like ions by numerical differentiation. The total energies were computed with and without the perturbation taking the interaction Hamiltonian $-D\mathcal{E}_z$, where $D$ is the induced electric dipole moment. We have also performed calculations with four different numbers of atomic orbitals using the Dyall's uncontracted correlation-consistent double-, triple-, and quadruple-$\zeta$ basis functions [40] (denoted by $X = 2, 3,$ and 4, respectively) from DIRAC code [39]. Electron correlation effects are incorporated by employing a singles and doubles approximated EOMCC (EOMCCSD) method to calculate the atomic wave functions and energies accurately. A description of this method in the calculation of atomic dipole polarizability is given in Ref. [38]. After obtaining $\alpha_{zz}(\gamma,J,M_J)$ values, we determine scalar polarizability by using the relation $\alpha^{(0)}(\gamma,J) = \Sigma_{M_J}\alpha_{zz}(\gamma,J,M_J)/(2J+1)$ and tensor polarizability of the $3p\,^2P_{3/2}$ state by $\alpha^{(2)}(\gamma,J) = \alpha_{zz}(\gamma,J,J) - \alpha^{(0)}(\gamma,J)$.

## III. RESULTS AND DISCUSSION

There are no experimental data or other theoretical calculations are available for the spectroscopic properties that are of our interest for investigating suitability of the considered ions as atomic clocks. To validate our calculations, we present EEs of many of the excited states of the considered Al-like ions in Table I. We compare our CCSD results with the values quoted in the National Institute of Science and Technology (NIST) database [41]. We have also given values obtained from the DHF method and considering the second-order many-body perturbation theory [MBPT(2) method]. The uncertainties in our CCSD values are quoted in the above table mainly due to the neglected triple excitations as discussed before. Though QED corrections are estimated approximately, we anticipate our calculations can be improved further by accounting QED corrections more accurately. As can be seen from this table, the CCSD values are very close to the NIST data and agree within 1% level. The fine structure splittings are observed to be large in the DHF and MBPT(2) methods, while the CCSD method brings them down close to the NIST data. However, the DHF results are found to be smaller than the NIST data, but the MBPT(2) method gives larger values for the other excited state. Then, the CCSD method cancels most of the correlation contributions from the MBPT(2) method to obtain values closer to the NIST data. For some states NIST data are unavailable, we expect that our calculations in these states are equally reliable like the other states. Importantly, it can be noticed that the wavelengths ($\lambda$), determined by taking inverse of the EEs, corresponding to the fine structure splitting of the ground state in all these considered ions are either in the optical region or close to the optical range. The $\lambda$ values of these transitions are also given in nm in Table II to highlight their values and for further uses. Particularly the transitions in the heavier ions such as $^{55}\mathrm{Mn}^{12+}$, $^{57}\mathrm{Fe}^{13+}$, $^{59}\mathrm{Co}^{14+}$, and $^{61}\mathrm{Ni}^{15+}$ seem to be in the optical region and can be used for frequency standards. Below, we also discuss about other properties of these ions and advantages of considering their fine structure splitting as possible frequency standards.

To ascertain the feasibility of considering the ions of our interest for atomic clocks, it is imperative to investigate some of the very crucial properties such as transition frequencies ($\nu$), which can be used as clock frequencies, transition probabilities ($A_{fi}$), lifetimes ($\tau_f$) of the excited states and natural line widths ($\Gamma$), and quality factors ($Q$) of the corresponding transitions. For this purpose we determine these properties of the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition in all the considered ions along with the transition probabilities and lifetimes of some of the other low-lying excited states that knowledge could also be useful in clock experiments such as populating more electrons to the $3p\,^2P_{3/2}$ state for reducing statistical uncertainty. The transition probabilities of the $f \rightarrow i$ transition due to the first three lower-order channels are evaluated using the expressions

$$A^{E1}_{fi} = \frac{2.02613 \times 10^{18}}{(2J_f+1)\lambda^3_{fi}} S^{E1}_{fi}, \tag{17}$$

$$A^{M1}_{fi} = \frac{2.69735 \times 10^{13}}{(2J_f+1)\lambda^3_{fi}} S^{M1}_{fi} \tag{18}$$

and

$$A^{E2}_{fi} = \frac{1.11995 \times 10^{18}}{(2J_f+1)\lambda^5_{fi}} S^{E2}_{fi}, \tag{19}$$

where the transition wavelength $\lambda_{fi}$ is used in Å, $J$ represents angular momentum of the state, $S^{O}_{fi} = |\langle J_f||\mathbf{O}||J_i\rangle|^2$ known as the line strength due to the transition operator $O$ of the corresponding channel that are used in atomic units (a.u.). The transition strengths are evaluated by calculating the reduced matrix element $\langle J_f||\mathbf{O}||J_i\rangle$ of $O$ using Eq. (15). Accumulating all possible transition probabilities from the $f$ state, the lifetime ($\tau_f$) of this state is determined by

$$\tau_f = \frac{1}{\sum_{i,O} A^{O}_{fi}}. \tag{20}$$

These values are obtained in second ($s$). In Table II, we present $\lambda$, $O$, and $A$ values for different transitions and channels from the $3p\,^2P_{3/2}$, $3d\,^2D_{3/2}$, and $3d\,^2D_{5/2}$ states. These values are expected to be within 2% accuracy as our calculated energies given in Table I are very accurate and the uncertainties to the transition amplitudes due to neglected triple excitations are found to be negligibly small. It can be seen from Table II, the allowed transition probabilities in the $3d\,^2D_{3/2}$ and $3d\,^2D_{5/2}$ states are very large and entirely responsible in the determination of the lifetimes of these states. However, the M1 channel among the forbidden channels place the dominant role estimating the lifetimes of the $3p\,^2P_{3/2}$ state. The lifetime of this state decreases almost by an order while going down from the Al-like $^{51}\mathrm{V}^{10+}$ to $^{63}\mathrm{Cu}^{16+}$ heavier ions. This suggests it has to be carefully decided about an ion of medium size having wavelength of the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition in the optical region and the lifetime of the $3p\,^2P_{3/2}$ state has to be sufficiently large during which $\nu$ can be measured within the required accuracy. The other important factors that are also relevant for carrying out measurement of $\nu$ precisely are the small $\Gamma$ value and large $Q$ value. We estimate $\Gamma$ and $Q$ values of the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition in the considered ions using the relations $\Gamma = 1/(2\pi \times \tau)$ in Hz and $Q = \nu/\Gamma$, respectively. From the values quoted

TABLE I. Excitation energies (in cm$^{-1}$) of low-lying states in the Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions relative to their ground states obtained using the DHF, MBPT(2), and CCSD methods. They are compared with the NIST database and differences between the CCSD and NIST values are given as "DIFF" in the last column (in %). The uncertainties in our CCSD values are quoted in parentheses due to the neglected triple excitations.

| Ion | Level | DHF | MBPT(2) | CCSD | NIST | DIFF |
|---|---|---|---|---|---|---|
| $^{51}$V$^{10+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 10123 | 10991 | 9727 (87) | 9696 | 0.32 |
| | $3d\,^2D_{3/2}$ | 363942 | 313478 | 380434 (4325) | 376897 | 0.94 |
| | $3d\,^2D_{5/2}$ | 364071 | 319060 | 381140 (4732) | 377650 | 0.92 |
| | $4s\,^2S_{1/2}$ | 935151 | 941007 | 936348 (1049) | 939500 | 0.34 |
| | $4p\,^2P_{1/2}$ | 1026047 | 1032081 | 1026596 (583) | | |
| | $4p\,^2P_{3/2}$ | 1029526 | 1035821 | 1029937 (545) | | |
| | $4d\,^2D_{3/2}$ | 1146444 | 1155386 | 1146927 (242) | 1147240 | 0.03 |
| | $4d\,^2D_{5/2}$ | 1146915 | 1155804 | 1147411 (239) | 1147770 | 0.03 |
| | $5s\,^2S_{1/2}$ | 1385307 | 1393379 | 1396537 (255) | | |
| $^{53}$Cr$^{11+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 12791 | 13667 | 12278 (68) | 12261 | 0.13 |
| | $3d\,^2D_{3/2}$ | 393834 | 345561 | 412317 (4426) | 408640 | 0.90 |
| | $3d\,^2D_{5/2}$ | 395388 | 346529 | 413297 (4927) | 409741 | 0.87 |
| | $4s\,^2S_{1/2}$ | 1087451 | 1093006 | 1086782 (1576) | | |
| | $4p\,^2P_{1/2}$ | 1186958 | 1192674 | 1186952 (662) | | |
| | $4p\,^2P_{3/2}$ | 1191424 | 1197397 | 1213711 (615) | | |
| | $4d\,^2D_{3/2}$ | 1318883 | 1324852 | 1318692 (272) | 1319000 | 0.02 |
| | $4d\,^2D_{5/2}$ | 1319532 | 1325651 | 1319359 (270) | 1319660 | 0.02 |
| | $5s\,^2S_{1/2}$ | 1610179 | 1612426 | 1619589 (422) | | |
| $^{55}$Mn$^{12+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 15942 | 16818 | 15292 (45) | 15295 | 0.20 |
| | $3d\,^2D_{3/2}$ | 424998 | 373481 | 444535 (4511) | 445322 | 0.86 |
| | $3d\,^2D_{5/2}$ | 427081 | 374624 | 445855 (5123) | 446836 | 0.82 |
| | $4s\,^2S_{1/2}$ | 1250787 | 1255623 | 1252347 (303) | | |
| | $4p\,^2P_{1/2}$ | 1358910 | 1364343 | 1358348 (740) | | |
| | $4p\,^2P_{3/2}$ | 1363625 | 1369358 | 1363734 (684) | | |
| | $4d\,^2D_{3/2}$ | 1502543 | 1508130 | 1501680 (305) | 1502090 | 0.03 |
| | $4d\,^2D_{5/2}$ | 1503412 | 1509169 | 1502575 (303) | 1503060 | 0.03 |
| | $5s\,^2S_{1/2}$ | 1850885 | 1835428 | 1859532 (538) | | |
| $^{57}$Fe$^{13+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 19629 | 20501 | 18825 (18) | 18852 | 0.14 |
| | $3d\,^2D_{3/2}$ | 456534 | 402079 | 477190 (4583) | 473223 | 0.84 |
| | $3d\,^2D_{5/2}$ | 459262 | 403426 | 478921 (5322) | 475202 | 0.78 |
| | $4s\,^2S_{1/2}$ | 1425241 | 1459184 | 1426004 (223) | 1435020 | 0.63 |
| | $4p\,^2P_{1/2}$ | 1541964 | 1547139 | 1540846 (819) | 1568840 | 1.78 |
| | $4p\,^2P_{3/2}$ | 1548984 | 1554403 | 1547540 (750) | 1574010 | 1.68 |
| | $4d\,^2D_{3/2}$ | 1697528 | 1702809 | 1695986 (340) | 1695980 | 0.0003 |
| | $4d\,^2D_{5/2}$ | 1698664 | 1704139 | 1697156 (339) | 1697290 | 0.008 |
| | $5s\,^2S_{1/2}$ | 2107708 | 2129982 | 2115860 (636) | | |
| $^{59}$Co$^{14+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 23912 | 24773 | 22932 (13) | 22979 | 0.20 |
| | $3d\,^2D_{3/2}$ | 488535 | 431422 | 510385 (4635) | 506230 | 0.82 |
| | $3d\,^2D_{5/2}$ | 492041 | 433006 | 512602 (5525) | 508793 | 0.75 |

TABLE I. *(continued.)*

| Ion | Level | DHF | MBPT(2) | CCSD | NIST | DIFF |
|---|---|---|---|---|---|---|
| | $4s\,^2S_{1/2}$ | 1610870 | 1617750 | 1611098 (428) | | |
| | $4p\,^2P_{1/2}$ | 1736208 | 1741135 | 1734524 (898) | | |
| | $4p\,^2P_{3/2}$ | 1744842 | 1750010 | 1742746 (815) | | |
| | $4d\,^2D_{3/2}$ | 1903908 | 1908903 | 1901667 (379) | 1901800 | 0.01 |
| | $4d\,^2D_{5/2}$ | 1905368 | 1910581 | 1903171 (378) | 1903600 | 0.02 |
| | $5s\,^2S_{1/2}$ | 2381096 | 2399116 | 2388851 (725) | | |
| $^{61}$Ni$^{15+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | 0 |
| | $3p\,^2P_{3/2}$ | 28852 | 29695 | 27674 (47) | 27760 | 0.31 |
| | $3d\,^2D_{3/2}$ | 521092 | 461568 | 544222 (4664) | 539839 | 0.81 |
| | $3d\,^2D_{5/2}$ | 525523 | 463431 | 547001 (5734) | 543107 | 0.72 |
| | $4s\,^2S_{1/2}$ | 1807686 | 1813910 | 1807530 (561) | | |
| | $4p\,^2P_{1/2}$ | 1941695 | 1946375 | 1939427 (978) | | |
| | $4p\,^2P_{3/2}$ | 1952203 | 1957100 | 1949426 (881) | | |
| | $4d\,^2D_{3/2}$ | 2121720 | 2126436 | 2118756 (419) | 2119400 | 0.03 |
| | $4d\,^2D_{5/2}$ | 2123566 | 2128526 | 2120656 (420) | 2121100 | 0.02 |
| | $5s\,^2S_{1/2}$ | 2671229 | 2687907 | 2678589 (810) | | |
| $^{63}$Cu$^{16+}$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | 0 | |
| | $3p\,^2P_{3/2}$ | 34512 | 35331 | 33113 (86) | 33239 | 0.38 |
| | $3d\,^2D_{3/2}$ | 554294 | 492576 | 578807 (4669) | 615888 | 0.81 |
| | $3d\,^2D_{5/2}$ | 557796 | 494768 | 582221 (5948) | 578243 | 0.69 |
| | $4s\,^2S_{1/2}$ | 2015676 | 2021576 | 2015155 (666) | 2026000 | 0.54 |
| | $4p\,^2P_{1/2}$ | 2158434 | 2162868 | 2155563 (892) | | |
| | $4p\,^2P_{3/2}$ | 2171106 | 2175736 | 2167612 (1062) | | |
| | $4d\,^2D_{3/2}$ | 2351009 | 2355451 | 2347297 (946) | 2336000 | 0.48 |
| | $4d\,^2D_{5/2}$ | 2353310 | 2358024 | 2349664 (463) | 2342000 | 0.33 |
| | $5s\,^2S_{1/2}$ | 2977918 | 2993954 | 2984841 (464) | | |

TABLE II. Transition wavelength λ (in nm), reduced transition matrix elements ($O$) due to different channels (in a.u.), and transition rates $A_{fi}$ (in $s^{-1}$) and lifetimes $\tau_f$ (in $s$) of the first three low-lying excited states $3p\,^2P_{3/2}$, $3d\,^2D_{3/2}$, and $3d\,^2D_{5/2}$ states of the Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions obtained using the CCSD method. The estimated natural linewidth Γ (in Hz), transition frequency $\nu$ (in Hz) and qualify factor $Q = \nu/\Gamma$ for the proposed M1 $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ clock transitions of the respective ions are also given. Numbers given in square brackets represent powers of 10. Wavelengths of clock transitions are highlighted in bold font.

| Ion | Level | Transition | λ | $O$ | $A_{fi}$ | $\tau_f$ | Γ | $\nu$ | $Q$ |
|---|---|---|---|---|---|---|---|---|---|
| $^{51}$V$^{10+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **1028.03** | 1.157 | 8.30 | 0.120 s | 1.32 | 2.92 [14] | 2.21 [14] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.679 | 1.12 [−8] | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 26.29 | 1.010 | 2.84 [10] | 0.028 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 26.98 | 0.542 | 7.59 [9] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 269.2 | 1.394 | 3.36 [10] | 0.030 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 141643 | 1.593 | 0.004 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.409 | 5.48 [−15] | | | | |
| $^{53}$Cr$^{11+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **814.49** | 1.156 | 16.70 | 0.060s | 2.66 | 3.68 [14] | 1.38 [14] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.594 | 0.0036 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 24.30 | 1.010 | 3.62 [10] | 0.022 ns | | | |

TABLE II. *(continued.)*

| Ion | Level | Transition | $\lambda$ | $O$ | $A_{fi}$ | $\tau_f$ | $\Gamma$ | $\nu$ | $Q$ |
|---|---|---|---|---|---|---|---|---|---|
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 25.00 | 0.542 | 9.53 [9] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 24.94 | 1.394 | 4.23 [10] | 0.024 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 10204.08 | 1.590 | 0.01 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | −0.350 | 2.82 [−9] | | | | |
| $^{55}$Mn$^{12+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **653.94** | 1.156 | 32.22 | 0.031s | 5.12 | 4.58 [14] | 8.95 [13] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.525 | 0.006 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 22.50 | 0.868 | 3.35 [10] | 0.023 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 23.30 | 0.488 | 9.54 [9] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 23.23 | 1.209 | 3.94 [10] | 0.025 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 7575.76 | 1.587 | 0.026 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.303 | 6.87 [−9] | | | | |
| $^{57}$Fe$^{13+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **531.21** | 1.156 | 60.117 | 0.017 s | 9.56 | 5.64 [14] | 5.90 [13] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.467 | 0.014 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 20.96 | 0.809 | 3.60 [10] | 0.021 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 21.82 | 0.471 | 1.08 [10] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 21.73 | 1.134 | 4.22 [10] | 0.024 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 5777.01 | 1.584 | 0.059 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.265 | 2.04 [−8] | | | | |
| $^{59}$Co$^{14+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **436.07** | 1.156 | 108.67 | 0.009 s | 17.28 | 6.88 [14] | 3.98 [13] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.419 | 0.03 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 19.29 | 0.756 | 3.85 [10] | 0.020 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 20.51 | 0.458 | 1.23 [10] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 20.42 | 1.068 | 4.522 [10] | 0.022 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 4510.60 | 1.581 | 0.122 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.233 | 5.427 [−8] | | | | |
| $^{61}$Ni$^{15+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **361.35** | 1.156 | 190.99 | 0.005 s | 30.38 | 8.30 [14] | 2.73 [13] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.377 | 0.06 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 18.37 | 0.707 | 4.08 [10] | 0.018 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 19.36 | 0.449 | 1.41 [10] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 19.26 | 1.010 | 4.8 [10] | 0.021 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 3598.42 | 1.157 | 0.129 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.207 | 1.33 [−7] | | | | |
| $^{63}$Cu$^{16+}$ | $3p\,^2P_{3/2}$ | $3p\,^2P_{3/2} \xrightarrow{M1} 3p\,^2P_{1/2}$ | **302.06** | 1.155 | 326.61 | 0.003 s | 51.95 | 9.93 [14] | 1.91 [13] |
| | | $3p\,^2P_{3/2} \xrightarrow{E2} 3p\,^2P_{1/2}$ | | 0.342 | 0.131 | | | | |
| | $3d\,^2D_{3/2}$ | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{1/2}$ | 17.28 | 0.662 | 4.31 [10] | 0.017 ns | | | |
| | | $3d\,^2D_{3/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 18.33 | 0.445 | 1.63 [10] | | | | |
| | $3d\,^2D_{5/2}$ | $3d\,^2D_{5/2} \xrightarrow{E1} 3p\,^2P_{3/2}$ | 18.21 | 0.958 | 5.13 [10] | 0.019 ns | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{M1} 3d\,^2D_{3/2}$ | 2929.12 | 1.572 | 0.442 | | | | |
| | | $3d\,^2D_{5/2} \xrightarrow{E2} 3d\,^2D_{3/2}$ | | 0.185 | 2.96 [−7] | | | | |

in Table II, we find that $\Gamma$ values increase with size of the ion while $Q$ values show the reverse trend. Therefore, it is necessary to choose an appropriate ion judiciously in which it is possible to attain moderate narrow natural linewidth and $Q$ value along with aforementioned criteria. In this point of view, we observe that the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition of the Al-like $^{53}\mathrm{Cr}^{11+}$, $^{55}\mathrm{Mn}^{12+}$, $^{57}\mathrm{Fe}^{13+}$, and $^{59}\mathrm{Co}^{14+}$ ions is suitable to be considered for atomic clocks.

After the above exploratory analysis for considering the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition for atomic clocks in many Al-like ions, we would like to now verify the typical order of systematics that these ions would exhibit while carrying out the frequency measurement of the above transition. The most common and significant systematics for an ionic clock are electric quadrupole shift, quadratic Stark shift, black-body radiation (BBR) shift, Zeeman shift, etc., which can be estimated either by carrying out independent experiments prior to measuring clock frequency or by performing precise calculations. Here, we assess these systematics by performing calculations by presuming typical strengths of electric and magnetic fields that are used for trapping ions. In fact, we present here the absolute magnitudes of the estimated systematics. However, uncertainties in these systematics are smaller than these values and can be reduced further by improving accuracies in the calculations when any one of these ions are pursued for atomic clock experiment. We discuss below these systematics one by one in the above transition of all the considered Al-like ions. It is worth mentioning here that some of the other systematics such as the Doppler effect and gravitational effects are generally negligibly small and will be below $10^{-19}$ level in the HCIs [13,24], so we are not concerned about these effects in the present work.

For estimating the interested systematics theoretically, knowledge of several spectroscopic properties are required. We have calculated electric quadrupole moments ($\Theta$), static $\alpha^{(0)}$ and $\alpha^{(2)}$ values, $g_J$ factors and magnetic dipole ($A_{hyf}$) and electric quadrupole ($B_{hyf}$) hyperfine structure constants of the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states. To determine $\alpha$ values, we have carried out calculations of change in EEs considering different strengths of electric field such as $\mathcal{E}_z = 0$, 0.0005, 0.001, and 0.002 a.u. in order to verify consistencies in the results. The final values were obtained from the resulting three energy shifts with finite electric fields assuming that they lie on a quartic polynomial. These results are given in Table III for all the considered Al-like ions. The uncertainty in our energy and polarizability data is mainly due to the finite basis set adopted in our calculation and neglected higher excited configurations in the EOMCCSD method. We give errors due to the finite basis sets as $\Delta P_{\text{basis}}$ in the above table by estimating differences in the energy and polarizability values obtained from the $X = 3$ and $X = 4$ basis set calculations. Previous studies on similar properties show negligible contributions due to higher-level excitations in the singly charged ions [38,48]. So for convenience, we assume total uncertainty to polarizabilities as twice of the errors coming due to use of finite basis sets. Other quantities such as $\Theta$, $g_J$, and $A_{hyf}$ and $B_{hyf}$ values are obtained using the CCSD method and quoted in Table IV along with the used nuclear spin ($I$), magnetic dipole moment ($\mu_I$) in unit of $\mu_N$, and electric quadrupole moment ($Q_I$) in barn ($b$) of the considered stable isotopes of the respective ions. Uncertainties in these quantities, apart for the $g_J$ values, are estimated by accounting the neglected triples contributions. Since $g_J$ factor and $A_{hyf}$ have similar mathematical expressions for their theoretical determination [49], we expect uncertainties to the calculated $g_J$ factors will be similar to the $A_{hyf}$ values of the respective states in each ion.

One of the most important and dominating systematic shifts in an atomic clock experiment is the electric quadrupole shift caused due to the gradient of electric field ($\nabla\mathcal{E}$) experienced by the atomic system during the measurement. This can be estimated by calculating the expectation value of the corresponding interaction Hamiltonian $H_Q = -\nabla\mathcal{E}\cdot\mathbf{\Theta}(\gamma,K)$ as

$$\Delta E_{\text{Quad}} = \langle \gamma K, M_K = K|H_Q|\gamma K, M_K = K\rangle, \tag{21}$$

where $K$ is the angular momentum of the state with its component $M_K$, $\gamma$ represents for other quantum numbers such as parity, and $\mathbf{\Theta}(\gamma,K)$ is known as the quadrupole moment, which is the expectation value of the electric quadrupole operator $\Theta = \frac{e}{2}(3z^2 - r^2)$, of the state. Using the Wigner-Eckart theorem, we can express

$$\begin{aligned}\mathbf{\Theta}(\gamma,K) &= \langle \gamma K K|\Theta|\gamma K K\rangle \\ &= \begin{pmatrix} K & 2 & K \\ -K & 0 & K\end{pmatrix}\langle \gamma K||\mathbf{\Theta}||\gamma K\rangle. \end{aligned}\tag{22}$$

According to the angular momentum selection rule of the above expression, $\Delta E_{\text{Quad}}$ will be zero for the $3p\,^2P_{1/2}$ state among the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition as its angular momentum $K \equiv J = 1/2$. However, we shall get the finite electric quadrupole shift from the atomic $3p\,^2P_{3/2}$ state owing to its angular momentum $J = 3/2$. However, it can be seen from Table IV that some of the considered Al-like ions have nuclear $I = 3/2$. As a result, the corresponding $3p\,^2P_{3/2}$ state can have hyperfine level $F = 0$. For the hyperfine level, $K \equiv F$, the quadrupole shift can be expressed by

$$E_{\text{Quad}}(\gamma J F M_F) = -K_1 K_2 \Theta(\gamma, J), \tag{23}$$

where

$$K_1 = \frac{2A_{\mathcal{E}}\left[3M_F^2 - F(F+1)\right]}{\sqrt{(2F+3)(2F+2)(2F+1)2F(2F-1)}}, \tag{24}$$

$$K_2 = (-1)^{I+J+F}(2F+1)\begin{Bmatrix} J & 2 & J \\ F & I & F\end{Bmatrix}\begin{pmatrix} J & 2 & J \\ -J & 0 & J\end{pmatrix}^{-1}, \tag{25}$$

where $\Theta(\gamma,J)$ is the atomic electric quadrupole moment, and $A_{\mathcal{E}}$ is the strength of the gradient of the applied electric field. The above expression still ensures that quadrupole shifts in any of the hyperfine levels of the $3p\,^2P_{1/2}$ state are zero. In addition, consideration of the $F = 0$ hyperfine level of the $3p\,^2P_{3/2}$ state in the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ transition can give zero quadrupole shift to the clock transition in the ions with $I = 3/2$. Among the other ions with different values of $I$, $^{51}\mathrm{V}^{10+}$, and $^{59}\mathrm{Co}^{14+}$ have $I = 7/2$, whereas $^{55}\mathrm{Mn}^{12+}$ has $I = 5/2$ and $^{57}\mathrm{Fe}^{13+}$ has $I = 1/2$. It can be noticed that $K_1$ of Eq. (23) is proportional to $3M_F^2 - F(F+1)$, which can vanish for $F = 3$ and $M_F = 2$ for the $3p\,^2P_{3/2}$ state. Therefore, if the condition that $M_F$ is zero is relaxed, we can choose the upper state of the clock transition to be $|^2P_{3/2}, F = 3, M_F = \pm 2\rangle$ for the $^{51}\mathrm{V}^{10+}$, $^{59}\mathrm{Co}^{14+}$, and $^{55}\mathrm{Mn}^{12+}$ ions. The corresponding lower state can be either

TABLE III. Energies and dipole polarizabilities obtained using Dyall's uncontracted correlation-consistent double-, triple-, and quadruple-$\zeta$ basis sets, which are labeled by dyall.cv$X$z with $X = 2$, 3, and 4, respectively, and the estimated uncertainties in values for the atomic states involved with the proposed clock transitions of the considered Al-like ions are given in cm$^{-1}$ and atomic unit (a.u.), respectively. Energies in the absence of electric fields obtained from different set of basis functions are compared with NIST data [41] and their differences from the NIST data are given as "DIFF" in percentage.

| Ion | Property | State | $X = 2$ | $X = 3$ | $X = 4$ | Uncertainty | NIST [41] | DIFF |
|---|---|---|---|---|---|---|---|---|
| $^{51}$V$^{10+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 9894 | 9918 | 9931 | 26 | 9696 | 2.4 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.58462 | 0.58582 | 0.58948 | 0.00732 | | |
| | | $3p\,^2P_{3/2}$ | 0.59004 | 0.58946 | 0.59323 | 0.00754 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00362 | 0.00375 | 0.00362 | 0.00022 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.05272 | 0.05263 | 0.05236 | 0.00054 | | |
| $^{53}$Cr$^{11+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 12506 | 12535 | 12549 | 28 | 12261 | 2.3 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.47444 | 0.47660 | 0.47724 | 0.00128 | | |
| | | $3p\,^2P_{3/2}$ | 0.47777 | 0.47982 | 0.48068 | 0.00172 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00333 | 0.00322 | 0.00344 | 0.00044 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.04383 | 0.04341 | 0.04334 | 0.00014 | | |
| $^{55}$Mn$^{12+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 15580 | 15627 | 15642 | 30 | 15295 | 2.3 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.38958 | 0.39106 | 0.39154 | 0.00096 | | |
| | | $3p\,^2P_{3/2}$ | 0.39271 | 0.39424 | 0.39475 | 0.00102 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00313 | 0.00318 | 0.00321 | 0.00006 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.03661 | 0.03642 | 0.03638 | 0.00008 | | |
| $^{57}$Fe$^{13+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 19191 | 19246 | 19262 | 32 | 18852 | 2.2 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.32354 | 0.32462 | 0.32500 | 0.00076 | | |
| | | $3p\,^2P_{3/2}$ | 0.32648 | 0.32760 | 0.32804 | 0.00088 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00294 | 0.00298 | 0.00304 | 0.00012 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.03091 | 0.03073 | 0.03068 | 0.00010 | | |
| $^{59}$Co$^{14+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 23389 | 23450 | 23466 | 32 | 22979 | 2.1 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.27144 | 0.27220 | 0.27240 | 0.00040 | | |
| | | $3p\,^2P_{3/2}$ | 0.27421 | 0.27502 | 0.27524 | 0.00044 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00277 | 0.00282 | 0.00284 | 0.00005 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.02633 | 0.02610 | 0.02609 | 0.00048 | | |
| $^{61}$Ni$^{15+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 28232 | 28301 | 28318 | 34 | 27760 | 2.0 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.22976 | 0.23026 | 0.23040 | 0.00028 | | |
| | | $3p\,^2P_{3/2}$ | 0.23241 | 0.23294 | 0.23312 | 0.00036 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00265 | 0.00268 | 0.00275 | 0.00005 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.02249 | 0.02241 | 0.02242 | 0.00002 | | |
| $^{63}$Cu$^{16+}$ | $E$ | $3p\,^2P_{1/2}$ | 0 | 0 | 0 | | 0 | |
| | | $3p\,^2P_{3/2}$ | 33786 | 33860 | 33881 | 42 | 33239 | 1.9 |
| | $\alpha^{(0)}(\gamma,J)$ | $3p\,^2P_{1/2}$ | 0.19602 | 0.19636 | 0.19651 | 0.00030 | | |
| | | $3p\,^2P_{3/2}$ | 0.19855 | 0.19894 | 0.19908 | 0.00028 | | |
| | $\delta\alpha^{(0)}(\gamma,J)$ | | 0.00253 | 0.00258 | 0.00258 | 0.00005 | | |
| | $\alpha^{(2)}(\gamma,J)$ | $3p\,^2P_{3/2}$ | 0.01941 | 0.01922 | 0.01929 | 0.00014 | | |

TABLE IV. Nuclear properties such as spin ($I$), magnetic moment ($\mu_I$ in $\mu_N$), and nuclear electric quadrupole moment ($Q_I$) in barn ($b$) are given from Ref. [42], and atomic properties such as quadrupole moment $\Theta(\gamma,J)$ (in a.u.), $g_J$ factor, magnetic dipole ($A_{hyf}$), and electric quadrupole ($B_{hyf}$) hyperfine-structure constants (in MHz) obtained using the CCSD method. Scalar and tensor dipole polarizabilities $\alpha^{(0)}(\gamma,J)$ and $\alpha^{(2)}(\gamma,J)$ of the atomic states (in a.u.) of the Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions obtained by the finite gradient approach are given using the EOMCCSD method. The uncertainties are given in parentheses.

| Ion | State | $I$ | $\mu_I$ | $Q_I$ | $\Theta(\gamma,J)$ | $\alpha^{(0)}(\gamma,J)$ | $\alpha^{(2)}(\gamma,J)$ | $g_J$ | $A_{hyf}$ | $B_{hyf}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $^{51}$V$^{10+}$ | $3p\,^2P_{1/2}$ | 7/2 | 5.148 | −0.043 | | 0.5858 (73) | | 0.665196 | 21456 (146) | |
| | $3p\,^2P_{3/2}$ | | | | 0.1530(3) | 0.5894 (75) | 0.0526 (5) | 1.333460 | 4342 (68) | −222 (6) |
| $^{53}$Cr$^{11+}$ | $3p\,^2P_{1/2}$ | 3/2 | 0.475 | −0.155 | | 0.4766 (13) | | 0.665081 | −5578 (30) | |
| | $3p\,^2P_{3/2}$ | | | | 0.1340(14) | 0.4798 (17) | 0.0434 (2) | 1.333363 | −1122 (14) | −964 (10) |
| $^{55}$Mn$^{12+}$ | $3p\,^2P_{1/2}$ | 5/2 | 3.453 | 0.427 | | 0.3911 (10) | | 0.664957 | 29096 (3) | |
| | $3p\,^2P_{3/2}$ | | | | 0.1180(11) | 0.3942 (10) | 0.0364 (1) | 1.333258 | 5821 (35) | 3162 (20) |
| $^{57}$Fe$^{13+}$ | $3p\,^2P_{1/2}$ | 1/2 | 0.091 | 0.11 | | 0.3246 (8) | | 0.664825 | 4509 (39) | |
| | $3p\,^2P_{3/2}$ | | | | 0.1055(4) | 0.3276 (9) | 0.0307 (1) | 1.333148 | 897 (2) | 961 (10) |
| $^{59}$Co$^{14+}$ | $3p\,^2P_{1/2}$ | 7/2 | 0.628 | 0.353 | | 0.2722 (4) | | 0.664684 | 5245 (42) | |
| | $3p\,^2P_{3/2}$ | | | | 0.0946(16) | 0.2750 (4) | 0.0261 (5) | 1.333032 | 1037 (47) | 3603 (40) |
| $^{61}$Ni$^{15+}$ | $3p\,^2P_{1/2}$ | 3/2 | −0.750 | 0.162 | | 0.2303 (3) | | 0.664536 | −17016 (66) | |
| | $3p\,^2P_{3/2}$ | | | | 0.0853(−11) | 0.2329 (4) | 0.0224 (1) | 1.332909 | −3345 (27) | 1918 (20) |
| $^{63}$Cu$^{16+}$ | $3p\,^2P_{1/2}$ | 3/2 | 2.227 | −0.221 | | 0.1964 (3) | | 0.664379 | 58412 (254) | |
| | $3p\,^2P_{3/2}$ | | | | 0.0774(57) | 0.1989 (3) | 0.0193(1) | 1.332779 | 11416 (511) | −3012 (60) |

the $|^2P_{1/2},F=3,M_F=\pm2\rangle$ or the $|^2P_{1/2},F=4,M_F=\pm2\rangle$ states in the $^{51}$V$^{10+}$ and $^{59}$Co$^{14+}$ ions while it could be either the $|^2P_{1/2},F=3,M_F=\pm2\rangle$ or the $|^2P_{1/2},F=2,M_F=\pm2\rangle$ states in the $^{55}$Mn$^{12+}$ ion. Any of these hyperfine levels of the ground state in the clock transitions of these ions will have the same Stark, BBR and Zeeman shifts due to absence of contribution from the tensor polarizability. The $^{57}$Fe$^{13+}$ ion does not have a proper combination of $F$ and $M_F$ values for which the quadrupole shift can be eliminated. The possible clock transitions in the $^{57}$Fe$^{13+}$ ion include the $|^2P_{1/2},F=0,M_F=0\rangle \rightarrow |^2P_{3/2},F=1,M_F=0\rangle$ or the $|^2P_{1/2},F=1,M_F=\pm1\rangle \rightarrow |^2P_{3/2},F=2,M_F=\pm1\rangle$ hyperfine transitions, in which it yields about $\delta E_{\text{Quad}} = 3.59$ Hz for a typical value of $A_{\mathcal{E}} = 10^8$ V/m$^2$. This corresponds to the fractional uncertainty to its clock frequency below $10^{-13}$ level. Even so, it is still possible to nullify technically this shift in $^{57}$Fe$^{13+}$, for example, by measuring clock frequencies in the three orthogonal directions of the quantizing external field and averaging out to attain the final clock transition frequency [43]. Any of such two types of transitions of $^{57}$Fe$^{13+}$ do not show great difference in the Stark, BBR, and Zeeman shifts, and therefore we pick up the $|^2P_{1/2},F=0,M_F=0\rangle \rightarrow |^2P_{3/2},F=1,M_F=0\rangle$ transition for $^{57}$Fe$^{13+}$ arbitrarily in Table IV.

The quadratic Stark shift of a hyperfine level $F$ with component $M_F$ can be evaluated by

$$\begin{aligned} E_{\text{Stark}}(\gamma,JF,M_F) &= -\frac{1}{2}\alpha(\gamma,J,F)\mathcal{E}^2 \\ &= -\frac{1}{2}\alpha^{(0)}(\gamma,J,F)\mathcal{E}_z^2 - \frac{1}{4}\alpha^{(2)}(\gamma,J,F) \\ &\quad\times \frac{[3M_F^2 - F(F+1)]}{F(2F-1)}(3\mathcal{E}_z^2 - \mathcal{E}^2), \end{aligned} \tag{26}$$

where $\mathcal{E}$ and $\mathcal{E}_z$ are the total strength and strength in the $z$ direction of the applied electric field strength, $\alpha^{(0)}(\gamma,J,F)$ and $\alpha^{(2)}(\gamma,J,F)$ are the scalar and tensor components of the polarizability $[\alpha(\gamma,J,F)]$ of the hyperfine level. These quantities can be related to their corresponding values in the atomic state as [43]

$$\alpha^{(0)}(\gamma,J,F) = \alpha^{(0)}(\gamma,J) \tag{27}$$

$$\begin{aligned} &\alpha^{(2)}(\gamma,J,F) \\ &\quad= (-1)^{I+J+F}\begin{Bmatrix} F & J & I \\ J & F & 2 \end{Bmatrix}\alpha^{(2)}(\gamma,J) \\ &\qquad\times\left[\frac{F(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}{(2F+3)(F+1)J(2J-1)}\right]^{1/2}. \end{aligned} \tag{28}$$

In Table IV, we have given our calculated $\alpha^{(0)}(\gamma,J)$ and $\alpha^{(2)}(\gamma,J)$ values of both the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states of the considered ions using the EOMCCSD method. These values are very small compared to typical values of the neutral atoms or singly charged ions. The tensor components of the $3p\,^2P_{3/2}$ states are found to be one order smaller than the scalar polarizabilities. Moreover, tensor polarizability contributions will not play any role in the $^{51}$V$^{10+}$, $^{59}$Co$^{14+}$, and $^{55}$Mn$^{12+}$ ions as we have proposed to consider $F=3$ and $M_F=\pm2$ hyperfine levels for the clock transition. Using the above relations and for a typical value of electric field strength $\mathcal{E} = 10$ V/m, we estimate the differential Stark shifts $\delta E_{\text{Stark}}$ to be about $3.73\times10^{-10}$ Hz, $1.99\times10^{-9}$ Hz, $1.98\times10^{-9}$ Hz, $1.85\times10^{-9}$ Hz, $1.75\times10^{-9}$ Hz, $1.67\times10^{-9}$ Hz, and $1.62\times10^{-9}$ Hz in the proposed clock transitions of the Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and

$^{63}$Cu$^{16+}$ ions, respectively. It corresponds to the fractional uncertainty to the clock frequencies below $10^{-23}$ level and given in Table V. This clearly shows that the Stark shifts are strongly suppressed in the proposed clock transitions of the investigated Al-like ions.

The BBR shift of hyperfine $F$ level can be estimated using the expression

$$\begin{aligned} E^{E1}_{BBR} &= -\frac{1}{2}(831.9\,\mathrm{V/m})^2\left[\frac{T(K)}{300}\right]^4\alpha^{(0)}(\gamma,J,F) \\ &= -\frac{1}{2}(831.9\,\mathrm{V/m})^2\left[\frac{T(K)}{300}\right]^4\alpha^{(0)}(\gamma,J), \end{aligned} \tag{29}$$

where $T$ in $K$ is the temperature at which the experiment to be conducted. Using the scalar polarizabilities of the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states given in Table IV and taking their differences, the BBR shifts in the $3p\,^2P_{1/2} \rightarrow 3p\,^2P_{3/2}$ clock transitions of the Al-like $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions are found to be within the $10^{-20}$–$10^{-21}$ level. Thus, uncertainties in the clock frequency measurements are expected to be below the level $10^{-19}$ supporting further the fact that the considered HCIs can be promising candidates for optical clocks. The BBR shift of $^{51}$V$^{10+}$ ion is slightly larger than $10^{-19}$. The environmental temperature in HCI clock is generally at temperatures far below the room temperature. In this situation, the BBR shift is not the limiting factor for HCI clocks.

The linear Zeeman shifts in the considered states can be avoided by selecting the $F = 0$ states when possible, otherwise $M_F = 0$ sublevel of a finite $F$ hyperfine state. For the finite $F$ state with nonzero $M_F$ sublevel, the linear Zeeman shift can also be removed technically by alternating $\pi$-polarized transitions with extreme states of opposite angular momentum ($M_F = \pm 2$) [44]. However, the ions would observe the second-order Zeeman shifts providing dominant sources due to the Zeeman effects. This shift of a hyperfine level $F$ with sublevel $M_F$ due to magnetic field strength $B$ is given by [45,46]

$$E^2_{\mathrm{Zeem}} = \beta_{\mathrm{Zeem}}(\gamma,J,F,M_F)B^2, \tag{30}$$

where

$$\beta_{\mathrm{Zeem}}(\gamma,J,F,M_F) = -\frac{(\mu_B g_J)^2}{\hbar}\sum_{F'}\frac{|\langle F'M_F|J_z|FM_F\rangle|^2}{E_{F'}-E_F}, \tag{31}$$

where $J_z$ is the $z$ component of $J$, $E_F$ is the hyperfine energy level and $F'$ corresponds to all allowed intermediate hyperfine levels. The hyperfine energy level is given by [47]

$$E_F = \frac{1}{2}A_{hyf}C + B_{hyf}\frac{\frac{3}{2}C(C+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}, \tag{32}$$

where $C = F(F+1) - I(I+1) - J(J+1)$. Since the dominant contributions to these shifts come only from the hyperfine splitting, we evaluate these shifts by determining $E_F$ values using the hyperfine structure constants $A_{hyf}$ and $B_{hyf}$ given in Table IV for the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ states. We also use the following identity here

$$\begin{aligned} &|\langle F'M_F|J_z|FM_F\rangle|^2 \\ &\quad = J(J+1)(2J+1)(2F+1)(2F'+1) \\ &\quad\times \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix}^2 \begin{Bmatrix} J & F & I \\ F' & J & 1 \end{Bmatrix}^2 \end{aligned} \tag{33}$$

to determine $\beta_{\mathrm{Zeem}}(\gamma,J,F,M_F)$ values and use $g_J$ factors given in Table IV. Considering the magnetic field strength

TABLE V. Fractional frequency shifts with respect to clock frequencies $\nu$ caused by electric quadrupole shifts $\delta E_{\mathrm{Quad}}$, quadratic Stark shifts $\delta E_{\mathrm{Stark}}$, BBR shifts $\delta E^{E1}_{BBR}$, and second-order Zeeman shifts $\delta E^2_{\mathrm{Zeem}}$ and the relativistic sensitive coefficient $q$ (in cm$^{-1}$) for the Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions. The parameter ($\beta_{\mathrm{Zeem}}$) is a coefficient related to estimate $\delta E^2_{\mathrm{Zeem}}$ (in $10^8$ Hz T$^{-2}$). Numbers given in brackets represent powers of 10.

| Ion | Transition | $\delta E_{\mathrm{Quad}}/\nu$ | $\delta E_{\mathrm{stark}}/\nu$ | $\delta E^{E1}_{BBR}/\nu$ | $\beta_{\mathrm{Zeem}}$ | $\delta E^2_{\mathrm{Zeem}}/\nu$ | $q$ |
|---|---|---|---|---|---|---|---|
| $^{51}$V$^{10+}$ | $\vert ^2P_{1/2},F=3,M_F=\pm2\rangle$ | 0 | 1.28 [−24] | 1.07 [−19] | −0.064 | 2.49 [−21] | −9085 |
| | $\rightarrow \vert ^2P_{3/2},F=3,M_F=\pm2\rangle$ | | | | 2.839 | | |
| $^{53}$Cr$^{11+}$ | $\vert ^2P_{1/2},F=1,M_F=0\rangle$ | 0 | 5.24 [−24] | 7.25 [−20] | 0.495 | 3.45 [−20] | −12352 |
| | $\rightarrow \vert ^2P_{3/2},F=0,M_F=0\rangle$ | | | | 52.92 | | |
| $^{55}$Mn$^{12+}$ | $\vert ^2P_{1/2},F=3,M_F=\pm2\rangle$ | 0 | 4.32 [−24] | 5.97 [−20] | 0.063 | 1.96 [−21] | −15440 |
| | $\rightarrow \vert ^2P_{3/2},F=3,M_F=\pm2\rangle$ | | | | 3.654 | | |
| $^{57}$Fe$^{13+}$ | $\vert ^2P_{1/2},F=0,M_F=0\rangle$ | 1.27 [−14] | 3.29 [−24] | 4.55 [−20] | −1.235 | −4.91 [−21] | −19069 |
| | $\rightarrow \vert ^2P_{3/2},F=1,M_F=0\rangle$ | | | | −12.31 | | |
| $^{59}$Co$^{14+}$ | $\vert ^2P_{1/2},F=3,M_F=\pm2\rangle$ | 0 | 2.55 [−24] | 3.53 [−20] | −0.263 | 5.03 [−20] | −23301 |
| | $\rightarrow \vert ^2P_{3/2},F=3,M_F=\pm2\rangle$ | | | | 137.96 | | |
| $^{61}$Ni$^{15+}$ | $\vert ^2P_{1/2},F=1,M_F=0\rangle$ | 0 | 2.01 [−24] | 2.78 [−20] | 0.016 | 6.27 [−21] | 89391 |
| | $\rightarrow \vert ^2P_{3/2},F=0,M_F=0\rangle$ | | | | 20.98 | | |
| $^{63}$Cu$^{16+}$ | $\vert ^2P_{1/2},F=1,M_F=0\rangle$ | 0 | 1.63 [−24] | 2.46 [−20] | −0.005 | −1.91 [−21] | 33836 |
| | $\rightarrow \vert ^2P_{3/2},F=0,M_F=0\rangle$ | | | | −7.650 | | |

to be $B = 5 \times 10^{-8}$ T as the case of the singly charged $\text{Al}^+$ ion clock [1], the differential second-order Zeeman shifts $\delta E^2_{\text{Zeem}}$ are estimated to be $7.26 \times 10^{-7}$ Hz, $-1.31 \times 10^{-5}$ Hz, $8.98 \times 10^{-7}$ Hz, $-2.77 \times 10^{-6}$ Hz, $3.46 \times 10^{-5}$ Hz, $5.20 \times 10^{-6}$ Hz, and $-1.91 \times 10^{-6}$ Hz in the proposed clock transitions of the Al-like $^{51}\text{V}^{10+}$, $^{53}\text{Cr}^{11+}$, $^{55}\text{Mn}^{12+}$, $^{57}\text{Fe}^{13+}$, $^{59}\text{Co}^{14+}$, $^{61}\text{Ni}^{15+}$, and $^{63}\text{Cu}^{16+}$ ions, respectively. This again lies within the $10^{-20} \sim 10^{-21}$ fractional uncertainty level of these clock frequencies, which are below the sought accuracy goal.

In order to address the sensitivity to the fine structure constant $\alpha_e$ variation in the $3p\,^2P_{1/2} \to 3p\,^2P_{3/2}$ clock transitions of the considered Al-like $^{51}\text{V}^{10+}$, $^{53}\text{Cr}^{11+}$, $^{55}\text{Mn}^{12+}$, $^{57}\text{Fe}^{13+}$, $^{59}\text{Co}^{14+}$, $^{61}\text{Ni}^{15+}$, and $^{63}\text{Cu}^{16+}$ ions, we calculate the relativistic $\alpha_e$ variation sensitive coefficient $q$ by defining as

$$\omega_t = \omega_0 + qx, \tag{34}$$

where $\omega_0$ is the angular frequency of the transition for the present-day value of the fine-structure constant $\alpha_e(0)$ and $\omega_t$ 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 $q$ parameters of the clock transitions using our CCSD method in Table V and they are found to be quite large. Moreover, some of them have positive signs while others have negative values. This is an advantage for probing variation in $\alpha_e$ using these clock transitions of the considered HCIs. In fact, these transitions can also be observed in the astrophysical objects. Thus, all the reported spectroscopic properties and the above $q$ parameters can also be very useful for astrophysical studies.

## IV. CONCLUSION

We have investigated the $3p\,^2P_{1/2} \to 3p\,^2P_{3/2}$ M1 transitions in the Al-like $^{51}\text{V}^{10+}$, $^{53}\text{Cr}^{11+}$, $^{55}\text{Mn}^{12+}$, $^{57}\text{Fe}^{13+}$, $^{59}\text{Co}^{14+}$, $^{61}\text{Ni}^{15+}$, and $^{63}\text{Cu}^{16+}$ ions as possible clock frequency standards. Many spectroscopic properties such as transition probabilities, lifetimes, electric quadrupole moments, electric dipole polarizabilities, hyperfine structure constants, and Lande $g_J$ factors of the low-lying atomic states are calculated using the CCSD and EOMCCSD method to find out the feasibility of considering the above transition in these ions for clocks. We find many of the dominant systematics in these ions are suppressed and it is plausible to attain the fractional systematic uncertainties to the clock frequencies below $10^{-19}$ levels. Many of these transitions are either in the optical region or close to the optical frequency domain. Moreover, the relativistic fine structure constant variation sensitive coefficients in these transitions are also found to be significantly large with opposite signs. All these findings strongly suggest the aptness of these HCIs as promising optical clocks with unprecedented accuracies.

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