Highly charged ion (HCI) clocks: Frontier candidates for testing variation of fine-structure constant

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Attempts are made to unify gravity with the other three fundamental forces of nature. As suggested by higher dimensional models, this unification may require space and time variation of some of the dimensionless fundamental constants. In this scenario, probing temporal variation of the electromagnetic fine structure constant ($\alpha = \frac{e^2}{\hbar c}$) in a low energy regime at the cosmological time scale is of immense interest. Atomic clocks are ideal candidates for probing α variation because their transition frequencies are measured with ultra-high precision. Since atomic transition frequency is a function of α, measurement of a clock frequency at different temporal and spatial locations can yield signatures to ascertain variation of α. Highly charged ions (HCIs) are very sensitive to variation of α and are least affected by external perturbations, making them excellent platforms for searching for temporal variation of α. In this work, we overview HCIs suitable for building atomic clocks because of their spectroscopic features and sensitivity to variation of α. The selection of HCI clock candidates is outlined based on two general rules—by analyzing trends in fine structure splitting and level-crossing patterns along a series of isoelectronic atomic systems of the periodic table. Two variants of relativistic many-body methods in the configuration interaction and coupled-cluster theory frameworks are employed to determine the properties of HCIs proposed for atomic clocks. These methods treat electronic correlation and relativistic effects under the frame of the Dirac-Coulomb Hamiltonian rigorously, while other higher-order relativistic effects are included approximately. Typical systematic effects of the HCI clock frequency measurements are discussed using the calculated atomic properties. This review will help understand limits and potentials of the proposed HCIs as the prospective atomic clock candidates and guide future HCI clock experiments.

1 Introduction

Atomic clocks, used for frequency standards, help us define the unit of time with very high precision so that they lose only one second over the age of our universe. These clocks are based on either neutral atoms or singly charged atomic ions. With the advent of recent laser cooling and trapping techniques of atomic systems, modern optical clock frequencies have been measured with uncertainties that are much lower than the present 10^{-16} level caesium microwave-based primary atomic clock [1–3]. Uncertainty of optical lattice clock based on ^{171}Yb atoms has reached an uncertainty of 1.4×10^{-18} [4, 5] whereas ^{87}Sr optical lattice clocks

TABLE 1 A summary of the sensitivity coefficients, q and K_α, of the clock transition frequency to variation of α, with definition given in text and the data source is taken from Ref. [11].

Z	Atoms	Clock transition	Energy (cm^{-1})	q (cm^{-1})	K_α (unit less)
13	Al$^+$	$3s^2\ ^1S_0 - 3s3p\ ^3P_0$	37393.03	146	0.008
20	Ca$^+$	$4s\ ^2S_{1/2} - 3d\ ^2D_{5/2}$	13710.89	1040	0.152
38	Sr	$5s^2\ ^1S_0 - 5s5p\ ^3P_0$	14317.52	443	0.062
70	Yb	$6s^2\ ^1S_0 - 6s6p\ ^3P_0$	17288.44	2714	0.314
70	Yb$^+$	$4f^{14}6s\ ^2S_{1/2} - 4f^{14}5d\ ^2D_{5/2}$	24332.69	12582	1.03
		$4f^{14}6s\ ^2S_{1/2} - 4f^{13}6s\ ^2F^{\circ}_{7/2}$	21418.75	−63752	−5.95
80	Hg	$6s^2\ ^1S_0 - 6s6p\ ^3P_0$	37645.08	15299	0.81
80	Hg$^+$	$5d^{10}6s\ ^2S_{1/2} - 5d^96s^2\ ^2D_{5/2}$	35514.62	−52200	−2.94

offer uncertainty of around 2.0×10^{-18} [6, 7]. Similarly, uncertainties of ^{171}Yb$^+$ and ^{40}Ca$^+$ ion clocks have both reached an accuracy of 3×10^{-18} [8, 9]. There have been continuous efforts to reduce uncertainties in the clock frequency measurements and miniaturize the atomic clocks, intending to utilize them in many sophisticated instruments and space science research.

Among various scientific applications of atomic clocks, see the review by Safronova et al [10] for more details, atomic clocks serve as an important tool to probe temporal and spatial variation of the fine-structure constant (α). Atomic energy levels are functions of α. Thus any variation in the α value will result in changes in the energy levels over time and space. Since optical clocks can measure atomic transition frequencies to ultra-high precision, they are the most suitable instruments for detecting any drift in the α value. The clock transitions have different sensitivity to variation of α. The sensitivity of an energy level to α variation is gauged through a relativistic sensitivity coefficient q by defining it as

$$\omega_t = \omega_0 + qx, \qquad (1)$$

where ω_0 is the angular frequency of the transition for the present-day value of the fine-structure constant $\alpha(0)$ and ω_t is the angular frequency of the transition corresponding to another value of $\alpha(t)$ at time t such that $x = (\alpha(t)/\alpha(0))^2 - 1 \approx 2(\alpha(t) - \alpha(0))/\alpha(0)$. Sometimes it is convenient to introduce a dimensionless sensitivity coefficient K_α by defining it as $K_\alpha = q/\omega_0$. Here, q and K_α are often referred to as a frequency's absolute and relative sensitivity factor to variation of α.

Table 1 summarizes the currently prevailing clock frequencies with regard to their sensitivity to variation of α. Some of them has low sensitivities to α variation, like the clock transition in Al$^+$, Ca$^+$, Sr and Yb, while the $4f^{14}6s\ ^2S_{1/2} - 4f^{13}6s\ ^2F^{\circ}_{7/2}$ transition in Yb$^+$ and the $5d^{10}6s\ ^2S_{1/2} - 5d^96s^2\ ^2D_{5/2}$ transition in Hg$^+$ have relatively higher

sensitivity coefficients to variation of α. Such contrast sensitivities to variation of α suggest different accuracy requirements in the frequency measurements if they are used for testing variation of α. Assuming the time variation rate of α per year is around 10^{-16} level, to detect such a small variation rate of α within a year time, minimum requirements of fractional uncertainties of the Sr, Yb, and Hg atomic clock frequencies would be about 8×10^{-17}, 5×10^{-17} and 2×10^{-18}, respectively, by considering their sensitivity coefficients to α variation. Thus, for any further constraining to the temporal variation of α lower than 10^{-16}, the aimed uncertainty level in the clock frequency measurement has to be less than 10^{-18} if an a-year-around experiment is planned. On the one hand, researchers endeavour to push for minimizing uncertainty levels further down in the clock frequency measurements to meet the requirement for inferring any signature of α variation from the measurements, and on the other hand, selecting a suitable pair of clock transitions having very different sensitivity to variation of α is a good option. To be specific, when a measurement of the frequency of an optical clock at the frequency f_1 relative to another optical clock at the frequency f_2 is conducted (the two optical clocks have different sensitivities to α variation), the time-variation of the ratio f_1/f_2 can be expressed as

$$\frac{\partial}{\partial t}\ln\frac{f_1}{f_2} = \frac{\partial}{\partial t}\ln R = \ln\dot{R} = [K_\alpha(1) - K_\alpha(2)]\frac{\partial}{\partial t}\ln\alpha, \qquad (2)$$

where $R = \frac{f_1}{f_2}$ is the frequency ratio, $K_\alpha(1)$ and $K_\alpha(2)$ are the sensitivity factors of the respective clock frequency. For example, the ^{199}Hg$^+$ and ^{27}Al$^+$ optical frequency standards have a big difference in K_α as $K_\alpha(\text{Al}^+)$-$K_\alpha(\text{Hg}^+) = 2.95$, and their frequency ratio of $f_{\text{Al}^+}/f_{\text{Hg}^+}$ has been measured over a timescale of about 1 year, yielding a drift rate of $f_{\text{Al}^+}/f_{\text{Hg}^+} = (-0.53 \pm 0.79) \times 10^{-16}$ and constrained the temporal variation of α as $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$ [12]. Similarly, Lange

in PTB compared two optical clocks based on the E2 and E3 transitions of ^{171}Yb$^+$ that have the difference in K_α as K_α(E3)-K_α(E2) = −6.95. The frequency ratio f_{E3}/f_{E2} was measured over 1,500 days, which determined $\dot{R}/R = -6.8\,(7.5) \times 10^{-18}$ per year and yield $\dot{\alpha}/\alpha = (1.0 \pm 1.1) \times 10^{-18}$ per year.

In the aim of ultimately observing the variation of α, it is necessary to improve the clock frequency measurements consistently. In this sense, even improving the limit on the constraint of α variation over time is meaningful. One way of proceeding with this task is to work hard to find ways to minimize uncertainties in the existing atomic clocks. Alternatively, we can look for other suitable candidates least influenced by stray electromagnetic fields. One such possibility is to use nuclear transitions for the clock frequency measurements. The presence of a low-lying metastable state in ^{229m}Th with excitation energy around 8 eV is identified to be the perfect choice for this purpose [14, 15]. Many efforts are already gone into directly detecting nuclear transition by measuring the isomeric state energy of ^{229m}Th precisely for achieving nuclear clock [16–19]. This transition has also been explored for testing variation of fundamental constants by different groups [20–23]. The other novel thought has been put into exploring highly charged ions (HCIs) for making atomic clocks [24]. Investigation of spectral properties of HCIs has a very long history, which is immensely interesting for identifying abundant elements in the solar corona and other astrophysical objects, describing exotic phenomena in the nuclear reactions, diagnosing plasma processes, etc. [25–28]. However, HCIs are recognized as potential candidates for making ultra-precise atomic clocks, developing tools for quantum information, and probing possible variations of α. Following the pioneering works by Berengut et al., which suggested enhanced sensitivity to variation of α in the HCIs [29–34], a long list of HCIs are being proposed [35–52] to select appropriate HCIs for consideration for the clock experiments. All these proposed HCI candidates appear promising for building atomic clocks and probing α variation, but there could be slight differences in setting up their experiments. Since the HCIs possess very compacted electron orbitals than their isoelectronic neutral atoms or singly charged ions, they can be strongly immune to external perturbations. Apart from this, it would be relatively easier to detect a signature of α variation in HCIs at the same level of accuracy in the clock frequency measurements with respect to optical lattice clocks or singly charged ion clocks owing to their enhanced sensitivity α coefficients.

In this brief review, we shortlist the HCIs that can be prospective candidates for optical atomic clocks other than those previously listed in a review by Safronova et al. [10]. Most of these HCIs have large α varying sensitivity coefficients for the clock transitions, which implies that they are excellent platforms for searching of temporal variation of α. Selection of HCIs for atomic clocks is further addressed based on the forbidden transitions within fine-structure splitting and those among interconfigurations that undergo orbital energy crossings. Relativistic many-body methods employed to calculate HCI properties are described briefly. Finally, prominent systematic effects of the HCI clock frequency measurements due to stray electromagnetic fields are discussed before summarizing the work.

2 Importance of α-variation studies

Actual values of many of the dimensionless physical constants need to be verified experimentally as their magnitudes are predicted differently by different models with strong scientific arguments. Though there has yet to be strong evidence to show that their values are not constant, there is also no strong scientific argument justifying that they have to be constants over time or space. Thus, any plausible signature in the temporal or spatial variation of fundamental physical constants would answer either of these questions. If slight temporal or spatial variation in the fundamental constants is possible, it will support some of the phenomena beyond the Standard Model of particle physics. This is why probing temporal and spatial variation of α is of immense interest to the research community [10, 28, 53, 54]. One of the biggest consequences of investigating the temporal and spatial variation of α is to support multidimensional theories that try to unify all four fundamental interactions [55–62]. Such theories also predict violation of Einstein's equivalence principle. Thus, any signature of variation in the α value can also imply violation of Einstein's equivalence principle.

In astronomy, observation of absorption spectral lines from distant astronomical objects such as quasars with large red shift constant (z) can be used directly for probing variation of α. Observations using the Kerk telescope suggest that the fractional drift in α is smaller by an amount $\Delta\alpha/\alpha = (\alpha_z - \alpha_0)/\alpha_0 = (0.543 \pm 0.116) \times 10^{-5}$ around 10^{10} years ago over the range $0.2 < z < 4.2$ [63, 64]. Observations of spectral lines from quasar J1120 + 0641 in the redshift range 5.5–7.1 using the Very Large Telescope (VLT) is used to search for variation of α. It is worth mentioning that observations at $z = 7.1$ correspond to the Universe about 0.8 billion years old. These observations reported the result as $\Delta\alpha/\alpha = (-2.18 \pm 7.27) \times 10^{-5}$, which is consistent with null temporal variation [65]. Very recently, Murphy et al. observed HE 0515–4414 by the VLT with the redshift range of 0.6–2.4. They combined their observed spectral lines data with 28 measurements from other spectrographs to mitigate the wavelength calibration errors and reported a weighted mean of $\Delta\alpha/\alpha = (-0.5 \pm 0.5_{stat} \pm 0.4_{sys})$ parts-per-million (ppm). Webb et al. proposed a theory of spatial dipole of α by analyzing observed data from both the Keck and VLT telescopes [28]. It does not seem to have strong evidence in favour of this theory as data from both the Keck and VLT observations used for this analysis had significant systematic effects [66, 67].

Another class of data is inferred from the geophysical data analysis from the Oklo natural fission reactor and cosmological observations, which correspond to a slightly smaller time scale than the astrophysical observations. The signature of temporal variation of α can be easily detected from events that correspond to the early epoch of the Universe. The data from the Oklo nuclear reactor offers a limit as $\Delta\alpha/\alpha < 1.1 \times 10^{-8}$ over a time span of 2 Gyr [68].

Laboratory-based atomic clocks provide measurements of the time variation of α in the present-day time scale. Table 2 summarizes the current most stringent limit to $(\Delta\alpha/\Delta t)/\alpha = \dot{\alpha}/\alpha$ per year, which is determined by the laboratory measurement of the ratio of two clock frequencies over a reasonably long time. It includes measurements of the clock frequency ratio of the Hg$^+$ and Al$^+$ optical clocks over the course of a year (Δt = 1yr), which yields as $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$ [12]. The other one is the ratio deduced from the electric quadrupole (E2) and electric octupole (E3) clock frequency measurements in Yb$^+$ over around 4 years (Δt = 4yr), which suggests $\dot{\alpha}/\alpha = (1.0 \pm 1.1) \times 10^{-18}$ per year [13], agreeing with the previous finding of null variation. Similar interpretations on the time variation of α have been made from the other clock frequency measurements found from Refs. [69–75].

Findings of variation of $\Delta\alpha$ from different studies have been reviewed in Refs. [11, 33, 53, 76, 77]. Table 3 compares limits to

TABLE 2 Time-varying frequency ratio R measurements using different combinations of optical atomic clocks (A_1 and A_2), and their corresponding α varying sensitivity coefficients from two separate works. The inferred limits on the time drift of α are also given from these works.

$A_1 - A_2$	$\dot{R}/R$	$K_\alpha(A_1) - K_\alpha(A_2)$	$\dot{\alpha}/\alpha$	Refs
Al⁺–Hg⁺	$(-0.53 \pm 0.79) \times 10^{-16}$	2.95	$-1.6 \pm 2.3 \times 10^{-17}$	[12]
Yb⁺ E2–E3	$(-6.8 \pm 7.5) \times 10^{-18}$	−6.95	$1.0 \pm 1.1 \times 10^{-18}$	[13]

TABLE 3 Comparison of various limits to variation in α with its absolute value ($\Delta\alpha/\alpha$) obtained from different types of works over a time interval Δt. The corresponding limits in annual fractional rate of change ($\dot{\alpha}/\alpha$), with a crude assumption of a linear change in time, are also given for the purpose of comparing them with the values given in Ref. [76] if one wishes to do so.

Source	$\Delta\alpha/\alpha$	Δt (year)	$\dot{\alpha}/\alpha$(year⁻¹)	Refs
Cosmological	$< 10^{-3}$	10^{10}	10^{-13}	[53]
Astrophysical (quasar)	$(2.18 \pm 7.18) \times 10^{-5}$	10^{10}	$(2.18 \pm 7.18) \times 10^{-15}$	[65]
Geophysical (Oklo)	$< 1.1 \times 10^{-8}$	2.1×10^9	$< 10^{-17}$	[68]
Laboratory			$(1.0 \pm 1.1) \times 10^{-18}$	[13]

the temporal variation in α from various sources. The interpretation of the astrophysical observations and geophysical data, principally the Oklo phenomenon, are highly dependent on many assumptions. Limits derived from the laboratory studies by comparing frequencies of the atomic clocks in that sense can be much less unambiguous. However, these results can only restricted to the present day phenomena and to the region of space of the earth's orbit. The time drift of the ratio of two atomic frequencies can also depend on the proton-to-electron mass ratio *via* $\mu_N/\mu_B = 1/\mu$ when at least one of the atomic clock frequencies is based on the hyperfine transition like the Rb and Cs microwave clocks [13, 71, 73, 74]. Together this quantity with α variation can tell us about possible variation of a strong-interaction parameter X_q, that denotes the ratio between the average quark mass and the quantum chromodynamic scale Λ_{QCD}. Therefore, comparison of two optical clock frequencies is quite important in order to infer directly signatures of the variation of the fundamental constants.

3 Potential candidates of HCI clocks

In the past decade, many HCIs have been proposed for making atomic clocks. A list of these ions and their proposed clock transitions are mentioned in Table 4. Transition energies and their sensitivity coefficients q and K are also given in the same table. The first optical HCI clock, based on the Ar¹³⁺ ions, has been demonstrated at the uncertainty level 2.2×10^{-17}. It used sympathetic cooling techniques to decrease temperature to milli-kelvin to cool the ions produced using the electron beam ion trap (EBIT). The accuracy of this HCI based optical clock is already comparable to that of many optical clocks in its first attempt itself [78, 79]. The clock transition in the Ar¹³⁺ ion was proposed by Yudin et al [37] in 2014, along with many other HCIs having magnetic-dipole (M1) transitions between the $np\ ^2P_{1/2} - {}^2P_{3/2}$ and among the np^2 $^3P_{0,1}$ fine structure splitting of many monovalent and divalent HCIs respectively. Later, we analyzed major systematics theoretically of clock transitions in the monovalent B-like, Al-like, and Ga-like ions [44, 46].

Based on the electric quadrupole (E2) transition between the np^4 $^3P_{0,2}$ fine structure splitting, the Ni¹²⁺ ion along with the other three

HCIs, Cu¹³⁺, Pd¹²⁺ and Ag¹³⁺, were proposed as promising candidates for making high-accuracy optical clocks [45]. The transition rate of the E2 transition is usually far slower than that of the M1 transition. Therefore the advantage of considering the E2 transitions in these ions for clocks is that they all possess larger quality factors than the M1 transitions between the $(np)^2P_{1/2,3/2}$ fine structure splittings. The spectroscopy lines of the Ni¹²⁺ ion in the EBIT has been identified by Liang et al. very recently [80]. Ba⁴⁺ with $5s^25p^4$ configuration was proposed by Beloy [48] as the mediumly ionized clock. The α varying sensitivity coefficients in the Ar¹³⁺, Ni¹²⁺ and Ba⁴⁺ ions are found to be much larger than most of the available singly charged ion and neutral atomic clocks except Hg⁺ and Yb⁺ clocks.

Among all the proposed HCIs, Ir¹⁷⁺ shows having the largest sensitivity to variation of α [30]. The double-hole configuration of Ir¹⁷⁺ offers several transitions in the optical range. Two of them, $4f^{13}5s$ $^3F^\circ_4 - 4f^{14}\ ^1S_0$ and $4f^{13}5s\ ^3F^\circ_4 - 4f^{12}5s^2\ ^3H_6$, are claimed to be suitable as clock transitions [30]. The optical lines in Ir¹⁷⁺ along with other Nd-like W, Re, Os, and Pt ions, have been identified by Winderger el al [81]. Their inferred transition energy of the $4f^{13}5s\ ^3F^\circ_4 - 4f^{12}5s^2\ ^3H_6$ transition lies between 4.0392 and 4.6397 eV. However, this value disagrees with the theoretical values that predict 3.7623 eV [82] and 3.003 eV [81]. Similarly, the $4f^{13}5s\ ^3F^\circ_4 - 4f^{14}\ ^1S_0$ transition that has been identified to have the largest q and K values are not observed experimentally, while transition energies from different theoretical results show about 20% difference [81, 82]. The Cf¹⁶⁺ and Cf¹⁷⁺ ions proposed by Berengut et al. [32] and the Cf¹⁵⁺ ion proposed by Dzuba [43] for atomic clocks also have relatively large q and K values. Porsev et al. have also explored the possibility of developing optical clocks using the Cf¹⁵⁺ and Cf¹⁷⁺ ions [47].

The ultra-narrow $5s_{1/2} - 5f_{5/2}$ optical transitions in Nd¹³⁺ and Sm¹⁵⁺ were proposed for the construction of the HCI clocks and search for variation of the fine-structure constant [36]. These lines have relatively large q and K values, but their transition wavelengths are about 170 and 180 nm, which are out of the accessible range of the currently available lasers. Safronova et al. searched for the visible lines in a series of the Ag-like, Cd-like, In-like, and Sn-like HCIs for the development of frequency standards and to probe variation of the fine-structure constant [38–40]. Among these ten HCIs recommended by

TABLE 4 A summary of the HCIs proposed for making optical clocks. The definition of q and K_α is given in text.

Z	Atoms	Clock transition	Energy (cm^{-1})	q (cm^{-1})	K_α (unit less)	Refs
18	Ar^{13+}	$2p_{1/2} - 2p_{3/2}$	22656.22	22137	1.95	[37, 79, 45]
28	Ni^{12+}	$3s^2 3p^4\ ^3P_2 - ^3P_0$	20060	14982	1.49	[45, 80]
56	Ba^{4+}	$5s^2 5p^4\ ^3P_2 - ^3P_0$	11302	5900	1.04	[48, 51]
82	Pb^{2+}	$6s^2\ ^1S_0\ 6s6p\ ^3P_0$	60397			[49]
77	Ir^{17+}	$4f^{13}5s^3 F^\circ_4 - 4f^{14}\ ^1S_0$	5055	367161	145.3	[30]
		$4f^{13}5s\ ^3F^\circ_4 - 4f^{12}5s^2\ ^3H_6$	35285	−385367	−21.84	
98	Cf^{15+}	$5f6p^2\ ^2F^\circ_{5/2} - 5f^26p\ ^2H^\circ_{9/2}$	13303	380000	57.1	[43]
			16170			[47]
98	Cf^{16+}	$5f6p\ J = 3 - 6p^2\ J = 0$	5267	370928	140.8	[32]
98	Cf^{17+}	$5f_{5/2} - 6p_{1/2}$	18686	449750	48.14	[32]
			20611			[47]
60	Nd^{13+}	$5s_{1/2} - 4f_{5/2}$	58897	106000	3.60	[36]
62	Sm^{15+}	$4f_{5/2} - 5s_{1/2}$	55675	−136000	−4.89	[36]
59	Pr^{9+}	$5p^2\ ^3P_0 - 5p4f\ ^3G_3$	20216	42721	4.23	[38]
			2201.36	69918	6.33	[83]
60	Nd^{9+}	$(5p^2 4f)^\circ_{5/2} - (5p4f^2)^\circ_{9/2}$	20594	67136	6.52	[50]
67	Ho^{14+}	$4f^6 5s\ ^8F_{1/2} - 4f^5 5s^2\ ^6H^\circ_{5/2}$	23823	−186000	7.81	[41]

them, the Pr^{9+} ion seems to be the more attractive, which has an optical transition $5p^2\ ^3P_0 - 5p4f\ ^3G_3$ between the ground and the first excited states. The lifetime of the excited clock state was estimated to be 10^{14} s, and it has a wavelength at 475 nm, which can be accessed by the currently available. Bekker et al. present the EBIT measurements of the spectra of Pr^{9+}, which refines the energy levels of such proposed nHz-wide clock line and demonstrates about Pr^{9+} having very large sensitivity coefficient to variation of α and variation of local Lorentz invariance probing coefficient [83]. The Sb-like Nd^{9+} ion was proposed by Yu et al. [50] as a possible HCI clock. The Nd^{9+} ion has the ground state configuration as $(5p^2 4f)^\circ_{5/2}$ and the first excited state configuration as $(5p4f^2)^\circ_{9/2}$. The E2 transition of $(5p^2 4f)^\circ_{5/2} - (5p4f^2)^\circ_{9/2}$ shows large q and K values and feasibility of making a high accuracy atomic clock.

Dzuba et al. studied the I-like Ho^{14+} ion as a possible candidate for an extremely accurate and stable optical clock which has q and K slightly larger than Pr^{9+} and Nd^{9+}. The Ho^{14+} ion has all the desired features, including relatively strong optical electric-dipole (E1) and M1 transitions can be used for cooling and detection. The electronic configuration of the ground state of this ion has seven valence electrons in the open s and f shells, which gives rise to a large number of fine structure splitting. Nakajima et al. have observed the visible spectra of the above ion using a compact electron beam ion trap [84]. They found that the ground state configuration of Ho^{14+} is [Kr]$4f^6 5s$ with 577 fine structure levels spreading over an energy range of about 40 eV, and the electronic configuration of the first-excited configuration of this ion [Kr]$4f^5 5s^2$, with 200 fine structure levels spreading over the similar energy range. Their results show a huge

number of emissions in the Ho^{14+} visible spectra, whereas these lines are challenging to distinguish while experimenting as they all have similar transition probabilities.

4 General directions for identifying HCI clock candidates

The HCIs have very compact sizes and wave functions compared with their counter neutral atoms and singly charged ions, which are accompanied with the scaling laws for energies and transition matrix elements with increasing the charge number Z_{ion} in an isoelectronic sequence [26, 85]. In order to understand the enhancement of q in the HCIs, Berengut et al suggested a simple analytical expression as [29, 85].

$$q_n \approx -I_n \frac{(Z\alpha)^2}{\nu(j+1/2)} \tag{3}$$

and

$$I_n = -E_n = \frac{Z_a^2}{2n^2} = \frac{(Z_{ion}+1)^2}{2\nu^2}, \tag{4}$$

where Z is the atomic number, j is the total angular momentum of the orbital, $I_n = -E_n$ represents the positive ionization potential energy of the electron in the electronic orbital, and n is the integer principal quantum number. The equality in Eq. (4) relates I_n to E_n by using an effective principle quantum number ν and an effective charge Z_a that the electron sees at larger distances, considering the screening in a multi-electron system. Eqs 3, 4 explain how enhancement of q increases with I_n, i.e., with larger Z_{ion}. Besides, q is related to j, which indicates that the excitation among orbitals with larger j differences can have bigger q. Appearance of Z means a heavy element is preferred, usually offering larger relativistic effects. Besides, the hole state in an otherwise filled external shell will have the highest q for particular values of Z and Z_a.

The energy scaling with Z_{ion} indicates that transitions in HCIs are frequently in the XUV and x-ray range unsuitable for making atomic clocks. However, we can realize that on occasions where HCIs have forbidden transitions can be in the optical region, as has been pointed out by the previous studies. Firstly, the energy interval between the fine structure and the hyperfine structure energy levels increase greatly with the charge number Z_{ion} in the HCI isoelectronic sequences, which leads to widening these level splitting. It causes transition lines to change from the microwave, as seen in the neutral atoms and singly charged ions, to the optical in HCIs. The other possible approach can be adopted to find suitable HCIs for clocks by analyzing the orbital energy crossings in the isoelectronic sequences of atomic systems. Near level crossings, frequencies of transitions involving the orbital sequence switching can be much smaller than the ionization potentials. This helps to distinguish suitable transitions that can be in the optical range in a prudent manner.

In the following, we overview two basic rules for selecting HCIs as candidates for making atomic clocks. In fact, from a general observation point of view of all the previously proposed HCI candidates for clocks, can be classified into two categories: HCIs with the M1 and E2 clock transitions among the fine structure splitting and HCIs with the forbidden transitions among the electronic configurations whose candidatures can be understood using orbital energy crossing scheme. Thus, we proceed further to investigate more HCIs along the same lines of thoughts to search for other suitable candidates for HCI clocks.

4.1 Forbidden transitions within fine-structure splitting

Studies of spectroscopic properties of forbidden lines are attractive for quite a long time in the fields of astronomical and laboratory research since they are frequently observed in astrophysical observations, e.g., in the solar corona and in solar flares, and high-temperature fusion plasma, where these forbidden lines are often used as diagnostic tools to find out temperature, constituents and ion densities [86–91]. The M1 transition lines occur amongst the fine-structure splitting of the HCI isoelectronic sequences and are usually found in the optical range. They are easier to observe in contrast to the resonant lines that appear in the far ultraviolet region. Biemont and coworkers have carried out comprehensive studies on many radiative properties of transition lines in HCIs having ground state configurations as $3p^k$, $4p^k$, $5p^k$, and $6p^k$ [92–102] with $k = 1, 2, 3, \cdots$ number of valence electrons.

Recently, many optical forbidden transitions between the fine-structure splitting in the HCIs are considered as clock transitions, and many of them are listed in Table 5. As can be seen from the above table, many proposals have considered the forbidden M1 transitions between the fine-structure splitting $^2P_{1/2}$ $-^2P_{3/2}$ in HCIs having single p-valence orbital and between the fine -structure splitting $^3P_0$ $-^3P_1$ in HCIs having two p valence electrons for making ultra-precise atomic clocks. Yu et al. have investigated B-, Al-, and Ga-like HCIs for making atomic clocks that have fine-structure splitting as $2p_{1/2,3/2}$, $3p_{1/2,3/2}$ and $4p_{1/2,3/2}$ respectively. It was found in this work that the M1 transitions between these fine structure splitting have appropriate wavelengths and quality factors as well as relatively smaller systematics (at the 10^{-19} level). Therefore, these ions are appeared to be excellent candidates to be considered for making atomic clocks [44, 45]. One can presume from these analyses that HCIs with np^k ground state configurations with $n \geq 5$ can have similar transition properties and be suitable for atomic clocks.

Compared with M1 transitions, wherever E2 transitions play important roles in deciding the lifetimes of an upper state, they can offer larger quality factors if considered as clock transitions. Yu et al. have proposed the S-like Ni^{12+} and Cu^{13+} ions having the $3p^4$ ground-state configurations, and the Se-like Pd^{12+} and Ag^{13+} ions having the $4p^4$ ground-state configurations as potential candidates for making an ultra-precise atomic clock, as listed in Table 5. The $^3P_2$ $-^3P_0$ transitions in the $^{58}Ni^{12+}$ and $^{106}Pd^{12+}$ ions with nuclear spin $I = 0$ and the $|^3P_2, F = 1/2\rangle - |^3P_0, F = 3/2\rangle$ transition in $^{63}Cu^{13+}$ with $I = 3/2$, and the $|^3P_2, F = 3/2\rangle - |^3P_0, F = 1/2\rangle$ transition in $^{107}Ag^{13+}$ with $I = 1/2$ can also be suitable for clock transitions, which can offer clock transitions with fractional uncertainties below 10^{-19} level. These HCIs have simple atomic energy level structures to carry out spectroscopic measurements, and the quality factors of the respective clock transitions are of the order 10^{15}–10^{16}. Allehabi et al. have identified $^3P_2$ $-^3P_0$ transitions from HCIs of group-16 elements that are governed by E2 channel and are in the optical region as possible high-accuracy optical clocks, including the S−, Se−, and Te-like systems, which have $3p^4$, $4p^4$, and $5p^4$ ground configurations [51] as listed in Table 5.

The forbidden transitions among the fine-structure splitting in HCIs possessing nd^k configuration in their ground state are more

TABLE 5 Summary of selected M1 and E2 HCI transitions of fine-structure splittings. a [b] should be read as $a \times 10^b$.

Ions	Z	Conf	Clock transition	Type	λ (nm)	Γ (Hz)	Q	q (cm^{-1})	K	Refs
S^{11+}	16	$2p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	760	3.27	1.2 [14]	12795	1.94	[37, 46]
Cl^{12+}	17	$2p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	574	7.59	6.9 [13]	16960	1.95	[37, 46]
Ar^{13+}	18	$2p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	441	16.71	4.1 [13]	22137	1.95	[37, 46]
K^{14+}	19	$2p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	345	35.07	2.5 [13]	28137	1.94	[37, 46]
Cr^{11+}	24	$3p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	816	2.66	1.4 [14]	−12352	−2.01	[37, 44]
Mn^{12+}	25	$3p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	654	5.12	9.0 [13]	−15440	−2.02	[37, 44]
Co^{14+}	27	$3p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	436	17.28	4.0 [13]	−23301	−2.03	[37, 44]
Cu^{16+}	29	$3p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	301	51.95	1.9 [13]	33836	2.04	[37, 44]
Nb^{10+}	41	$4p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	418	19.76	3.6 [13]	23928	2.00	[37, 46]
Ru^{13+}	44	$4p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	255	87.01	1.4 [13]	41741	2.13	[37, 46]
Xe^{5+}	54	$5p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	641	5.43	8.6 [13]			[37]
Ba^{7+}	56	$5p$	$^2P^o_{1/2}-^2P^o_{3/2}$	M1	424	18.80	3.8 [13]			[37]
Ni^{14+}	28	$2p^2$	$^3P_0-^3P_1$	M1	670	9.5	4.7 [13]			[37]
Br^{3+}	35	$3p^2$	$^3P_0-^3P_1$	M1	3814	0.05	1.6 [15]			[37]
Rb^{5+}	37	$4p^2$	$^3P_0-^3P_1$	M1	1946	0.39	4.0 [14]			[37]
Xe^{4+}	54	$5p^2$	$^3P_0-^3P_1$	M1	1076	2.3	1.2 [14]			[37]
Ba^{6+}	56	$5p^2$	$^3P_0-^3P_1$	M1	645	10.7	4.3 [13]			[37]
Ni^{12+}	28	$3p^4$	$^3P_2-^3P_0$	E2	498	0.008	7.2 [16]	22473	2.3	[45, 80]
Cu^{13+}	29	$3p^4$	$^3P_2-^3P_0$	E2	431	0.011	6.6 [16]			[45]
Pd^{12+}	46	$4p^4$	$^3P_2-^3P_0$	E2	396	0.080	9.5 [15]			[45]
Ag^{13+}	47	$4p^4$	$^3P_2-^3P_0$	E2	367	0.100	8.2 [15]			[45]
Xe^{2+}	54	$5p^4$	$^3P_2-^3P_0$	E2	1230	0.006	3.8 [16]	5611	1.38	[51]
Ba^{4+}	56	$5p^4$	$^3P_2-^3P_0$	E2	885	0.018	1.9 [16]	5976	1.06	[51]
Ce^{6+}	58	$5p^4$	$^3P_2-^3P_0$	E2	704	0.034	1.2 [16]	5907	0.83	[51]
Zr^{6+}	40	$4p^4$	$^3P_2-^3P_0$	E2	816	0.007	5.2 [16]	8939	1.42	[51]
Cd^{14+}	48	$4p^4$	$^3P_2-^3P_0$	E2	347	0.12	7.1 [15]	8837	0.61	[51]
Ge^{16+}	32	$3p^4$	$^3P_2-^3P_0$	E2	300	0.038	2.6 [16]	18484	1.11	[51]
Kr^{20+}	36	$3p^4$	$^3P_2-^3P_0$	E2	213	0.13	1.1 [16]	17252	0.74	[51]
Sr^{22+}	38	$3p^4$	$^3P_2-^3P_0$	E2	187	0.20	8.1 [15]	14130	0.53	[51]
Cu^{10+}	29	$3d$	$^2D_{3/2}-^2D_{5/2}$	M1	2465	0.114	1.1 [15]			[112]
Ga^{12+}	31	$3d$	$^2D_{3/2}-^2D_{5/2}$	M1	1585	0.430	4.4 [14]			[112]
As^{14+}	33	$3d$	$^2D_{3/2}-^2D_{5/2}$	M1	1071	1.394	2.0 [14]			[112]
Se^{15+}	34	$3d$	$^2D_{3/2}-^2D_{5/2}$	M1	893	2.403	1.4 [14]			[112]
Hf^{12+}	72	$4f^{12}$	$^3H_6-^3F_4$	E2	1168	9.5 [−6]	2.7 [19]			[35]
Os^{18+}	76	$4f^{12}$	$^3H_6-^3F_4$	E2	1008	1.4 [−5]	2.2 [19]			[35]
Hg^{22+}	80	$4f^{12}$	$^3H_6-^3F_4$	E2	922	1.3 [−5]	2.4 [19]			[35]
Po^{26+}	84	$4f^{12}$	$^3H_6-^3F_4$	E2	860	1.2 [−5]	2.9 [19]			[35]
Ra^{30+}	88	$4f^{12}$	$^3H_6-^3F_4$	E2	814	1.1 [−5]	3.2 [19]			[35]
U^{34+}	92	$4f^{12}$	$^3H_6-^3F_4$	E2	778	1.1 [−5]	3.8 [19]			[35]

complicated to study than the HCIs having np^k configurations in the ground state. The reason is d-orbitals have many subshells bestowing strong open-shell problems. As a result, it is challenging to study transition properties among the fine-structure splitting of these HCIs, even using the available sophisticated atomic many-body methods. Some of these transitions are found to be useful in the production processes 13.5-nm-wavelength extreme ultraviolet (EUV) radiation for nanolithographic applications [103]. They also give rise EUV spectra between 10 and 25 nm in the tungsten HCIs from the $3d$ open-shell configurations as listed in the NIST database [104]. It is natural to anticipate that some of these transitions could be considered for atomic clocks. Theoretical studies carried out in Refs. [105–111] support this idea. A wide range of calculations on the M1 and E2 transition probabilities among the fine-structure splitting of the $3d\ ^2D_{3/2} - 3d\ ^2D_{5/2}$ transitions are performed in the K-like sequence HCIs to find out their feasibility for using optical clocks [112]. Some of them are listed in Table 5.

Now we turn to the transitions involving fine-structure partners of open $4f$ shells. For the reason mentioned above in the case of the nd^k configurations, theoretical studies of these transitions are even more complicated than the open p- and d-shells. Electrons from the open-shell $4f$ orbitals usually show strong correlation effects with the inner s, p, and d shells. Historically, the forbidden transitions among the fine structures of the open f-shell configurations are widely investigated for various applications such as carrying out temperature and density diagnostics of plasma, and astronomical spectral identifications [113–117]. A series of HCIs from Hf^{12+} to U^{34+} that have $4f^{12}$ valence shells were proposed to be excellent candidates for building exceptionally accurate atomic clocks by Derevianko et al. [35, 118]. Some of them are listed in Table 5. In addition to the highly forbidden laser-accessible transitions within the $4f^{12}$ ground-state configurations that can be used to be the clock transitions, these ions also have additional M1 and E2 transitions along with the M1 clock transitions that can be used for cooling ions during the measurement.

In Table 5, we compare the q and K values for the proposed candidates of the HCI clocks when they are reported earlier. Most of them have larger q and K values than their isoelectronic neutral atoms and singly charged ions, however, are still less than the singly charged ions Hg^+ and Yb^+. It indicates that q and K are not significantly prominent in the M1 and E2 transitions between the fine-structure splittings.

4.2 Orbital energy crossings in complex HCIs

Generally, the ordering of energy levels in neutral atoms follows the $n + l$ and n orbital filling scheme (often referred to as Madelung rule [119]), where n and l are the principles and angular quantum numbers. According to this rule, we can assume that the order of the atomic orbital filling in the neutral and singly charged ions would be $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 5f \rightarrow 6d \rightarrow 7p\cdots$. However, this rule is violated in the hydrogen-like ions, in which the filling order of the orbitals complies with the Coulombic ordering. That is, orbitals with smaller n are filled first, and for equal n, the orbitals with smaller l are filled. If we follow this ordering, then nd orbitals are filled first instead of $(n + 1)s$ orbitals after the np orbitals. Similarly, nf orbitals are filled first instead of $(n + 1)s$ orbitals after the nd. The phenomenon of the orbital energy of nd and nf diving down while $(n + 1)s$ and also $(n + 1)p$ rising up as

the Z and Z_{ion} increasing in an isoelectronic sequence is referred to as the orbital energy crossing, which is first investigated by Berengut, et al., [34]. They exterminated all the energy crossing in the periodical table. The previously proposed HCIs for making atomic clocks are mostly concentrated on the $nd - (n + 1)s$ crossing and the $4f - 5s$ crossing.

4.2.1 The $nd - (n + 1)s$ level crossings

Table 6 summarizes the $3d - 4s$ energy level-crossing occurring in the K-like and Ca-like isoelectronic sequences and the isoelectronic sequences of the elements belonging to the $3d$ metals. The ground state configurations of the singly charged ions belonging to these elements are generally $3d^{x-1}4s$, while the ground state configuration of their double charged ions happens to be $3d^x$ with x denoting the number of the valence electrons that is one ($x = 1$) for the K-like isoelectronic sequence, two ($x = 2$) for the Ca-like isoelectronic sequences, and so on till $x = 10$ for the Ni-like isoelectronic sequences. So one would anticipate that the $3d - 4s$ energy level crossing can occur in these isoelectronic sequences when the charges of the ions increase further. However, there have been several exceptions seen where no $3d - 4s$ level-crossings have occurred in these isoelectronic sequences, such as HCIs belonging to the Ti-like and V-like isoelectronic sequences which have the number of the valence electrons close to half-filling and to the Fe-, Co-, and Ni-like isoelectronic sequences that are close to full-filling. In these cases, the ground state configuration is preferred to be $3d^x$. Table 7 summarizes the $4d - 5s$ energy level-crossings that occur in a series of isoelectronic sequences of elements from the fifth row of the periodic table. The $4d - 5s$ energy level-crossings are observed in the Rb-, Sr-, and Y-like isoelectronic sequences with $x = 1-3$ and in the Mo-like isoelectronic sequence with $x = 6$. However, no such energy level crossings are seen in the isoelectronic sequences with the number of valence electrons close to half- or fully-filled. i.e., for $x = 4, 5, 7, 8, 9, 10$. For the elements belonging to the sixth row of the periodic table, the $5d - 6s$ energy level crossings are observed in some isoelectronic sequences, shown in Table 8, such as in the Tm-, Yb-, Lu-, Ta-, W-, and Ir-like isoelectronic sequences.

As shown in Tables 6, Tables 7, Tables 8, the $nd - (n + 1)\ s$ energy level-crossings happen often in the doubly-charged ions. In these doubly-charged ions, transition wavelengths between their ground and first excited states in these ions are within the optical range. Such transitions are accompanied by changes in the electronic angular momenta from the s to d orbitals. Thus, considering these HCIs as atomic clocks would offer substantial relativistic sensitivity coefficients to probe α variation. For example, The Ac^{2+}, Zr^{2+}, Hf^{2+}, and Hg^{2+} has been suggested as suitable candidate for laboratory searches of space-time variation of α [31]. We find that many double charged HCI ions have similar transitions, such as the $3d^2 - 3d4s$ transition in Ti^{2+}, the $3d^3 - 3d^24s$ transition in V^{2+}, the $4d^3 - 4d^25s$ transition in Nb^{2+}, the $5d^5 - 5d^46s$ transition in Re^{2+}, the $5d^6 - 5d^56s$ transition in Os^{2+}, and the $5d^9 - 5d^86s$ transition in Au^{2+}, which could be the promising HCIs for the study of possible temporal variation of α. The singly and triply charged ions also have some new interesting optical transitions, for example, Allehabi, et al. have demonstrated that the metastable excited state in Hf^+ and Hf^{3+} may be good clock states having sufficiently long-lived upper states, insensitive to the external perturbations, and additional E1 cooling line available [52].

4.2.2 The $4f - 5s$ and $4f - 5p$ level crossings

The $4f - 5s$ orbital energy crossing frequently occurs in the isoelectronic sequences of the electronic configuration containing open-shelled $5s$ and $4f$ orbital. Table 9 lists some HCIs in such

TABLE 6 The energy levels of some ions in the K-like ($N = 19$), Ca-like ($N = 20$), and the forth row transition metals from Sc-to Ni-like ($N = 21 - 28$) isoelectronic sequence HCIs, where N is the number of the electron, Z is the atomic number, and x is the number of valence electrons. The closed-shell configuration is [Ar] $\equiv 1s^22s^22p^63s^23p^6$. The data are taken from the NIST database [120], and units are in cm^{-1}.

N	Z	x	Ion	Configuration	State	Energy	N	Z	x	Ion	Configuration	State	Energy
			K-like isoelectronic sequences							Ca-like isoelectronic sequences			
19	20	1	Ca$^+$	[Ar]$4s$	$^2S_{1/2}$	0	20	21	2	Sc$^+$	[Ar]$3d4s$	$^3D_1$	0
				[Ar]$3d$	$^2D_{3/2}$	13650					[Ar]$3d^2$	$^3F_2$	4803
	21	1	Sc^{2+}	[Ar]$3d$	$^2D_{3/2}$	0		22	2	Ti^{2+}	[Ar]$3d^2$	$^3F_2$	0
				[Ar]$4s$	$^2S_{1/2}$	25539					[Ar]$3d4s$	$^3D_1$	38064
	22	1	Ti^{3+}	[Ar]$3d$	$^2D_{3/2}$	0		23	2	V^{3+}	[Ar]$3d^2$	$^3F_2$	0
				[Ar]$4s$	$^2S_{1/2}$	80389					[Ar]$3d4s$	$^3D_1$	96196
			Sc-like isoelectronic sequences							Ti-like isoelectronic sequences			
21	22	3	Ti$^+$	[Ar]$3d^24s$	$^4F_{3/2}$	0	22	23	4	V$^+$	[Ar]$3d^4$	$^5D_0$	0
				[Ar]$3d^3$	$^4F_{3/2}$	908					[Ar]$3d^34s$	$^5F_1$	2604
	23	3	V^{2+}	[Ar]$3d^3$	$^4F_{3/2}$	0		24	4	Cr^{2+}	[Ar]$3d^4$	$^5D_0$	0
				[Ar]$3d^24s$	$^4F_{3/2}$	43942					[Ar]$3d^34s$	$^5F_1$	49492
	24	3	Cr^{3+}	[Ar]$3d^3$	$^4F_{3/2}$	0		25	4	Mn^{3+}	[Ar]$3d^4$	$^5D_0$	0
				[Ar]$3d^24s$	$^4F_{3/2}$	103996					[Ar]$3d^34s$	$^5F_1$	111506
			V-like isoelectronic sequences							Cr-like isoelectronic sequences			
23	24	5	Cr$^+$	[Ar]$3d^5$	$^6S_{5/2}$	0	24	25	6	Mn$^+$	[Ar]$3d^54s$	$^7S_3$	0
				[Ar]$3d^44s$	$^6D_{1/2}$	11961					[Ar]$3d^6$	$^5D_4$	14326
	25	5	Mn^{2+}	[Ar]$3d^5$	$^6S_{5/2}$	0		26	6	Fe^{2+}	[Ar]$3d^6$	$^5D_4$	0
				[Ar]$3d^44s$	$^6D_{1/2}$	62457					[Ar]$3d^54s$	$^5S_2$	41000
	26	5	Fe^{3+}	[Ar]$3d^5$	$^6S_{5/2}$	0		27	6	Co^{3+}	[Ar]$3d^6$	$^5D_4$	0
				[Ar]$3d^44s$	$^6D_{1/2}$	127766					[Ar]$3d^54s$	$^5S_2$	102774
			Mn-like isoelectronic sequences							Fe-like isoelectronic sequences			
25	26	7	Fe$^+$	[Ar]$3d^64s$	$^6D_{9/2}$	0	26	27	8	Co$^+$	[Ar]$3d^8$	$^3F_4$	0
				[Ar]$3d^7$	$^4F_{9/2}$	1872					[Ar]$3d^74s$	$^3F_4$	9814
	27	7	Co^{2+}	[Ar]$3d^7$	$^4F_{9/2}$	0		28	8	Ni^{2+}	[Ar]$3d^8$	$^3F_4$	0
				[Ar]$3d^64s$	$^4D_{7/2}$	55729					[Ar]$3d^74s$	$^5F_4$	61338
	28	7	Ni^{3+}	[Ar]$3d^7$	$^4F_{9/2}$	0		29	8	Cu^{3+}	[Ar]$3d^8$	$^3F_4$	0
				[Ar]$3d^64s$	$^4D_{7/2}$	120909					[Ar]$3d^74s$	$^5F_4$	128343
			Co-like isoelectronic sequences							Ni-like isoelectronic sequences			
27	28	9	Ni$^+$	[Ar]$3d^9$	$^2D_{5/2}$	0	28	29	10	Cu$^+$	[Ar]$3d^{10}$	$^1S_0$	0
				[Ar]$3d^84s$	$^2F_{7/2}$	13550					[Ar]$3d^94s$	$^1D_2$	26264
	29	9	Cu^{2+}	[Ar]$3d^9$	$^2D_{5/2}$	0		30	10	Zn^{2+}	[Ar]$3d^{10}$	$^1S_0$	0
				[Ar]$3d^84s$	$^2F_{7/2}$	67017					[Ar]$3d^94s$	$^1D_2$	83500
	30	9	Zn^{3+}	[Ar]$3d^9$	$^2D_{5/2}$	0		31	10	Ga^{3+}	[Ar]$3d^{10}$	$^1S_0$	0
				[Ar]$3d^84s$	$^2F_{7/2}$	135951					[Ar]$3d^94s$	$^1D_2$	156025

kinds of isoelectronic sequences. This type of HCIs usually has the large number of charge, larger than 10 in most cases. The Ag-, Cd-, In-, Sn-like HCIs containing one, two, three, and four valence electrons have been investigated by Safronova, et al [38–40]. When valence electrons are larger than 4, the electronic configuration becomes far more complicated. Therefore there is little data available for such kind

TABLE 7 The energy level of some ions in the Rb-like ($N = 37$), Sr-like ($N = 38$), and the fifth row transition metals from Y- to Pd-like ($N = 39 - 46$) isoelectronic sequence HCIs, where N is the number of the electron, Z is the atomic number, and x is the number of valence electron. $[Kr] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$. The data are from the NIST database [120] and in cm^{-1}.

N	Z	x	Ion	Configuration	State	Energy	N	Z	x	Ion	Configuration	State	Energy
			Rb-like isoelectronic sequences							Sr-like isoelectronic sequences			
37	38	1	Sr$^+$	[Kr]$5s$	$^2S_{1/2}$	0	38	39	2	Y$^+$	[Kr]$5s^2$	$^1S_0$	0
				[Kr]$4d$	$^2D_{3/2}$	14555					[Kr]$4d^2$	$^1D_2$	14833
	39	1	Y^{2+}	[Kr]$4d$	$^2D_{3/2}$	0		40	2	Zr^{2+}	[Kr]$4d^2$	$^3F_2$	0
				[Kr]$5s$	$^2P_{1/2}$	7467					[Kr]$5s^2$	$^1S_0$	48506
	40	1	Zr^{3+}	[Kr]$4d$	$^2D_{3/2}$	0		41	2	Nb^{3+}	[Kr]$4d^2$	$^3F_2$	0
				[Kr]$5s$	$^2S_{1/2}$	38253					[Kr]$4d5s$	$^3D_1$	52064
			Y-like isoelectronic sequences							Zr-like isoelectronic sequences			
39	40	3	Zr$^+$	[Kr]$4d^2 5s$	$^4F_{3/2}$	0	40	41	4	Nb$^+$	[Kr]$4d^4$	$^5D_0$	0
				[Kr]$4d5s^2$	$^2D_{3/2}$	14298					[Kr]$4d^3 5s$	$^5F_1$	2356
	41	3	Nb^{2+}	[Kr]$4d^3$	$^4F_{3/2}$	0		42	4	Mo^{2+}	[Kr]$4d^4$	$^5D_0$	0
				[Kr]$4d^2 5s$	$^4F_{3/2}$	25220					[Kr]$4d^3 5s$	$^5F_1$	32419
	42	3	Mo^{3+}	[Kr]$4d^3$	$^4F_{3/2}$	0		43	4	Tc^{3+}	[Kr]$4d^4$	$^5D_0$	0
				[Kr]$4d^2 5s$	$^4F_{3/2}$	6					[Kr]$4d^3 5s$	$^5F_1$	71139
			Nb-like isoelectronic sequences							Mo-like isoelectronic s sequences			
41	42	5	Mo$^+$	[Kr]$4d^5$	$^6D_{5/2}$	0	42	43	6	Tc$^+$	[Kr]$4d^5 5s$	$^7S_3$	0
				[Kr]$4d^4 5s$	$^6D_{1/2}$	11783					[Kr]$4d^6$	$^5D_4$	3461
	43	5	Tc^{2+}	[Kr]$4d^5$	$^6D_{5/2}$	0		44	6	Ru^{2+}	[Kr]$4d^6$	$^5D_4$	0
				[Kr]$4d^4 5s$	$^6D_{1/2}$	44254					[Kr]$4d^5 5s$	$^5S_2$	41112
			Tc-like isoelectronic sequences							Ru-like isoelectronic s sequences			
43	44	7	Ru$^+$	[Kr]$4d^7$	$^4F_{9/2}$	0	44	45	8	Rh$^+$	[Kr]$4d^8$	$^3F_4$	0
				[Kr]$4d^6 5s$	$^4D_{7/2}$	19379					[Kr]$4d^7 5s$	$^3F_4$	25376
	45	7	Rh^{2+}	[Kr]$4d^7$	$^4F_{9/2}$	0		46	8	Pd^{2+}	[Kr]$4d^8$	$^3F_4$	0
				[Kr]$4d^6 5s$	$^4D_{7/2}$	54632					[Kr]$4d^7 5s$	$^3F_4$	62561
			Rh-like isoelectronic sequences							Pd-like isoelectronic s sequences			
45	46	9	Pd$^+$	[Kr]$4d^9$	$^2D_{5/2}$	0	46	47	10	Ag$^+$	[Kr]$4d^{10}$	$^1S_0$	0
				[Kr]$4d^8 5s$	$^2F_{7/2}$	32281					[Kr]$4d^9 5s$	$^3D_3$	39168
	47	9	Ag^{2+}	[Kr]$4d^9$	$^2D_{5/2}$	0		48	10	Cd^{2+}	[Kr]$4d^{10}$	$^1S_0$	0
				[Kr]$4d^8 5s$	$^2F_{9/2}$	63246					[Kr]$4d^9 5s$	$^3D_3$	80454

of HCIs. Dzuba has investigated the energy levels of the I-like Ho^{14+} and Xe-like Er^{15+} with $x = 6$ and 7, which are proposed as candidates for an extremely accurate and stable optical atomic clock which is found to have large values of q and K suitable for the study of time variation of α. When $x \geq 12$, there observed some HCIs having the $4f - 5s$ crossing in the hole states of the $5s$ and $4f$ shells, as listed in Table 9. For example, the Ir^{17+} ion has been proposed for the search of variation of α, and its hole state of $5s4f^{14}$ has extremely high values of q and K, indicating the hole states can dramatically enhance the sensitivity to α variation [30]. Nandy and Sahoo have also investigated the W^{13+}, Ir^{16+}

and Pt^{17+} HCIs with ground state configurations $4f^{13}$ as promising optical clock candidates to probe variation of α [124].

The $4f - 5p$ energy level-crossing occurs in the isoelectronic sequences containing the open-shelled $5p$ and $4f$ configurations, and this type of HCIs usually have mediated number of charge, around ten or lower. Table 10 lists some of these kinds of HCIs. Safronova et al. have proposed In-like Pr^{10+} and Sn-like Pr^{9+} and Nd^{10+} as the potential candidates for atomic clocks [38–40]. Berengnut et al. have also proposed Sn-like Pr^{9+} as a promising candidate for developing an extremely accurate atomic clock for

TABLE 8 The energy levels of some ions in the isoelectronic (Isoelec.) sequences of several sixth row transition metals, where N is the number of the electron, Z is the atomic number, and x is the number of valence electron. $[Xe] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$. The data is taken from the NIST database unless cited others. Units for all the values are in cm^{-1}.

Isoelec. Sequences	N	Z	x	Ion	Configuration	State	Energy
Tm-like	69	70	1	Yb$^+$	$[Xe]4f^{14}6s$	$^2S_{1/2}$	0
					$[Xe]4f^{14}5d$	$^2D_{3/2}$	22961
Tm-like	69	71	1	Lu^{2+}	$[Xe]4f^{14}6s$	$^2S_{1/2}$	0
					$[Xe]4f^{14}5d$	$^2D_{3/2}$	5708
Tm-like	69	72	1	Hf^{3+}	$[Xe]4f^{14}5d$	$^2D_{3/2}$	0
					$[Xe]4f^{14}6s$	$^2S_{1/2}$	18380 [52]
Yb-like	70	71	2	Lu$^+$	$[Xe]4f^{14}6s^2$	$^1S_0$	0
					$[Xe]4f^{14}5d^2$	$^3P_0$	35652
Yb-like	70	72	2	Hf^{2+}	$[Xe]4f^{14}5d^2$	$^3F_2$	0
					$[Xe]4f^{14}5d6s$	$^3D_1$	2652 [31]
Lu-like	71	72	3	Hf$^+$	$[Xe]4f^{14}6s^25d$	$^2D_{3/2}$	0
					$[Xe]4f^{14}6s5d^2$	$^2F_{5/2}$	12070
Lu-like	71	74	3	W^{3+}	$[Xe]4f^{14}5d^3$	$^4F_{3/2}$	0
					$[Xe]4f^{14}5d^26s$	$^4F_{3/2}$	32692
Ta-like	73	74	5	W$^+$	$[Xe]4f^{14}5d^46s$	$^6D_{1/2}$	0
					$[Xe]4f^{14}5d^5$	$^6S_{5/2}$	7420
Ta-like	73	75	5	Re^{2+}	$[Xe]4f^{14}5d^5$	$^6S_{5/2}$	0
					$[Xe]4f^{14}5d^46s$	$^6D_{1/2}$	143961
W-like	74	75	6	Re$^+$	$[Xe]4f^{14}5d^56s$	$^7S_3$	0
					$[Xe]4f^{14}5d^46s^2$	$^5D_0$	13777
W-like	74	76	6	Os^{2+}	$[Xe]4f^{14}5d^6$	$^5D_4$	0
					$[Xe]4f^{14}5d^56s$	$^7S_3$	4578
W-like	74	77	6	Ir^{3+}	$[Xe]4f^{14}5d^6$	$^5D_4$	0
					$[Xe]4f^{14}5d^6$	$^3H_4$	14546
Ir-like	77	78	9	Pt$^+$	$[Xe]4f^{14}5d^9$	$^2D_{5/2}$	0
					$[Xe]4f^{14}5d^86s$	$^4F_{9/2}$	4787
Ir-like	77	79	9	Au^{2+}	$[Xe]4f^{14}5d^9$	$^2D_{5/2}$	0
					$[Xe]4f^{14}5d^86s$	$^4F_{9/2}$	50818 [121]

the measurement of sensitivity to variation of α. Yu et al. have calculated the atomic energy levels of Sb-like Nd^{9+} and suggested Nd^{9+} as a potential candidate for making an atomic clock [50]. The In-, Sn-, and Sb-like HCIs with mediated number of charge contain one, two, and three valence electrons distributing on the $5p$ and $4f$ shells. However, accurate calculation of such systems also needs to take into two inner occupied $5s$ electrons, which makes multi-valent systems containing three to five valence electrons distributing on 11 orbitals of $5s$, $5p$, and $4f$. Their complex electronic configurations make studying spectroscopic properties from theoretical and experimental viewpoints challenging. Due to the scarcity of data on energy level, isoelectronic sequences with x larger than 3 are not in

Table 10. When $x \geq 14$, there observed the hole state of $4f$ shell in some HCIs, for example W$^{(8-13)+}$ ions, as listed in 10. Their $4f$- or $5p$ − excitation causes a lot of transitions with energies in the optical range. There has been greatly renewed interest in the spectral emission of tungsten from high-temperature plasma [116, 126, 128–132].

Tables 6, Tables 7, Tables 8, Tables 9, Tables 10 compile a series of HCIs that underline the orbital energy-crossings in their electronic configurations. Many of these HCIs show optical transitions between the ground and low-lying excited states. Although the exact values of q and K for these transitions are mostly absent in the literature, their values can be conjectured to be very large from the characterstics of the $s − f$ and $p − f$ inter-configuration transitions.

TABLE 9 The energy level of HCIs in the isoelectronic sequences containing the different number of 5s and 4f valence electrons x, where N is the number of the electron, Z is the atomic number. $[Kr] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$. Units for values are in cm^{-1}.

Isoelec	N	Z	X	Ion	Configuration	State	Energy
Ag-like	47	60	1	Nd^{13+}	$[Kr]4d^{10}5s$	$^2S_{1/2}$	0
					$[Kr]4d^{10}4f^1$	$^2F^o_{5/2}$	55706 [39]
Ag-like	47	61	1	Pm^{14+}	$[Kr]4d^{10}5s$	$^2S_{1/2}$	0
					$[Kr]4d^{10}4f^1$	$^2F^o_{5/2}$	8902 [34]
Ag-like	47	62	1	Sm^{15+}	$[Kr]4d^{10}4f^1$	$^2F^o_{5/2}$	0
					$[Kr]4d^{10}5s$	$^2S_{1/2}$	60517 [34]
Cd-like	48	61	2	Pm^{13+}	$[Kr]4d^{10}5s^2$	$^1S_0$	0
					$[Kr]4d^{10}5s4f$	$^3F^o_2$	86136 [34]
Cd-like	48	62	2	Sm^{14+}	$[Kr]4d^{10}4f^2$	$^3H_4$	0
					$[Kr]4d^{10}5s4f$	$^3F^o_2$	2172 [40]
Cd-like	48	63	2	Eu^{15+}	$[Kr]4d^{10}4f^2$	$^3H_4$	0
					$[Kr]4d^{10}5s4f$	$^3F^o_2$	48780 [34]
In-like	49	62	3	Sm^{13+}	$[Kr]4d^{10}5s^24f$	$^2F^o_{5/2}$	0
					$[Kr]4d^{10}5s4f^2$	$^4H_{7/2}$	20254 [39]
In-like	49	63	3	Eu^{14+}	$[Kr]4d^{10}4f^25s$	$J = 3.5$	0
					$[Kr]4d^{10}4f5s^2$	$J = 3.5$ (odd)	24854 [34]
In-like	49	64	3	Gd^{15+}	$[Kr]4d^{10}4f^3$	$J = 4.5$ (odd)	0
					$[Kr]4d^{10}4f^25s$	$J = 3.5$	30172 [34]
I-like	53	67	7	Ho^{14+}	$[Kr]4d^{10}5s4f^6$	$^8F_{1/2}$	0
					$[Kr]4d^{10}5s^24f^5$	$^6H^o_{5/2}$	23800 [41]
Xe-like	54	68	8	Er^{14+}	$[Kr]4d^{10}5s4f^7$	$^9S^o_4$	0
					$[Kr]4d^{10}5s^24f^6$	$^7F_0$	18555 [41]
Ce-like	58	74	12	W^{16+}	$[Kr]4d^{10}5s4f^{11}$	$^5I^o_8$	0
					$[Kr]4d^{10}5s^24f^{10}$	$^5I_8$	19000 [120]
Pr-like	59	77	13	Ir^{18+}	$Kr]4d^{10}4f^{13}$	$^2F^o_{7/2}$	0
					$Kr]4d^{10}5s4f^{12}$	$^4F_{9/2}$	70096 [122]
Nd-like	60	74	14	Os^{16+}	$[Kr]4d^{10}5s^24f^{12}$	$^3H_6$	0
					$[Kr]4d^{10}5s4f^{13}$	$^3F^o_4$	37460 [81]
Nd-like	60	77	14	Ir^{17+}	$[Kr]4d^{10}5s4f^{13}$	$^3F^o_4$	0
					$[Kr]4d^{10}4f^{14}$	$^1S_0$	13530 [81]
Nd-like	60	78	14	Pt^{18+}	$[Kr]4d^{10}4f^{14}$	$^1S_0$	0
					$[Kr]4d^{10}5s4f^{13}$	$^3F^o_4$	48809 [81]
Pm-like	61	74	15	W^{13+}	$[Kr]4d^{10}5s^24f^{13}$	$^2F^o_{7/2}$	0
					$[Kr]4d^{10}5s^24f^{13}$	$^2F^o_{5/2}$	26000 [120–123]
Sm-like	61	77	15	Ir^{16+}	$[Kr]4d^{10}5s^24f^{13}$	$^2F^o_{7/2}$	0
					$[Kr]4d^{10}5s^24f^{13}$	$^2F^o_{5/2}$	25023 [124]
Sm-like	61	78	15	Pt^{17+}	$[Kr]4d^{10}5s4f^{14}$	$^2S_{1/2}$	0
					$[Kr]4d^{10}5s^24f^{13}$	$^2F^o_{7/2}$	24860 [124]

TABLE10 The energy level of HCIs in the isoelectronic sequences containing the different number of 5p and 4f valence electrons x, where N is the number of the electron, Z is the atomic number. [Kr] ≡ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ and [Cd] ≡ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$. Units of all values are in cm^{-1}.

Isoelec	N	Z	x	Ion	Configuration	State	Energy
In-like	49	58	1	Ce^{11+}	[Kr]$5p$	$^2P^o_{1/2}$	0
					[Kr]$5p$	$^2P^o_{3/2}$	33427 [39]
					[Kr]$4f$	$^2F^o_{5/2}$	54947 [39]
In-like	49	59	1	Pr^{10+}	[Kr]$5p$	$^2P^o_{1/2}$	0
					[Kr]$4f$	$^2F^o_{5/2}$	3958 [39]
					[Kr]$5p$	$^2P^o_{3/2}$	39084 [39]
In-like	49	60	1	Nd^{11+}	[Kr]$4f$	$^2F^o_{5/2}$	0
					[Kr]$4f$	$^2F^o_{7/2}$	4566 [39]
					[Kr]$5p$	$^2P^o_{1/2}$	53491 [39]
Sn-like	50	59	2	Pr^{9+}	[Kr]$5p^2$	^3P_o	0
					[Kr]$5p4f$	$^3G_3$	22101 [83]
					[Kr]$5p^2$	$^3P_1$	28561 [83]
Sn-like	50	60	2	Nd^{10+}	[Kr]$4f^2$	$^3H_4$	0
					[Kr]$5p4f$	$^3G_3$	2605 [40]
					[Kr]$4f^2$	$^3H_5$	3432 [40]
Sb-like	51	59	3	Pr^{8+}	[Kr]$5p^3$	$^4S^o_{3/2}$	0
					[Kr]$5p^2 4f$	$^4G^o_{5/2}$	18386 [125]
					[Kr]$5p^3$	$^2D_{3/2}$	24348 [125]
Sb-like	51	60	3	Nd^{9+}	[Kr]$5p^2 4f$	$J = 5/2$	0
					[Kr]$5p^2 4f$	$J = 7/2$	6524 [50]
					[Kr]$4f^2 5p$	$J = 9/2$	20594 [50]
Sb-like	51	61	3	Pm^{10+}	[Kr]$4f^2 5p$	$J = 9/2$	0
					[Kr]$4f^3$	$J = 9/2$	5296 [125]
Sb-like	51	62	3	Sm^{11+}	[Kr]$4f^3$	$^4I^o_{9/2}$	0
					[Kr]$4f^3$	$^4I^o_{11/2}$	3063 [125]
Sm-like	62	74	14	W^{12+}	[Cd]$4f^{14}$	$^1S_0$	0
					[Cd]$4f^{13}5p$	$^3D_3$	4016 [126]
Eu-like	63	74	15	W^{11+}	[Cd]$4f^{13}5p^2$	$^4F^o_{7/2}$	0
					[Cd]$4f^{14}5p$	$^2P^o_{1/2}$	11000 [120, 127, 128]
Gd-like	64	74	16	W^{10+}	[Cd]$4f^{14}5p^2$	$^3P_2$	0
					[Cd]$4f^{13}5p^3$	$^3G_5$	44614 [129]
Tb-like	65	74	17	W^{9+}	[Cd]$4f^{14}5p^3$	$^2P^o_{3/2}$	0
					[Cd]$4f^{13}5p^3$	$^3G^o_5$	44614 [116]
Dy-like	66	74	18	W^{8+}	[Cd]$4f^{14}5p^4$	$^3P_2$	0
					[Cd]$4f^{13}5p^5$	$^3F_4$	14000 [120, 116]

Such features in atomic clocks are useful for probing α variation. It is, therefore, necessary to estimate energies and other spectroscopic properties of these relevant for estimating systematic errors if they are undertaken for atomic clocks.

5 Relativistic many-body methods

There is a great need to determine the energies and radiative properties of the HCIs to determine their suitability for atomic clocks.

Again, their high-accuracy estimations are also essential for gauging the atomic clocks' systematic effects. The required atomic data include energy level structures, atomic polarizabilities, hyperfine structure constants, Landé g_J factors, quadrupole moments, etc., which are unknown for many HCIs. For theoretical evaluation of these quantities, it is necessary to employ methods that can reliably estimate them. Though relativistic contributions from the Breit and quantum electrodynamics (QED) effects would be significant in the HCIs, Coulomb interactions still play decisive roles in accurately determining properties of the interested HCIs for finding their aptness to make atomic clocks. Thus, we adopt relativistic many-body methods that can estimate atomic properties with reasonable accuracy in HCIs, and corrections from the higher-order relativistic effects are estimated approximately wherever required. Again, it is impossible to employ a single many-body method to all the HCIs undertaken here for investigation due to their multi-valence electronic configurations. We choose a method that can be applied aptly in HCIs with a particular electronic configuration class. In this view, we have considered methods like the configuration interaction (CI) method, general active space configuration interaction (GASCI) method and Fock-space relativistic coupled-cluster (FS-RCC) theory in the present work. In all the methods, wave functions obtained using the Dirac-Hartree-Fock (DHF) method are considered the starting point. Correlation effects due to the residual Coulomb interactions are included through the many-body approaches.

5.1 Approximations in the Hamiltonian

To take into account the major relativistic effects and electron correlation effects in the HCIs, we first consider the Dirac-Coulomb (DC) Hamiltonian in our calculations which in atomic units (a.u.) is given by

$$H^{DC} = \sum_i \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_{nuc}(r_i) \right] + \sum_{i,j>i} \frac{1}{r_{ij}}$$
$$= \sum_i h_i + \sum_{i,j>i} g_{ij}, \tag{5}$$

where the rest mass energies of the electrons are subtracted. In this expression c is the speed of light, $V_{nuc}(r)$ is the nuclear potential and $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are the 4×4 Dirac matrices with the components

$$\alpha_x = \begin{pmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{pmatrix}, \alpha_y = \begin{pmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{pmatrix}, \alpha_z = \begin{pmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}, \tag{6}$$

for the identity matrix I and the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \text{ and } \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{7}$$

In our calculations, we adopt either the Gaussian or Fermi nuclear charge distribution [133] to obtain the nuclear potentials of the heavier HCIs. The Gaussian nuclear charge distribution is defined by

$$\rho(r) = \left(\frac{\eta}{\pi}\right)^{\frac{3}{2}} e^{-\eta r^2} \tag{8}$$

with $\eta = \frac{3}{2} R_{rms}^{-2}$, where R_{rms} is the root mean square (rms) nuclear charge radius of the atomic nucleus. This leads to the expression for nuclear potential observed by an electron as

$$V_{nuc}(r) = -\frac{Z}{r} \, erf\left(\sqrt{\eta}\, r\right). \tag{9}$$

In the Fermi nuclear charge distribution, it is given as

$$\rho(r) = \frac{\rho_0}{1 + e^{(r-b)/a}}, \tag{10}$$

where ρ_0 is the normalization constant, b is the half-charge radius and $a = 2.3/4 \ln 3$ is known as the skin thickness. We obtain the b value using the relation

$$b = \sqrt{\frac{5}{3} R_{rms}^2 - \frac{7}{3} a^2 \pi^2} \tag{11}$$

and rms charge radius of a given nucleus with atomic mass A is estimated in fm by

$$R_{rms} = 0.836 A^{1/3} + 0.570. \tag{12}$$

The above expression gives the nuclear potential expression as

$$V_{nuc}(r) = -\frac{Z}{\mathcal{N}r} \begin{cases} \frac{1}{b}\left(\frac{3}{2} + \frac{a^2\pi^2}{2b^2} - \frac{r^2}{2b^2} + \frac{3a^2}{b^2}P_2^+ \frac{6a^3}{b^2 r}\left(S_3 - P_3^+\right)\right) & \text{for } r_i \le b \\ \frac{1}{r_i}\left(1 + \frac{a62\pi^2}{b^2} - \frac{3a^2 r}{b^3}P_2^- + \frac{6a^3}{b^3}\left(S_3 - P_3^-\right)\right) & \text{for } r_i > b, \end{cases} \tag{13}$$

where the factors are

$$\mathcal{N} = 1 + \frac{a^2\pi^2}{b^2} + \frac{6a^3}{b^3}S_3 \quad \text{with} \quad S_k = \sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^k} e^{-lb/a} \quad \text{and}$$
$$P_k^\pm = \sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^k} e^{\pm l(r-b)/a}. \tag{14}$$

Whenever necessary, we add the potential (V^B) due to the Breit interaction to the DC Hamiltonian to take into account the contribution from this higher-order relativistic effect and is given by

$$V^B = -\sum_{j>i} \frac{\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \hat{\mathbf{r}}_{ij})(\boldsymbol{\alpha}_j \cdot \hat{\mathbf{r}}_{ij})\right]}{2r_{ij}}, \tag{15}$$

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

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

$$V^{Uehl} = -\frac{2}{3}\sum_i \frac{\alpha^2}{r_i}\int_0^\infty dx\, x\, \rho_n(x)\int_1^\infty dt\sqrt{t^2 - 1}\left(\frac{1}{t^3} + \frac{1}{2t^5}\right)$$
$$\times \left[e^{-2ct|r_i - x|} - e^{-2ct(r_i + x)}\right] \tag{16}$$

and

$$V^{WK} = \sum_i \frac{0.368 Z^2}{9\pi c^3 \left(1 + (1.62cr_i)^4\right)} \rho(r_i), \tag{17}$$

respectively. The SE contribution V_{SE} is estimated by including two parts as

$$V_{\mathrm{SE}}^{ef} = A_l \sum_i \frac{2\pi Z\alpha^3}{r_i} I_1^{ef}(r_i) - B_l \sum_i \frac{\alpha}{r_i} I_2^{ef}(r_i) \tag{18}$$

known as effective electric form factor part and

$$V_{\mathrm{SE}}^{mg} = -\sum_k \frac{i\alpha^3}{4} \boldsymbol{\gamma} \cdot \boldsymbol{\nabla}_k \frac{1}{r_k} \int_0^\infty dx \, x \, \rho_n(x) \int_1^\infty dt \frac{1}{t^3\sqrt{t^2-1}}$$
$$\times \left[e^{-2ct|r_k-x|} - e^{-2ct(r_k+x)} - 2ct(r_k + x - |r_k - x|) \right], \tag{19}$$

known as the effective magnetic form factor part. In the above expressions, we use

$$A_l = \begin{cases} 0.074 + 0.35Z\alpha & \text{for } l = 0, 1 \\ 0.056 + 0.05Z\alpha + 0.195Z^2\alpha^2 & \text{for } l = 2, \end{cases} \tag{20}$$

and

$$B_l = \begin{cases} 1.071 - 1.97x^2 - 2.128x^3 + 0.169x^4 & \text{for } l = 0, 1 \\ 0 & \text{for } l \ge 2. \end{cases} \tag{21}$$

The integrals are given by

$$I_1^{ef}(r) = \int_0^\infty dx \, x \, \rho_n(x)$$
$$\times \left[(Z|r-x| + 1)e^{-Z|r-x|} - (Z(r+x) + 1)e^{-2ct(r+x)} \right] \tag{22}$$

and

$$I_2^{ef}(r) = \int_0^\infty dx \, x \, \rho_n(x) \int_1^\infty dt \frac{1}{\sqrt{t^2-1}}$$
$$\left\{ \left(1 - \frac{1}{2t^2}\right)\left[\ln(t^2-1) + 4\ln\left(\frac{1}{Z\alpha} + \frac{1}{2}\right)\right] - \frac{3}{2} + \frac{1}{t^2} \right\} \left\{ \frac{\alpha}{t}\left[e^{-2ct|r-x|} - e^{-2ct(r+x)}\right] \right.$$
$$\left. + 2r_A e^{2r_A ct} \left[E_1(2ct(|r-x| + r_A)) - E_1(2ct(r+x+r_A)) \right] \right\} \tag{23}$$

with the orbital quantum number l of the system, $x = (Z - 80)\alpha$, $r_A = 0.07Z^2\alpha^3$, and the exponential integral $E_1(r) = \int_r^\infty ds e^{-s}/s$.

The atomic Hamiltonian given by Eq. 5 can be expressed in the second-quantization formalism as

$$H^{DC} = \sum_{pq} h_q^p a_p^+ a_q + \frac{1}{4} \sum_{pqrs} V_{qs}^{pr} a_p^+ a_r^+ a_s a_q, \tag{24}$$

where $h_q^p = \langle p|\hat{h}|q\rangle$ and $V_{qs}^{pr} = \langle pr|\hat{g}|qs\rangle - \langle pr|\hat{g}|sq\rangle$ with the indices $\{p, q, r, s\}$ denote atomic orbitals. Due to the presence of two-body Coulomb (and also Breit and QED) interactions, it is not possible to obtain atomic wave functions of multi-electron systems exactly. In practice, it is dealt with by dividing the atomic Hamiltonian into an effective one-body term and residual interactions; i.e. $H = H_0 + V_{es}$. As mentioned earlier, the one-body part H_0 is constructed using the DHF method in this work while correlation contributions from V_{es} are included at different levels of approximations through various methods that are outlined briefly below.

5.2 CI and GASCI methods

The DHF method is a good starting point to construct the exact atomic wave functions in a many-electron system. The complete spectrum of single-particle solutions obtained from the DHF procedure constitutes a one-particle basis from which one may construct determinants that approximate the wave function for an atomic closed-shell system through an anti-symmetric Hartree-product (Slater determinant) of four-spinors

$$\Phi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}) = \mathbf{A}(\psi_1(\mathbf{r_1}), \psi_2(\mathbf{r_1}), \ldots, \psi_N(\mathbf{r_N})). \tag{25}$$

In the CI method, the exact wave function $|\Psi\rangle$ of an atomic state (known as atomic state function (ASF)) is constructed by expressing it as a linear sum of all possible singly, doubly up to N-tuple excited Slater determinants (referred as configuration state functions (CSFs)) with respect to the DHF wave function ($|\Phi_0\rangle$). i.e.

$$|\Psi\rangle = C_0|\Phi_0\rangle + \sum_I C_I|\Phi_I\rangle + \sum_{II} |\Phi_{II}\rangle + \cdots, \tag{26}$$

where C_n with $n = 0, I, II, \cdots$ are the CSF mixing coefficients for the respective CSFs $|\Phi_n\rangle$. In the second-quantization form, we can express as [134].

$$|\Psi\rangle = \left(C_0 + \sum_{ai} c_i^a a_a^+ a_i + \sum_{a>b,i>j} c_{ij}^{ab} a_a^+ a_b^+ a_i a_j + \cdots \right)|\Phi_0\rangle. \tag{27}$$

The second and the third terms within the brackets are the single and double excitations, respectively, expressed in terms of creation (a^+) and annihilation (a) operators. The coefficients of Eq. 27 are obtained by solving

$$\mathbf{HC} = E_{\mathbf{CI}}\mathbf{C}, \tag{28}$$

where $\mathbf{H}$ is the matrix of the atomic Hamiltonian and $\mathbf{C}$ is the matrix of the expansion coefficients. The diagonalization of the Hamiltonian $\mathbf{H}$ matrix gives the spectrum of exact eigenvalues $E_{\mathbf{CI}}$ for the system for a given basis set.

In practice, carrying out a full CI is impossible, so we have to choose only a small subset of determinants that carries most of the correlation energies. This is generally done by truncating the CI expansion. Usually, the singly and doubly excited configurations are retained and this truncated CI method is referred to as CISD, where 'S' and 'D' stand for the single and double excitations, respectively. Correlation energy that arises from the excitations from the single reference DHF determinant is often referred to as dynamic correlation energy. In many situations, multi-reference determinant states are considered to take into account static correlation effects by simultaneously exciting electrons from all the determinants [135]. In the CI approach, such a selection of reference is referred to as multi-reference CI (MRCI) method. This is more effective, and the diagonalization of Eq. 28 can converge faster.

A restricted active space CI (RASCI) method has been developed to account for both the dynamics and static correlations rigorously [136]. In the RASCI, the active orbital space is divided into three subspace: RAS1, RAS2, and RAS3. RAS1 is the occupied space in which at the most two electron holes are created; RAS3 is the unoccupied space that receives at most two electrons from RAS1 and eventually from RAS2; RAS2 is the current active space in which all the possible excitations are considered is formed by both the occupied and unoccupied orbitals. Better choice of reference wave functions can be made through the GASCI method [137–139]. The GASCI can be considered as the complete generalization of the RASCI method. In this method, the number of subspaces and the number of excited electrons can be arbitrary in contrast to the restriction on the number of the subspace and the number of the excited electrons having two in the RASCI method. So the approximation made to the wave function in the CI method can be improved through the inclusion of more core-valence and core-core correlation space.

To illustrate the application of the GASCI method, we take an example of the Ni^{12+} HCI and demonstrate how the CSFs are decided. We may consider its valence configuration $3p^4$ with the core occupation

TABLE 11 Demonstration of GASCI scheme for Ni^{12+}, where 'min' and 'max' denote the minimal and maximal number of accumulated electrons occupied in the respective core, valence, and virtual orbitals.

Gas no.	Min	Max	Number of orbitals	Orbitals	Type
I	2	4	2	1s, 2s	core
II	8	10	3	2p	core
III	10	12	1	3s	core
IV	13	16	3	3p	valence
V	16	16	150	n (s, p, $\cdots$i) with $n \geq 4$	virtual

$1s^2 2s^2 2p^6 3s^2$. The scheme of the GASCI employed for Ni^{12+} is shown in Table 11. Here, the correlated orbitals are divided into five subsets I-V, which correspond to the core ($1s$, $2s$, $2p$, and $3s$), the valence ($3p$), and the rest (virtual) orbitals, receptively. The 'minimal' (min) and 'maximal' (max) number of electrons (min, max) in the I, II, and III types of space are (2, 4), (6, 8), and (10, 12), respectively. That is to say, only single and double excitations are allowed in core orbitals. When the valance orbitals $3p$ (space IV) are included, at most three electrons are allowed to excite out of the total core + valance space. According to this GASCI scheme, the possible excitations are 1) single or double excitations from the core with no excitation from the valence space; 2) single excitations from the core and single excitations from the valance space; 3) single excitations from the core and double excitations from the valance space; 4) double excitations from the core and single excitations from the valance space; and 5) no excitation from the core but singles, doubles and/or triple excitations from the valance space. Combining all of those possible occupations from the core, valence and virtual orbitals forms a CI space with about 7×10^9 determinants in Ni^{12+}, which includes the most dominant core-core, core-valence, and valence-valance correlations. This means that the GASCI scheme can design a complete and near-complete core and valence spaces based on the multi-reference configurations of CI method.

The GASCI method is well suited to apply to the multi-valence atomic systems having open-shell configurations in the p, d, and f shells. This method is also apt to employ to the HCIs exhibiting strong degeneracy among the energy levels due to level-crossings [50]. The GASCI can be employed using the relativistic quantum chemistry code package DIRAC [140, 141]. This method has been applied to calculate atomic properties of the Sb-like Nd^{9+} ion.

5.3 FS-RCC method

The FS-RCC method is an all-order perturbative method, and different contributions arising through the FS-RCC calculations can be understood through perturbative analysis. To understand this point, we start with the basic formulation of many-body perturbation theory to derive the expression for the ASF in the FS-RCC method. The FS-RCC method are well adaptive to the study of the single-particle or hole system, for example the B-, Al-, and Ga-like HCIs of one p valence and the W^{13+}, Ir^{16+}, and Pt^{18+} ions of one $4f$ hole.

The ASF $|\Psi_v\rangle$ of an atomic system with a closed-core and a valence orbital v can be expressed by

$$|\Psi_v\rangle = \Omega_v |\Phi_v\rangle, \tag{29}$$

where Ω_v and $|\Phi_v\rangle$ are referred to as the wave operator and the reference state respectively. For the computational simplicity we choose the working reference state as the DHF wave function $|\Phi_c\rangle$ for the closed core, then the actual reference state is constructed from it as $|\Phi_v\rangle = a_v^\dagger |\Phi_c\rangle$ for the respective state with the valence orbital v.

Following the form of the reference states in our approach, Ω_v can now be divided as

$$\Omega_v = 1 + \chi_c + \chi_v, \tag{30}$$

where χ_c and χ_v are responsible for carrying out the excitations from $|\Phi_c\rangle$ and $|\Phi_v\rangle$, respectively, due to the residual interaction $V_r = H - H_0$ for the DHF Hamiltonian H_0. In a perturbative series expansion, we can express as

$$\chi_c = \sum_k \chi_c^{(k)} \quad \text{and} \quad \chi_v = \sum_k \chi_v^{(k)}, \tag{31}$$

where the superscript k refers to the number of times V_r is considered. The kth order amplitudes for the χ_c and χ_v operators are obtained by solving the equations

$$\left[\chi_c^{(k)}, H_0\right] P = Q V_r \left(1 + \chi_c^{(k-1)}\right) P \tag{32}$$

and

$$\begin{aligned}\left[\chi_v^{(k)}, H_0\right] P = &\, Q V_r \left(1 + \chi_c^{(k-1)} + \chi_v^{(k-1)}\right) P - \sum_{m=1}^{k-1} \chi_v^{(k-m)} \\ &\times P V_r \left(1 + \chi_c^{(m-1)} + \chi_v^{(m-1)}\right) P,\end{aligned} \tag{33}$$

where the projection operators $P = |\Phi_c\rangle\langle\Phi_c|$ and $Q = 1 - P$ describe the model space and the orthogonal space of the DHF Hamiltonian H_0 respectively. The energy of the state $|\Psi_v\rangle$ is evaluated by using an effective Hamiltonian

$$H_v^{eff} = P a_v H \Omega_v a_v^\dagger P. \tag{34}$$

Using the normal order Hamiltonian $H_N = H - PHP$ in place of H in the above expression, the attachment energy of a state with the valence orbital v is evaluated.

The above formulation is generalized to all-orders in the FS-RCC method as

$$|\Psi_v\rangle \equiv \Omega_v |\Phi_v\rangle = e^T \{1 + S_v\} |\Phi_v\rangle \tag{35}$$

with $\chi_c = e^T - 1$ and $\chi_v = e^T S_v - 1$, where T and S_v are the CC excitation operators that excite electrons from the core and core along with the valence orbitals to the virtual space respectively. In the singles and doubles approximation (RCCSD method), it is given as

$$T = T_1 + T_2 \quad \text{and} \quad S_v = S_{1v} + S_{2v}. \tag{36}$$

The amplitudes of these operators are evaluated using the equations

$$\langle \Phi_c^* | \bar{H}_N | \Phi_c \rangle = 0 \qquad (37)$$

and

$$\langle \Phi_v^* | (\bar{H}_N - \Delta E_v) S_v | \Phi_v \rangle = -\langle \Phi_v^* | \bar{H}_N | \Phi_v \rangle, \qquad (38)$$

where $|\Phi_c^*\rangle$ and $|\Phi_v^*\rangle$ is the excited state configurations for the DHF states $|\Phi_c\rangle$ and $|\Phi_v\rangle$ respectively and $\bar{H}_N = (H_N e^T)_l$ with subscript l represents for the linked terms only. Here $\Delta E_v = H_v^{eff} - H_c^{eff}$ is the attachment energy of the electron in the valence orbital v with $H_c^{eff} = PH(1 + \chi_c)P$. Following Eq. 34, expression for ΔE_v is given by

$$\Delta E_v = \langle \Phi_v | \bar{H}_N \{1 + S_v\} | \Phi_v \rangle. \qquad (39)$$

Contributions from important triply excited configurations can be included at the cost of RCCSD method computation by defining perturbative operators as

$$T_3^{pert} = \frac{1}{6} \sum_{abc,pqr} \frac{(H_N T_2)_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \qquad (40)$$

and

$$S_{3v}^{pert} = \frac{1}{4} \sum_{ab,pqr} \frac{(H_N T_2 + H_N S_{2v})_{abv}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_v - \epsilon_p - \epsilon_q - \epsilon_r}, \qquad (41)$$

where $\{a, b, c\}$ and $\{p, q, r\}$ represent the occupied and virtual orbitals, respectively, and ϵs are their corresponding DHF orbital energies.

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

$$\frac{\langle \Psi_f | O | \Psi_i \rangle}{\sqrt{\langle \Psi_i | \Psi_i \rangle \langle \Psi_f | \Psi_f \rangle}} = \frac{\langle \Phi_f | \tilde{O}_{fi} | \Phi_i \rangle}{\sqrt{\langle \Phi_i | \tilde{N}_i | \Phi_i \rangle \langle \Phi_f | \tilde{N}_f | \Phi_f \rangle}} \qquad (42)$$

where $\tilde{O}_{fi} = \{1 + S_f^\dagger\} e^{T^\dagger} O e^T \{1 + S_i\}$ and $\tilde{N}_{k=f,i} = \{1 + S_k^+\} e^{T^\dagger} e^T \{1 + S_k\}$. In the expectation value evaluation, it turns out to be $|\Psi_i\rangle = |\Psi_f\rangle$. We adopt iterative procedures [142, 143] to account for contributions from both the non-terminating series $e^{T^\dagger} O e^T$ and $e^{T^\dagger} e^T$ that appear in Eq. 42.

6 Systematics of HCI clocks

One of the most important aspects of modern atomic clocks is to achieve very high-precision measurements such that they can be applied for probing fundamental physics, including the variation of α. Thus, systematic effects observed in an experiment play essential roles in deciding whether a transition frequency measurement in an atomic system is suitable for undertaking the task. From this point of view, it is imperative to determine the significance of some of the noted systematics that needs to be analyzed in atomic systems before considering them in the experiments. The major systematics responsible for deciding an HCI clock's accuracy is Stark shifts due to lasers, BBR shifts, thermal radiation shifts, magnetic field shifts, motion-induced shifts, micromotion shifts, collisional shifts, etc., to cite a few. These systematics are also commonly seen in the neutral atom and singly charged ion-based atomic clocks. Determining each of these effects would require performing separate experiments. However, as discussed earlier, they can be estimated quite accurately by employing potential relativistic many-body methods. In fact, prior theoretical studies can also guide the

experimental to decide about the conditions like the ac and dc electric field strengths, gradient, orientation, and polarization of the quantized field, etc., in an atomic clock experiment. Though the general perception is that HCIs can have small systematics on the ground that their orbitals are very much contracted, in some cases, one of the systematics can be too large due to either degeneracy of the states or other factors. Therefore, it is essential to analyze the above systematics *a prior* by employing reliable many-body methods before a HCI is undertaken in the experiment to achieve clock frequency measurement below 10^{-19} level. Here we discuss the formulations of some of the aforementioned systems and how they are determined theoretically. Other systematics, such as the motional and collisional shifts, are non-trivial to estimate theoretically and depend on environmental conditions and are not discussed here. Still, they can be controlled well by utilizing currently available well-advanced ion trap techniques [12, 144–147].

6.1 Electric quadrupole shift

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 the electric field (∇E) experienced by the atomic states of the clock transition during the measurement. This can be estimated by calculating the expectation value of the corresponding interaction Hamiltonian $H_Q = -\nabla E \cdot \Theta(\gamma, K)$ as

$$\Delta E_{Quad} = \langle \gamma K, M_K = K | H_Q | \gamma K, M_K = K \rangle, \qquad (43)$$

where K is the angular momentum of the state with its component M_K, γ represents for other quantum numbers such as parity and $\Theta(\gamma, K)$ is known as 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. The electric quadrupole moment can be written as

$$\begin{aligned} \Theta(\gamma, K) &= \langle \gamma K K | \Theta | \gamma K K \rangle \\ &= \begin{pmatrix} K & 2 & K \\ -K & 0 & K \end{pmatrix} \langle \gamma K \| \Theta \| \gamma K \rangle. \end{aligned} \qquad (44)$$

For the hyperfine level, $K \equiv F$, the quadrupole shift can be expressed as

$$E_{Quad}(\gamma J F M_F) = -K_1 K_2 \Theta(\gamma, J), \qquad (45)$$

where

$$K_1 = \frac{2 A_E [3 M_F^2 - F(F+1)]}{\sqrt{(2F+3)(2F+2)(2F+1)2F(2F-1)}} \qquad (46)$$

and

$$K_2 = (-1)^{I+J+F} (2F+1) \begin{Bmatrix} J & 2 & J \\ F & I & F \end{Bmatrix} \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}^{-1}, \qquad (47)$$

for A_E representing the strength of the gradient of the applied electric field. According to the angular momentum selection rules for the above expression, ΔE_{Quad} will be zero for the states with $J = 1/2$ and $J = 0$. The expression in Eq. 47 ensures that quadrupole shifts in any of the hyperfine levels of the $J = 1/2, 0$ state is zero. However, a finite electric quadrupole shift still exists for those states of J with values other than 0 and 1/2. In such cases, it is possible to design experimental schemes to cancel out the electric quadrupole shift by choosing appropriate hyperfine levels or averaging out the measurements. For those ions that do not have a proper combination of F and M_F values for the zero quadrupole shift, experimental techniques can be adopted like

averaging the clock frequencies measured in the three orthogonal directions of the quantizing external field to suppress the electric quadrupole shift down to the limit below 10^{-19} level [148, 149].

6.2 Quadratic stark shift

The quadratic Stark shift of a level level (γ, J, F, M_F) with component M_F can be evaluated by

$$
\begin{aligned}
E_{Stark}\left(\gamma, J, F, M_F\right) &= -\frac{1}{2}\alpha\left(\gamma, J, F\right)\mathcal{E}^2 \\
&= -\frac{1}{2}\alpha^{(0)}\left(\gamma, J, F\right)\mathcal{E}_z^2 - \frac{1}{4}\alpha^{(2)}\left(\gamma, J, F\right)\frac{\left[3M_F^2 - F(F+1)\right]}{F(2F-1)}\left(3\mathcal{E}_z^2 - \mathcal{E}^2\right),
\end{aligned}
\tag{48}
$$

where $\mathcal{E}$ and $\mathcal{E}_z$ are the total strength and strength in the z-direction of the applied electric field, $\alpha^{(0)}(\gamma, J, F)$ and $\alpha^{(2)}(\gamma, J, F)$ are the scalar and tensor components of the total polarizability $\alpha(\gamma, J, F)$ of the hyperfine level. These quantities can be related to their corresponding values in the atomic state as [148].

$$
\alpha^{(0)}\left(\gamma, J, F\right) = \alpha^{(0)}\left(\gamma, J\right)
\tag{49}
$$

and

$$
\begin{aligned}
\alpha^{(2)}\left(\gamma, J, F\right) &= (-1)^{I+J+F}\begin{Bmatrix} F & J & I \\ J & F & 2 \end{Bmatrix}\alpha^{(2)}\left(\gamma, J\right) \\
&\times \left[\frac{F(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}{(2F+3)(F+1)J(2J-1)}\right]^{1/2}.
\end{aligned}
\tag{50}
$$

The differential values of $\alpha^{(0)}$ and $\alpha^{(2)}$ in clock transitions of HCIs are usually very small compared to the typical values obtained in the neutral atom or singly charged ion clocks. For example, for a typical value of electric field strength $E = 10$ V/m, the differential Stark shift for most previously proposed HCIs can be estimated using the above relation to be far below 10^{-19} level.

6.3 BBR shift

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

$$
\begin{aligned}
E_{BBR}^{E1} &= -\frac{1}{2}(831.9V/m)^2\left[\frac{T(K)}{300}\right]^4\alpha^{(0)}\left(\gamma, J, F\right) \\
&= -\frac{1}{2}(831.9V/m)^2\left[\frac{T(K)}{300}\right]^4\alpha^{(0)}\left(\gamma, J\right),
\end{aligned}
\tag{51}
$$

where T in K is the temperature at which the experiment is to be conducted. Using the scalar polarizabilities of the interesting clock states, the BBR shift can be estimated. It can be noticed that BBR shifts for atomic states and their hyperfine levels are the same. The environmental temperature in the HCI clock is generally far below the room temperature. In this situation, the BBR shifts are not the major limiting factors for the HCI clocks.

6.4 Zeeman shift

The linear Zeeman shifts in the clock transitions can be avoided by selecting $F = 0$ hyperfine levels wherever possible, else $M_F = 0$ sublevels of

finite F hyperfine levels. For the finite F levels with non-zero M_F sublevel, the linear Zeeman shift can also be removed technically by alternating π-polarized transitions with extreme angular momentum states with two opposite sublevels (e.g. $M_F = \pm2$) during the measurements [12]. However, it is not possible to get rid-off the second-order Zeeman shifts in such situations and they would provide the dominant uncertainties due to the Zeeman effects. The second-order Zeeman shift of a hyperfine level F with sublevel M_F due to magnetic field strength $\mathcal{B}$ is given by [150].

$$
E_{Zeem}^2 = \beta_{Zeem}\left(\gamma, J, F, M_F\right)\mathcal{B}^2,
\tag{52}
$$

where

$$
\beta_{Zeem}\left(\gamma, J, F, M_F\right) = -\frac{\left(\mu_B g_J\right)^2}{\hbar}\sum_{F'}\frac{|\langle F'M_F|J_z|FM_F\rangle|^2}{E_{F'} - E_F},
\tag{53}
$$

with J_z denoting the z-component of J, E_F is the hyperfine energy level and F' corresponds to all possible intermediate hyperfine levels. The hyperfine energy level is given by [151].

$$
E_F = \frac{1}{2}A_{hyf}C + B_{hyf}\frac{\frac{3}{2}C(C+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)},
\tag{54}
$$

where $C = F(F+1) - I(I+1) - J(J+1)$. The E_F values can be determined using the hyperfine structure constants A_{hyf} and B_{hyf}. The angular momentum matrix element is given by

$$
\begin{aligned}
|\langle F'M_{F'}|J_z|FM_F\rangle|^2 &= J(J+1)(2J+1)(2F+1) \\
&\times (2F'+1)\begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix}^2\begin{Bmatrix} J & F & I \\ F' & J & 1 \end{Bmatrix}^2.
\end{aligned}
\tag{55}
$$

Thus, $\beta_{Zeem}\left(\gamma, J, F, M_F\right)$ of a hyperfine level can be determined if Landé g_J factor of the atomic state is known. For a given typical experimental condition, $\mathcal{B}$ value can be decided suitably to estimate the second-order Zeeman shift. It is, in principle, possible to control the strength of the magnetic field in experiments to reduce uncertainties due to the Zeeman shifts to achieve the clock frequency measurements to the intended level of precision.

7 Summary

A new generation of atomic clocks that would provide ultra-precise clock frequency measurements is highly required to probe many subtle effects supporting physics beyond the Standard Model of particle physics. Atomic clocks based on highly charged ions, having a high sensitivity to variation of α and extremely low sensitivity to external perturbations, are understood to possess such potentials.

In the past decade, many HCIs have been proposed as candidates for making an ultra-precise atomic clock, which has highly stable laser-accessible clock transition, enhanced sensitivity to variation of α, and advantageous atomic properties to inhibit external perturbations. Based on two basic rules that outline the M1 and E2 forbidden transition in fine-structure splittings and the higher order forbidden transition in complex configuration accompanied with orbital crossing, a shortlist of HCI clock candidates are summarized, which includes Ar^{13+}, Ni^{12+}, Ba^{4+}, Pb^{2+}, Ir^{17+}, Cf^{15-17+}, Nd^{13}, Sm^{15+}, Pr^{9+}, Nd^{9+}, Ho^{14+}, etc., The first atomic clock based on Ar^{13+} has been realized now and reached 10^{-17} frequency uncertainty at the moment. The other ions aside from Ar^{13+} can offer better frequency stability and higher sensitivity to variation of α, indicating a new

possibility for making atomic clocks. These discussions would help understand the merits and dis-merits of those HCIs and also guide seeking new highly charged ions candidates for clock and applications in searching for the variation of α.

Knowledge of spectroscopic data essential to analyze the feasibility of considering a highly charged ion for an atomic clock experiment is currently limited. In order to realize those proposed HCI clocks, more efforts are needed, including more accurate data prediction for energies that help identify clock transition lines and various atomic properties needed for a full assessment of the systematic shifts. High-accuracy relativistic many-body methods are employed to fulfil such tasks by using variants of relativistic configuration and coupled-cluster methods. The challenges are the complete treatment of the complex electron correlation often met in strongly open $4f$-shelled configurations mixed with the $5s$ and $5p$ valence electrons. Rigorous treatment contributions from QED in fine structure splitting require accurate determination of energies and transition probabilities.

The proposed HCIs are the prospective candidates who offer the most precise frequency standards. With theoretical and experimental progress, the atomic clock based on new HCI candidates will lead to ideal platforms to probe temporal variation of α. Upon the fruitful accomplishment of such clocks, they can promote other high-precision experiments and invoke new exciting avenues for researching fundamental physics.

Author contributions

Y-MY and BS contribute equally to this work and share the first authorship. B-bS contributed to the part contents of the CI method as well as the relativistic effects and level-crossings in HCIs.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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