Highly Charged Ion (HCl) Clocks: Frontier candidates for testing variation of fine-structure constant

Yan-Mei Yu, B. K. Sahoo, and Bing-Bing Suo

1 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
2 Atomic, Molecular and Optical Physics Division, Physical Research Laboratory, Navrangpura, Ahmedabad 380009, India
3 Institute of Modern Physics, Northwest University, Xi’an, Shaanxi 710069, China
4 University of Chinese Academy of Sciences, Beijing 100049, China

Correspondence*: Yan-Mei Yu
ymyu@iphy.ac.cn
B. K. Sahoo
bijaya@prl.res.in

ABSTRACT

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 $\alpha$ variation because their transition frequencies are measured with ultra-high precision. Since atomic transition frequency is a function of $\alpha$, measurement of a clock frequency at different temporal and spatial locations can yield signatures to ascertain variation of $\alpha$. Highly charged ions (HCIs) are very sensitive to variation of $\alpha$ and are least affected by external perturbations, making them excellent platforms for searching for temporal variation of $\alpha$. In this work, we overview HCIs suitable for building atomic clocks because of their spectroscopic features and sensitivity to variation of $\alpha$. 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, 2, 3]. Uncertainty of optical lattice clock based on $^{171}$Yb atoms has reached an uncertainty of $1.4 \times 10^{-18}$ [4, 5] whereas $^{87}$Sr optical lattice clocks offer uncertainty of around $2.0 \times 10^{-18}$ [6, 7]. Similarly, uncertainties of $^{171}$Yb$^+$ and $^{40}$Ca$^+$ ion clocks have both reached an accuracy of $3 \times 10^{-18}$ [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 ($\alpha$). Atomic energy levels are functions of $\alpha$. Thus any variation in the $\alpha$ 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 $\alpha$ value. The clock transitions have different sensitivity to variation of $\alpha$. The sensitivity of an energy level to $\alpha$ variation is gauged through a relativistic sensitivity coefficient $q$ by defining it as

$$\omega_t = \omega_0 + qx,$$  \hspace{1cm} (1)

where $\omega_0$ is the angular frequency of the transition for the present-day value of the fine-structure constant $\alpha(0)$ and $\omega_t$ 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 $K_\alpha$ by defining it as $K_\alpha = q/\omega_0$. Here, $q$ and $K_\alpha$ are often referred to as a frequency’s absolute and relative sensitivity factor to variation of $\alpha$.

Table I summarizes the currently prevailing clock frequencies with regard to their sensitivity to variation of $\alpha$. Some of them has low sensitivities to $\alpha$ variation, like the clock transition in Al$^+$, Ca$^+$, Sr and Yb, while the $4f^{14}6s^2S_{1/2} - 4f^{13}6s^2F_{7/2}^0$ 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 $\alpha$. Such contrast sensitivities to variation of $\alpha$ suggest different accuracy requirements in the frequency measurements if they are used for testing variation of $\alpha$. Assuming the time variation rate of $\alpha$ per year is around $10^{-16}$ level, to detect such a small variation rate of $\alpha$ within a year time, minimum requirements of fractional uncertainties of the Sr, Yb, and Hg atomic clock frequencies would be about $8 \times 10^{-17}$, $5 \times 10^{-17}$ and $2 \times 10^{-18}$, respectively, by considering their sensitivity coefficients to $\alpha$ variation. Thus, for any further constraining to the temporal variation of $\alpha$ 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 $\alpha$ variation from the measurements, and on the other hand, selecting a suitable pair of clock transitions having very different sensitivity to variation of $\alpha$ is a good option. To be specific, when a measurement of the frequency of an optical clock at the frequency $f_1$
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 \(^{199}\text{Hg}^+\) and \(^{27}\text{Al}^+\) optical frequency standards have a big difference in \( K_\alpha \) 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 one year, yielding a drift rate of \( \dot{\alpha}/\alpha = (-0.53 \pm 0.79) \times 10^{-16} \) and constrained the temporal variation of \( \alpha \) 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 \(^{171}\text{Yb}^+\) that have the difference in \( K_\alpha \) as \( K_\alpha(\text{E3})-K_\alpha(\text{E2})= -6.95. \) The frequency ratio \( f_{\text{E3}}/f_{\text{E2}} \) was measured over 1500 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 \( \alpha \), it is necessary to improve the clock frequency measurements consistently. In this sense, even improving the limit on the constraint of \( \alpha \) 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 \(^{229m}\text{Th} \) with excitation energy

### Table 1

A summary of the sensitivity coefficients, \( q \) and \( K_\alpha \), of the clock transition frequency to variation of \( \alpha \), with definition given in text and the data source is taken from Ref. \(^{[11]}\)

| \( Z \) | atoms | Clock transition | Energy (cm\(^{-1}\)) | \( q \) (cm\(^{-1}\)) | \( K_\alpha \) (unit less) |
|-------|-------|------------------|----------------------|----------------|----------------------|
| 13    | Al\(^+\) | \( 3s^21S_0-3s3p^3P_0 \) | 37393.03 | 146 | 0.008 |
| 20    | Ca\(^+\) | \( 4s^22S_{1/2}-3d^2D_{5/2} \) | 13710.89 | 1040 | 0.152 |
| 38    | Sr    | \( 5s^21S_0-5s5p^3P_0 \) | 14317.52 | 443 | 0.062 |
| 70    | Yb    | \( 6s^21S_0-6s6p^3P_0 \) | 17288.44 | 2714 | 0.314 |
| 70    | Yb\(^+\) | \( 4f^{14}6s^22S_{1/2}-4f^{14}5d^2D_{5/2} \) | 24332.69 | 12582 | 1.03 |
|       |       | \( 4f^{14}6s^22S_{1/2}-4f^{13}6s^2F_{7/2} \) | 21418.75 | -63752 | -5.95 |
| 80    | Hg\(^+\) | \( 6s^21S_0-6s6p^3P_0 \) | 37645.08 | 15299 | 0.81 |
| 80    | Hg\(^+\) | \( 5d^{10}6s^22S_{1/2}-5d^96s^22D_{5/2} \) | 35514.62 | -52200 | -2.94 |

### Table 2

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

| \( A_1-A_2 \) | \( \frac{R}{R} \) | \( K_\alpha(A_1)-K_\alpha(A_2) \) | \( \dot{\alpha}/\alpha \) |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} | \(^{[13]}\) |

relative to another optical clock at the frequency \( f_2 \) is conducted (the two optical clocks have different sensitivities to \( \alpha \) variation), the time-variation of the ratio \( f_1/f_2 \) can be expressed as

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

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 \(^{199}\text{Hg}^+\) and \(^{27}\text{Al}^+\) optical frequency standards have a big difference in \( K_\alpha \) 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 one year, yielding a drift rate of \( \dot{\alpha}/\alpha = (-0.53 \pm 0.79) \times 10^{-16} \) and constrained the temporal variation of \( \alpha \) 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 \(^{171}\text{Yb}^+\) that have the difference in \( K_\alpha \) as \( K_\alpha(\text{E3})-K_\alpha(\text{E2})= -6.95. \) The frequency ratio \( f_{\text{E3}}/f_{\text{E2}} \) was measured over 1500 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.
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, 17, 18, 19]. This transition has also been explored for testing variation of fundamental constants by different groups [20, 21, 22, 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, 26, 27, 28]. However, HCIs are recognized as potential candidates for making ultra-precise atomic clocks, developing tools for quantum information, and probing possible variations of $\alpha$. Following the pioneering works by Berengut et al., which suggested enhanced sensitivity to variation of $\alpha$ in the HCIs [29, 30, 31, 32, 33, 34], a long list of HCIs are being proposed [35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52] to select appropriate HCIs for consideration for the clock experiments. All these proposed HCI candidates appear promising for building atomic clocks and probing $\alpha$ 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 $\alpha$ 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 $\alpha$ 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 $\alpha$ varying sensitivity coefficients for the clock transitions, which implies that they are excellent platforms for searching of temporal variation of $\alpha$. 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 $\alpha$-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 $\alpha$ is of immense interest to the research community [53, 54, 28, 10]. One of the biggest consequences of investigating the temporal and spatial variation of $\alpha$ is to support multidimensional theories that try to unify all four fundamental interactions [55, 56, 57, 58, 59, 60, 61, 62]. Such theories also predict violation of Einstein’s equivalence principle. Thus, any signature of variation in the $\alpha$ 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 $\alpha$. Observations using the Kerk telescope suggest that the fractional drift in $\alpha$ is smaller by an amount $\Delta \alpha/\alpha = (\alpha_z - \alpha_0)/\alpha_0 = (0.543 \pm$
Table 3. Comparison of various limits to variation in $\alpha$ with its absolute value ($\Delta \alpha/\alpha$) obtained from different types of works over a time interval $\Delta t$. 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                  | $\Delta \alpha/\alpha$ | $\Delta t$ (year) | $\dot{\alpha}/\alpha$ (year$^{-1}$) | Refs. |
|-------------------------|-------------------------|-------------------|---------------------------------------|-------|
| Cosmological            | $< 10^{-3}$             | $10^{10}$         | $10^{-14}$                            | [53]  |
| Astrophysical(quasar)   | $(2.18 \pm 7.27) \times 10^{-5}$ | $10^{10}$         | $(2.18 \pm 7.27) \times 10^{-15}$    | [65]  |
| Geophysical(Oklo)       | $< 1.1 \times 10^{-8}$  | $2.1 \times 10^{9}$ | $< 10^{-17}$                         | [68]  |
| Laboratory              | $(1.0 \pm 1.1) \times 10^{-18}$ |                  |                                       | [13]  |

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 to 7.1 using the Very Large Telescope (VLT) is used to search for variation of $\alpha$. 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 [63]. 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 $\Delta \alpha/\alpha = (-0.5 \pm 0.5_{\text{stat}} \pm 0.4_{\text{sys}})$ parts-per-million (ppm). Webb et al. proposed a theory of spatial dipole of $\alpha$ 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 $\alpha$ 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 $\alpha$ 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 ($\Delta t = 1$yr), 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 four years ($\Delta t = 4$yr), 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 $\alpha$ have been made from the other clock frequency measurements found from Refs. [69, 70, 71, 72, 73, 74, 75].

Findings of variation of $\Delta \alpha$ from different studies have been reviewed in Refs. [53, 77, 76, 11, 33]. Table 3 compares limits to the temporal variation in $\alpha$ 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
The ultra-narrow $5s_{1/2} - 4f_{5/2}$ optical transitions in Nd$^{13+}$ and Sm$^{15+}$ 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 nm 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, 39, 40]. Among these ten HCIs recommended by...
Table 4. A summary of the HCIs proposed for making optical clocks. The definition of \( q \) and \( K_\alpha \) is given in text.

| \( Z \) | atoms | Clock transition       | Energy (cm\(^{-1}\)) | \( q \) (cm\(^{-1}\)) | \( K_\alpha \) (unit less) | Refs. |
|-----|-------|------------------------|-----------------------|-------------------------|--------------------------|-------|
| 18  | Ar\(^{18}\)+ | 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\(^3\)P\(_0\) | 60397                 |                      |                           | [49] |
| 77  | Ir\(^{17}\)+ | 4f\(^{13}\)5s\(^3\)F\(_{4}\) - 4f\(^{14}\)1S\(_0\) | 5055                  | 367161                  | 145.3                    | [30] |
| 98  | Cr\(^{15}\)+ | \( 5f6p^22F_{5/2}^o \) - \( 5f^26p^22H_{9/2}^o \) | 13303                 | 380000                  | 57.1                     | [43] |
|     |        |                        |                       |                         |                          | [47] |
| 98  | Cr\(^{16}\)+ | 5f\(_{6p}\) J=3 - 6p\(^2\) J=0 | 5267                  | 370928                  | 140.8                    | [32] |
| 98  | Cr\(^{17}\)+ | 5f\(_{5/2}\) - 6p\(_{1/2}\) | 18686                 | 449750                  | 48.14                    | [32] |
|     |        |                        |                       |                         |                          | [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\(^3\)G\(_3\) | 20216                 | 42721                   | 4.23                     | [38] |
|     |        |                        |                       |                         |                          | [83] |
| 60  | Nd\(^{9}\)+ | \( (5p^24f)^{6}_{5/2} \) - \( (5p4f^2)^{9}_{9/2} \) | 20594                 | 67136                   | 6.52                     | [50] |
| 67  | Ho\(^{14}\)+ | 4f\(^6\)5s\(^8\)F\(_{1/2}\) - 4f\(^5\)5s\(^2\)6H\(_{5/2}\) | 23823                 | -186000                 | 7.81                     | [41] |

Then, the Pr\(^{9}\)+ ion seems to be the more attractive, which has an optical transition \( 5p^2\)3P\(_0\) - 5p4f\(^3\)G\(_3\) 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 \( \alpha \) 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\(^{11}\)+ ion has the ground state configuration as \( (5p^24f)^{5}_{5/2} \) and the first excited state configuration as \( (5p4f^2)^{9}_{9/2} \). The E2 transition of \( (5p^24f)^{6}_{5/2} - (5p4f^2)^{9}_{9/2} \) 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\textsuperscript{14+} is [Kr]4\textit{f}\textsuperscript{6}5\textit{s} 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]4\textit{f}\textsuperscript{5}5\textit{s}\textsuperscript{2}, with 200 fine structure levels spreading over the similar energy range. Their results show a huge number of emissions in the Ho\textsuperscript{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 \(Z_{\text{ion}}\) 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 \[85, 29\]

\[
q_n \approx -I_n \frac{(Z\alpha)^2}{\nu(j + 1/2)},
\]

and

\[
I_n = -E_n = \frac{Z^2_a}{2n^2} = \frac{(Z_{\text{ion}} + 1)^2}{2\nu^2},
\]

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 \(\nu\) and an effective charge \(Z_a\) that the electron sees at larger distances, considering the screening in a multi-electron system. Eqs. (3) and (4) explain how enhancement of \(q\) increases with \(I_n\), i.e., with larger \(Z_{\text{ion}}\). 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 \(Z_{\text{ion}}\) 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 \(Z_{\text{ion}}\) 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. 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. BERMONT 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 with k = 1, 2, 3, · · ·, 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. One can presume from these analyses that HCIs with np^k ground state configurations with n ≥ 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 58Ni^{12+} and 106Pd^{12+} ions with nuclear spin I = 0 and the (3P_2, F = 1/2) - (3P_0, F = 3/2) transition in 63Cu^{13+} with I = 3/2, and the (3P_2, F = 3/2) - (3P_0, F = 1/2) transition in 107Ag^{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 as listed in Table 5.

The forbidden transitions among the fine-structure splitting in HCIs possessing np^k configuration in their ground state are more 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. 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. It is natural to anticipate that some of these transitions could be considered for atomic clocks. Theoretical studies carried out in Refs. 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 reasons 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, 114, 115, 116, 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. [118, 35]. 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 $1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p → 5s → 4d → 5p → 6s → 4f → 5d → 6p → 7s → 5f → 6d → 7p \ldots$. 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, 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 $(n + 1)s$ orbitals 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 \(3d^9\). 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.
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 $[\text{Ar}]\equiv 1s^22s^22p^63s^23p^6$. 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 |
|-----|-----|-----|-----|-------------|-------|--------|-----|-----|-----|-----|-------------|-------|--------|
| 19  | 20  | 1   | Ca$^+$ | [Ar]4s | $^2S_{1/2}$ | 0     | 20  | 21  | 2   | Sc$^{2+}$ | [Ar]3d4s | $^3D_1$ | 0     |
|     |     |     |       | [Ar]3d | $^2D_{3/2}$ | 13650 | 22  | 2   | Ti$^{2+}$ | [Ar]3d | $^3D_2$ | 3F_2 | 4803 |
|     |     |     |       | [Ar]4s | $^2S_{1/2}$ | 25539 |     |     |     | [Ar]3d4s | $^3D_1$ | 38064 |
|     |     |     |       | [Ar]4s | $^2D_{3/2}$ | 80389 | 23  | 2   | V$^{3+}$ | [Ar]3d | $^3F_2$ | 0     |     |
|     |     |     |       | [Ar]4s | $^2S_{1/2}$ |     | 24  | 2   | Cr$^{3+}$ | [Ar]3d4s | $^3F_2$ | 96196 |

| 21  | 22  | 3   | Ti$^+$ | [Ar]3d$^2$4s | $^4F_{3/2}$ | 0     | 22  | 23  | 4   | V$^+$ | [Ar]3d | $^3D_0$ | 0     |
|     |     |     |       | [Ar]3d$^3$ | $^4F_{3/2}$ | 908   | 24  | 2   | Cr$^{2+}$ | [Ar]3d$^3$ | $^4F_{3/2}$ | 0     |
|     |     |     |       | [Ar]3d$^2$4s | $^4F_{3/2}$ | 43942 |     |     |     | [Ar]3d$^3$ | $^4F_{3/2}$ | 94992 |
|     |     |     |       | [Ar]3d$^3$ | $^4F_{3/2}$ | 103996| 25  | 4   | Mn$^{3+}$ | [Ar]3d$^4$s | $^4F_{3/2}$ | 0     |

| 23  | 24  | 5   | Cr$^+$ | [Ar]3d$^5$ | $^6S_{5/2}$ | 0     | 24  | 25  | 6   | Mn$^+$ | [Ar]3d$^5$ | $^7S_3$ | 0     |
|     |     |     |       | [Ar]3d$^4$4s | $^6D_{1/2}$ | 11961 | 26  | 2   | Fe$^{2+}$ | [Ar]3d$^5$ | $^7D_4$ | 14326 |
|     |     |     |       | [Ar]3d$^5$ | $^6S_{5/2}$ | 62457 |     |     |     | [Ar]3d$^5$ | $^7D_4$ | 0     |
|     |     |     |       | [Ar]3d$^4$4s | $^6D_{1/2}$ | 127766| 27  | 6   | Co$^{3+}$ | [Ar]3d$^6$ | $^7D_4$ | 0     |

| 25  | 26  | 7   | Fe$^+$ | [Ar]3d$^6$4s | $^6D_{9/2}$ | 0     | 26  | 27  | 8   | Co$^+$ | [Ar]3d$^7$4s | $^3F_4$ | 0     |
|     |     |     |       | [Ar]3d$^7$ | $^4F_{9/2}$ | 1872  | 28  | 2   | Ni$^{2+}$ | [Ar]3d$^7$4s | $^3F_4$ | 9814  |
|     |     |     |       | [Ar]3d$^8$4s | $^4D_{7/2}$ | 55729 |     |     |     | [Ar]3d$^8$4s | $^5F_4$ | 61338 |
|     |     |     |       | [Ar]3d$^7$ | $^4F_{9/2}$ | 120909| 29  | 8   | Cu$^{3+}$ | [Ar]3d$^8$ | $^3F_4$ | 0     |

| 27  | 28  | 9   | Ni$^+$ | [Ar]3d$^9$ | $^2D_{5/2}$ | 0     | 28  | 29  | 10  | Cu$^{2+}$ | [Ar]3d$^{10}$ | $^1S_0$ | 0     |
|     |     |     |       | [Ar]3d$^9$4s | $^2F_{7/2}$ | 13550 | 30  | 9   | Zn$^{3+}$ | [Ar]3d$^{10}$ | $^1S_0$ | 0     |
|     |     |     |       | [Ar]3d$^9$ | $^2F_{7/2}$ | 67017 |     |     |     | [Ar]3d$^{10}$ | $^1D_2$ | 83500 |
|     |     |     |       | [Ar]3d$^9$4s | $^2F_{7/2}$ | 135951| 31  | 10  | Ga$^{3+}$ | [Ar]3d$^{10}$ | $^1S_0$ | 0     |

As shown in Tables 6, 7, and 8 the $n(d−(n+1)s$ 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

Frontiers 12
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]$=1s^22s^22p^63s^23p^63d^{10}4s^24p^6$. The data are from the NIST database [120] and in cm$^{-1}$.

| $N$ | $Z$ | Ion                    | Configuration | State   | Energy | $N$ | $Z$ | Ion                    | Configuration | State   | Energy |
|----|----|------------------------|---------------|---------|--------|----|----|------------------------|---------------|---------|--------|
|    | 37 | 38 1 Sr$^+$             | [Kr]$5s$      | $2S_{1/2}$ | 0      | 38 | 39 2 Y$^+$             | [Kr]$5s^2$   | $1S_0$  | 0      |
|    |    | 39 1 Y$^{2+}$          | [Kr]$4d$      | $2D_{3/2}$ | 14555  | 40 2 Zr$^{2+}$         | [Kr]$4d^2$   | $1D_2$  | 14833  |
|    |    | 40 1 Zr$^{3+}$         | [Kr]$4d$      | $2D_{3/2}$ | 0      | 41 2 Nb$^{3+}$         | [Kr]$5s^2$   | $1S_0$  | 48506  |
|    |    |                        | [Kr]$5s$      | $2S_{1/2}$ | 7467   |        |        |                        | [Kr]$4d^2$   | $3F_3$  | 0      |
|    | 39 | 40 3 Zr$^{+}$          | [Kr]$4d^25s$  | $4F_{3/2}$ | 0      | 40 | 41 4 Nb$^{+}$          | [Kr]$4d^4$   | $5D_0$  | 0      |
|    |    | 41 3 Nb$^{2+}$         | [Kr]$4d^5s^2$ | $2D_{3/2}$ | 14298  | 42 4 Mo$^{2+}$         | [Kr]$4d^4$   | $5D_0$  | 0      |
|    |    | 42 3 Mo$^{3+}$         | [Kr]$4d^4s^2$ | $4F_{3/2}$ | 25220  |        |        |                        | [Kr]$4d^5s_5$| $5F_1$  | 32419  |
|    |    |                        | [Kr]$4d^25s$  | $4F_{3/2}$ | 60896  |        |        |                        | [Kr]$4d^5s_5$| $3D_1$  | 71139  |
|    | 41 | 42 5 Mo$^+$            | [Kr]$4d^5$    | $6D_{5/2}$ | 0      | 42 | 43 6 Te$^+$            | [Kr]$4d^5s_5$| $7S_0$  | 0      |
|    |    | 43 5 Tc$^{2+}$         | [Kr]$4d^5s$   | $6D_{1/2}$ | 11783  |        |        |                        | [Kr]$4d^6$   | $5D_4$  | 3461   |
|    |    |                        | [Kr]$4d^5s^2$ | $4D_{7/2}$ | 19379  |        |        |                        | [Kr]$4d^6$   | $5D_4$  | 0      |
|    |    |                        | [Kr]$4d^5s_5$ | $4D_{7/2}$ | 44254  |        |        |                        | [Kr]$4d^5s_5$| $5S_2$  | 41112  |
|    | 43 | 44 7 Ru$^+$            | [Kr]$4d^7$    | $4F_{9/2}$ | 0      | 44 | 45 8 Rh$^+$            | [Kr]$4d^8$   | $3F_4$  | 0      |
|    |    | 45 7 Rh$^{2+}$         | [Kr]$4d^6s$   | $4D_{7/2}$ | 19379  |        |        |                        | [Kr]$4d^7s_5$| $3F_4$  | 25376  |
|    |    |                        | [Kr]$4d^6s^2$ | $4D_{7/2}$ | 54632  |        |        |                        | [Kr]$4d^7s_5$| $3F_4$  | 0      |
|    |    |                        | [Kr]$4d^6s_5$ | $4D_{7/2}$ | 44254  |        |        |                        | [Kr]$4d^5s_5$| $5S_2$  | 41112  |
|    | 45 | 46 9 Pd$^+$            | [Kr]$4d^9$    | $2D_{5/2}$ | 0      | 46 | 47 10 Ag$^+$           | [Kr]$4d^{10}$| $1S_0$  | 0      |
|    |    | 47 9 Ag$^{2+}$         | [Kr]$4d^8s$   | $2D_{5/2}$ | 0      |        |        |                        | [Kr]$4d^{10}$| $5D_3$  | 39168  |
|    |    |                        | [Kr]$4d^8s^2$ | $2D_{5/2}$ | 32281  |        |        |                        | [Kr]$4d^{10}$| $3D_3$  | 0      |
|    |    |                        | [Kr]$4d^8s_5$ | $2D_{5/2}$ | 63246  |        |        |                        | [Kr]$4d^8s_5$| $3D_3$  | 80454  |

Angular momenta from the $s$ to $d$ orbitals. Thus, considering these HCIs as atomic clocks would offer substantial relativistic sensitivity coefficients to probe $\alpha$ 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 $\alpha$ [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 $5d^6 - 5d^56s$ transition in Au$^{2+}$, which could be the promising HCIs for the study of possible temporal variation of $\alpha$. The singly and triply charged ions also have some interesting optical transitions, for example, Allehab, 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 kinds of isoelectronic sequences. This type of HCIs usually has the large number of charge, larger than 10 in
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. \([\text{Xe}]\equiv 1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6\). The data is taken from the NIST database unless cited others. Units for all the values are in \( \text{cm}^{-1} \).

| Isoelec. Sequences | \( N \) | \( Z \) | \( x \) | Ion | Configuration | State | Energy |
|--------------------|------|------|-----|-----|-------------|------|-------|
| Tm-like | 69 | 70 | 1 | Yb\(^+\) | \([\text{Xe}]4f^{14}6s\) | \(2S_{1/2}\) | 0 |
| Tm-like | 69 | 71 | 1 | Lu\(^{2+}\) | \([\text{Xe}]4f^{14}5d\) | \(2D_{3/2}\) | 22961 |
| Tm-like | 69 | 72 | 1 | Hf\(^{3+}\) | \([\text{Xe}]4f^{14}5d\) | \(2D_{3/2}\) | 5708 |
| Yb-like | 70 | 71 | 2 | Lu\(^+\) | \([\text{Xe}]4f^{14}6s^2\) | \(1S_0\) | 0 |
| Yb-like | 70 | 72 | 2 | Hf\(^{2+}\) | \([\text{Xe}]4f^{14}5d^2\) | \(3F_{2}\) | 35652 |
| Lu-like | 71 | 72 | 3 | Hf\(^+\) | \([\text{Xe}]4f^{14}6s5d\) | \(2F_{3/2}\) | 2652 |
| Lu-like | 71 | 74 | 3 | W\(^{4+}\) | \([\text{Xe}]4f^{14}5d^3\) | \(4F_{3/2}\) | 0 |
| Ta-like | 73 | 74 | 5 | W\(^+\) | \([\text{Xe}]4f^{14}5d^6\) | \(4F_{3/2}\) | 32692 |
| Ta-like | 73 | 75 | 5 | Re\(^{2+}\) | \([\text{Xe}]4f^{14}5d^5\) | \(6D_{1/2}\) | 0 |
| W-like | 74 | 75 | 6 | Re\(^+\) | \([\text{Xe}]4f^{14}5d^5\) | \(7S_3\) | 143961 |
| W-like | 74 | 76 | 6 | Os\(^{2+}\) | \([\text{Xe}]4f^{14}5d^6\) | \(5D_0\) | 13777 |
| W-like | 74 | 77 | 6 | Ir\(^{3+}\) | \([\text{Xe}]4f^{14}5d^6\) | \(7S_3\) | 4578 |
| Ir-like | 77 | 78 | 9 | Pt\(^+\) | \([\text{Xe}]4f^{14}5d^9\) | \(3H_4\) | 14546 |
| Ir-like | 77 | 79 | 9 | Au\(^{2+}\) | \([\text{Xe}]4f^{14}5d^8\) | \(2D_{5/2}\) | 0 |

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, 39, 40]. When valence electrons are larger than 4, the electronic configuration becomes far more complicated. Therefore, there is little data available for such kinds of HCIs. Dzuba has investigated the energy levels of the I-like \( \text{Ho}^{14+} \) and Xe-like \( \text{E}^{15+} \) with \( x = 6 \) and 7, which are proposed as candidates for an extremely accurate and stable optical atomic clock which is found to have extremely high values of \( q \) and \( K \) suitable for the study of time variation of \( \alpha \). 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 \( \text{Ir}^{17+} \) ion has been proposed for the search of variation of \( \alpha \), 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 \( \alpha \) variation [30]. Nandy and Sahoo have also investigated the \( \text{W}^{13+} \), \( \text{Ir}^{16+} \) and \( \text{Pt}^{17+} \) HCIs with ground state configurations \( 4f^{13} \) as promising optical clock candidates to probe variation of \( \alpha \) [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 meditated number of charge, around ten or
Table 9. The energy level of HClms 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. \([\text{Kr}] \equiv 1s^22s^22p^63s^23p^63d^{10}4s^24p^6\). Units for values are in cm\(^{-1}\).

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

lower. Table 10 lists some of these kinds of HClms. Safronova et al. have proposed In-like Pr\(^{10+}\) and Sn-like P\(^{9+}\) and Nd\(^{10+}\) as the potential candidates for atomic clocks [39, 40, 38]. Berengnut et al. have also proposed Sn-like Pr\(^{9+}\) as a promising candidate for developing an extremely accurate atomic clock for the measurement of sensitivity to variation of \(\alpha\). 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 HClms with mediated number of charge contain one, two, and three valence electrons distributing...
Table 10. The energy level of HCl 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. \([\text{Kr}]=1s^22s^22p^63s^23p^63d^{10}4s^24p^6\) and \([\text{Cd}]=1s^22s^22p^63s^23p^63d^{10}4s^24p^6\). Units of all values are in cm$^{-1}$.

| Isoelec. | $N$ | $Z$ | $x$ | Ion | Configuration | State | Energy |
|----------|-----|-----|-----|-----|---------------|-------|--------|
| In-like  | 49  | 58  | 1   | Ce$^{1+}$ | [Kr]$5p_{2}$ | $^2P_{1/2}$ | 0 |
|          |     |     |     |      | [Kr]$5p_{3/2}$ | 33427 [39] |
|          |     |     |     |      | [Kr]$4f_{5/2}$ | 54947 [39] |
| In-like  | 49  | 59  | 1   | Pr$^{10+}$ | [Kr]$5p_{2}$ | $^2P_{1/2}$ | 0 |
|          |     |     |     |      | [Kr]$5p_{3/2}$ | 3958 [39] |
| In-like  | 49  | 60  | 1   | Nd$^{11+}$ | [Kr]$4f_{2}$ | $^2P_{1/2}$ | 4566 [39] |
| Sn-like  | 50  | 59  | 2   | Pr$^{9+}$ | [Kr]$5p_{2}^2$ | $^3P_{0}$ | 0 |
|          |     |     |     |      | [Kr]$5p_{4}f_{4}$ | $^3G_{3}$ | 22101 [83] |
|          |     |     |     |      | [Kr]$5p_{2}f_{2}$ | $^3P_{1}$ | 28561 [83] |
| Sn-like  | 50  | 60  | 2   | Nd$^{10+}$ | [Kr]$4f_{2}^2$ | $^3H_{4}$ | 0 |
|          |     |     |     |      | [Kr]$5p_{4}f_{4}$ | $^3G_{3}$ | 2605 [40] |
|          |     |     |     |      | [Kr]$4f_{2}f_{2}$ | $^3H_{5}$ | 3432 [40] |
| Sb-like  | 51  | 59  | 3   | Pr$^{8+}$ | [Kr]$5p_{3}^2$ | $^4S_{3/2}$ | 0 |
|          |     |     |     |      | [Kr]$5p_{2}^2f_{4}$ | $^4G_{5/2}$ | 18386 [125] |
|          |     |     |     |      | [Kr]$5p_{3}^2$ | $^2D_{3/2}$ | 24348 [125] |
| Sb-like  | 51  | 60  | 3   | Nd$^{9+}$ | [Kr]$5p_{2}^2f_{4}$ | $J = 5/2$ | 0 |
|          |     |     |     |      | [Kr]$5p_{2}^2f_{4}$ | $J = 7/2$ | 6524 [50] |
|          |     |     |     |      | [Kr]$4f_{2}^2f_{0}$ | $J = 9/2$ | 20594 [50] |
| Sb-like  | 51  | 61  | 3   | Pm$^{10+}$ | [Kr]$4f_{2}^2f_{0}$ | $J = 9/2$ | 0 |
|          |     |     |     |      | [Kr]$4f_{2}^2f_{0}$ | $J = 9/2$ | 5296 [125] |
| Sb-like  | 51  | 62  | 3   | Sm$^{11+}$ | [Kr]$4f_{2}^3$ | $^4I_{9/2}$ | 0 |
|          |     |     |     |      | [Kr]$4f_{2}^3$ | $^4I_{11/2}$ | 3063 [125] |
| Sm-like  | 62  | 74  | 14  | W$^{12+}$ | [Cd]$4f_{14}^{13}$ | $^1S_{0}$ | 0 |
|          |     |     |     |      | [Cd]$4f_{15}^{13}p_{5}$ | $^3D_{3}$ | 4016 [126] |
| Eu-like  | 63  | 74  | 15  | W$^{11+}$ | [Cd]$4f_{14}^{15}p_{5}$ | $^2P_{1/2}$ | 11000 [120, 127, 128] |
|          |     |     |     |      | [Cd]$4f_{14}^{15}p_{2}^2$ | $^2P_{1/2}$ | 11000 [120, 127, 128] |
| Gd-like  | 64  | 74  | 16  | W$^{10+}$ | [Cd]$4f_{14}^{15}p_{2}^2$ | $^3P_{2}$ | 0 |
|          |     |     |     |      | [Cd]$4f_{14}^{15}p_{3}^2$ | $^3G_{5}$ | 44614 [129] |
| Tb-like  | 65  | 74  | 17  | W$^{9+}$ | [Cd]$4f_{14}^{15}p_{3}^2$ | $^2P_{2}$ | 0 |
|          |     |     |     |      | [Cd]$4f_{14}^{15}p_{3}^2$ | $^3F_{3}$ | 14000 [120, 116] |
| Dy-like  | 66  | 74  | 18  | W$^{8+}$ | [Cd]$4f_{14}^{15}p_{4}$ | $^3P_{2}$ | 0 |

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 3-5 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 $x ≥ 14$, there observed the hole state of $4f$ shell in some HCl, 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, 130, 129, 131, 132, 126, 128].

Tables 6, 7, 8, 9, and 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 characteristics of the $s - f$ and $p - f$ inter-configuration transitions. Such features in atomic clocks are useful for probing $\alpha$ 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

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

$$= \sum_i \hbar_i + \sum_{i,j>i} g_{ij}, \quad (5)$$

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 $\alpha = (\alpha_x, \alpha_y, \alpha_z)$ and $\beta$ are the $4 \times 4$ Dirac matrices with the components

$$\alpha_x = \begin{pmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{pmatrix}, \alpha_y = \begin{pmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{pmatrix}, \alpha_z = \begin{pmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}, \quad (6)$$
for the identity matrix \( I \) and the Pauli spin matrices

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\] (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

\[
\rho(r) = \left( \frac{\eta}{\pi} \right)^{3/2} e^{-\eta r^2}
\] (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

\[
V_{\text{nuc}}(r) = -\frac{Z}{r} \text{erf} \left( \sqrt{\eta} r \right).
\] (9)

In the Fermi nuclear charge distribution, it is given as

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

where \( \rho_0 \) 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

\[
b = \sqrt{\frac{5 \cdot 3}{3} R_{rms}^2 - \frac{7}{3} a^2 \pi^2}
\] (11)

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

\[
R_{rms} = 0.836 A^{1/3} + 0.570.
\] (12)

The above expression gives the nuclear potential expression as

\[
V_{\text{nuc}}(r) = -\frac{Z}{\mathcal{N} r} \left\{ \frac{1}{2} \left( \frac{3}{2} + \frac{a^2 \pi^2}{2 b^2} - \frac{2}{2 b^2} + \frac{3a^2}{b^2} P_2 + \frac{6a^3}{b^4} (S_3 - P_3^+) \right) \right\} \quad \text{for} \ r_i \leq b
\]

\[
\frac{1}{2} \left( 1 + \frac{6a^2 \pi^2}{b^2} - \frac{3a^2}{b^2} P_2 + \frac{6a^3}{b^4} (S_3 - P_3^-) \right) \quad \text{for} \ r_i > b,
\] (13)

where the factors are

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

\[
V^B = -\sum_{j>i} \frac{[\alpha_i \cdot \alpha_j + (\alpha_i \cdot \hat{r}_{ij})(\alpha_j \cdot \hat{r}_{ij})]}{2 r_{ij}},
\] (15)
where \( \hat{r}_{ij} \) is the unit vector along the inter-electronic distance \( r_{ij} \).

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

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

and

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

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

\[
V^{ef}_{SE} = A_l \sum_i \frac{2\pi Z\alpha^3}{r_i} I^{ef}_1(r_i) - B_l \sum_i \frac{\alpha}{r_i} I^{ef}_2(r_i)
\]

known as effective electric form factor part and

\[
V^{mq}_{SE} = -\sum_k \frac{i\alpha^3}{4} \gamma \cdot \nabla_k \frac{1}{r_k} \int_0^\infty dx \, x \rho_n(x) \int_1^\infty dt \frac{1}{t^3\sqrt{t^2 - 1}} \times \left[ e^{-2ct|r_k-x|} - e^{-2ct(r_k+x)} - 2ct(r_k + x - |r_k - x|) \right],
\]

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

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

and

\[
B_l = \begin{cases} 
1.071 - 1.97x^2 - 2.128x^3 + 0.169x^4 & \text{for } l = 0, 1 \\
0 & \text{for } l \geq 2.
\end{cases}
\]

The integrals are given by

\[
I^{ef}_1(r) = \int_0^\infty dx \, x \rho_n(x)[(Z|r - x| + 1)e^{-Z|r-x|} - (Z(r + x) + 1)e^{-2ct(r+x)}]
\]
As mentioned earlier, the one-body part \( H_C \)
where

\[
H_C = \sum_{l} \frac{1}{2l^2 - 1} \left\{ \ln(t^2 - 1) + 4 \ln \left( \frac{1}{Z} + \frac{1}{2} \right) - \frac{3}{2} + \frac{1}{t^2} \right\}
\]

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

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

\[
H^{DC} = \sum_{pq} h^0_p a^+_p a^q + \sum_{pqrst} \frac{1}{4} V^pqr^+ s a^+_p a^+_q a^r a^s,
\]

where \( h^0_p = \langle p|\hat{h}|q \rangle \) and \( V^pqr^+ s = \langle pr|\hat{g}|qs \rangle - \langle pr|\hat{g}|sq \rangle \) 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

\[
\Phi(r_1, r_2, \ldots, r_N) = \mathbf{A}(\psi_1(r_1), \psi_2(r_2), \ldots, \psi_N(r_N)).
\]

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 \( |\Phi_0\rangle \).

\[
|\Psi\rangle = C_0|\Phi_0\rangle + \sum_{I} C_I|\Phi_I\rangle + \sum_{II} |\Phi_{II}\rangle + \cdots,
\]

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

\[
|\Psi\rangle = (C_0 + \sum_{ai} c^a_{i} a^+_i a^a_i + \sum_{a>b,i>j} c^{ab}_{ij} a^+_a a^+_b a^a_i a^b_j + \cdots)|\Phi_0\rangle.
\]

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.
Table 11. Demonstration of GASCI scheme for Ni$_{12}^{12+}$, 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    | virtual   |
| V       | 16    | 16    | 150                | $n(s, p, \cdots i)$ with $n \geq 4$ | virtual   |

by solving

$$\mathbf{HC} = E_{\text{CI}} \mathbf{C},$$

(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 $E_{\text{CI}}$ 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, 138, 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 2 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$_{12}^{12+}$ HCI and demonstrate how the CSFs are decided. We may consider its valence configuration $3p^4$ with the core occupation $1s^2 2s^2 2p^6 3s^2$. The scheme of the GASCI employed for Ni$_{12}^{12+}$ 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, respectively. 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+valence space.
According to this G ASCI 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 valence space; (3) single excitations from the core and double excitations from the valence space; (4) double excitations from the core and single excitations from the valence space; and (5) no excitation from the core but singles, doubles and/or triple excitations from the valence space. Combining all of those possible occupations from the core, valence and virtual orbitals forms a CI space with about $7 \times 10^9$ determinants in Ni$^{12+}$, which includes the most dominant core-core, core-valence, and valence-valence correlations. This means that the G ASCI scheme can design a complete and near-complete core and valence spaces based on the multi-reference configurations of CI method.

The G ASCI 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 G ASCI 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$^{3+}$ 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 4$f$ hole.

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

$$|\Psi_v\rangle = \Omega_v |\Phi_v\rangle,$$

where $\Omega_v$ 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, $\Omega_v$ can now be divided as

$$\Omega_v = 1 + \chi_c + \chi_v,$$

where $\chi_c$ and $\chi_v$ 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

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

where the superscript $k$ refers to the number of times $V_r$ is considered. The $k$th order amplitudes for the $\chi_c$ and $\chi_v$ operators are obtained by solving the equations

$$[\chi_c^{(k)}, H_0]P = QV_r (1 + \chi_c^{(k-1)}) P$$
and

\[ [\chi_v^{(k)}, H_0]P = QV_v (1 + \chi_c^{(k-1)} + \chi_v^{(k-1)}) P - \sum_{m=1}^{k-1} \chi_v^{(k-m)} \times PV_v (1 + \chi_c^{(m-1)} + \chi_v^{(m-1)}) P, \]  

(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

\[ H_v^{eff} = P a_v H \Omega_v a_v^\dagger P. \]  

(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

\[ |\Psi_v\rangle \equiv \Omega_v |\Phi_v\rangle = e^T \{1 + S_v\} |\Phi_v\rangle \]  

(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

\[ T = T_1 + T_2 \quad \text{and} \quad S_v = S_{1v} + S_{2v}. \]  

(36)

The amplitudes of these operators are evaluated using the equations

\[ \langle \Phi_c^* | T_N | \Phi_c \rangle = 0 \]  

(37)

and

\[ \langle \Phi_c^* | (T_N - \Delta E_v) S_v | \Phi_c \rangle = -\langle \Phi_v^* | T_N | \Phi_v \rangle, \]  

(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 \( T_N = (H_N e^T)_l \) 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 \( H_c^{eff} = PHP (1 + \chi_c) P \). Following Eq. (34), expression for \( \Delta E_v \) is given by

\[ \Delta E_v = \langle \Phi_v | T_N \{1 + S_v\} | \Phi_v \rangle. \]  

(39)

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

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

(40)
and

$$S_{3v}^{\text{pert}} = \frac{1}{4} \sum_{ab, pqr} \langle H_N T_2 + H_N S_{2v_{ab}} \rangle_{pqr}^{abv} \left( \epsilon_a + \epsilon_b + \epsilon_v - \epsilon_p - \epsilon_q - \epsilon_r \right), \quad (41)$$

where \( \{a, b, c\} \) and \( \{p, q, r\} \) represent the occupied and virtual orbitals, respectively, and \( \epsilon \)s 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

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

where \( \tilde{O}_{fi} = \{1 + S_f^2\} e^{T^+} O e^T \{1 + S_i\} \) and \( \tilde{N}_{k{=}f, i} = \{1 + S_k^2\} e^{T^+} e^T \{1 + S_k\} \). 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 \( e^{T^+} O e^T \) and \( e^{T^+} e^T \) 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 \( \alpha \). 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 \textit{a priori} 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 [144, 145, 146, 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 (\( \nabla E \)) 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

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

(43)

where $K$ is the angular momentum of the state with its component $M_K$, $\gamma$ 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

$$\Theta(\gamma, K) = \langle KK | \Theta | KK \rangle$$

$$= \left( \begin{array}{cc} K & 2 & K \\ -K & 0 & K \end{array} \right) \langle \gamma K | \Theta | \gamma K \rangle.$$

(44)

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

$$E_{\text{Quad}}(\gamma J FM_F) = -K_1 K_2 \Theta(\gamma, J),$$

(45)

where

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

(46)

and

$$K_2 = (-1)^{I+J+F}(2F + 1) \left\{ \begin{array}{ccc} J & 2 & J \\ F & I & F \end{array} \right\} \left( \begin{array}{ccc} J & 2 & J \\ -J & 0 & J \end{array} \right)^{-1},$$

(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, $\Delta E_{\text{Quad}}$ 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 $(\gamma, J, F, M_F)$ with component $M_F$ can be evaluated by

$$E_{\text{Stark}}(\gamma, J, F, M_F) = -\frac{1}{2} \alpha(\gamma, J, F) \mathcal{E}^2$$

$$= -\frac{1}{2} \alpha^{(0)}(\gamma, J, F) \mathcal{E}^2 - \frac{1}{4} \alpha^{(2)}(\gamma, J, F) \frac{[3M_F^2 - F(F + 1)]}{F(2F - 1)} (3\mathcal{E}^2 - \mathcal{E}^2),$$

(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
\[ \alpha^{(0)}(\gamma, J, F) = \alpha^{(0)}(\gamma, J) \]  

(49)

and

\[ \alpha^{(2)}(\gamma, J, F) = (-1)^{I+J+F} \left\{ \begin{array}{ccc} F & J & I \\ J & F & 2 \end{array} \right\} \alpha^{(2)}(\gamma, J) \]

\[ \times \left[ \frac{F(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}{(2F+3)(F+1)J(2J-1)} \right]^{1/2}. \]  

(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 \( E = 10 \text{ V/m} \), 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

\[ E^{E1}_{BBR} = -\frac{1}{2}(831.9 \text{V/m})^2 \left[ \frac{T(K)}{300} \right]^4 \alpha^{(0)}(\gamma, J, F) \]

\[ = -\frac{1}{2}(831.9 \text{V/m})^2 \left[ \frac{T(K)}{300} \right]^4 \alpha^{(0)}(\gamma, J), \]

(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 \( \pi \)-polarized transitions with extreme angular momentum states with two opposite sublevels (e.g. \( M_F = \pm 2 \)) 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 \( B \) is given by [150]

\[ E^2_{Zeem} = \beta_{Zeem}(\gamma, J, F, M_F)B^2, \]

(52)

where

\[ \beta_{Zeem}(\gamma, J, F, M_F) = -\frac{(\mu_Jg_J)^2}{\hbar} \sum_{F'} \frac{|\langle F'M_F|J_z|FM_F\rangle|^2}{E_{F'} - E_F}. \]

(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]

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

$$|\langle F'M_F'|J_z|FM_F\rangle|^2 = J(J+1)(2J+1)(2F+1)(2F'+1) \left\{ \begin{array}{ccc} F & 1 & F' \\ -M_F & 0 & M_F \end{array} \right\}^2 \left\{ \begin{array}{ccc} J & F & I \\ F' & J & 1 \end{array} \right\}^2.$$ (55)

Thus, $\beta_{Zeem}(\gamma, J, F, M_F)$ of a hyperfine level can be determined if Landé $g_J$ factor of the atomic state is known. For a given typical experimental condition, $B$ 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 $\alpha$ 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 $\alpha$, 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$^{17+}$, Cr$^{15-17+}$, 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 $\alpha$, 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 $\alpha$.

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 4$f$-shelled configurations mixed with the 5$s$ and 5$p$ 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 $\alpha$. Upon the fruitful accomplishment of such clocks, they can promote other high-precision experiments and invoke new exciting avenues for researching fundamental physics.

**CONFLICT OF INTEREST STATEMENT**

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.

**AUTHOR CONTRIBUTIONS**

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

**FUNDING**

This work is supported by The National Key Research and Development Program of China (2021YFA1402104) and the National Natural Science Foundation of China under Grant No. 11874064, and Project supported by the Space Application System of China Manned Space Program. B.K.S. would like to acknowledge use of Vikram-100 HPC of Physical Research Laboratory (PRL), Ahmedabad.

**REFERENCES**

[1] Lodewyck J, Bilicki S, Bookjans E, Robyr JL, Shi CY, Vallet G, et al. Optical to microwave clock frequency ratios with a nearly continuous strontium optical lattice clock. *Metrologia*, 53(4):1123, 2016.

[2] Riehle F, Gill P, Arias F, and Robertsson L. The CIPM list of recommended frequency standard values: guidelines and procedures. *Metrologia*, 55(2):188, 2018.

[3] Boulder Atomic Clock Optical Network (BACON) Collaboration. Frequency ratio measurements at 18-digit accuracy using an optical clock network. *Nature*, 591(7851):564–569, 2021.

[4] Schioppo M, Brown RC, McGrew WF, Hinkley N, Fasano RJ, Beloy K, et al. Ultrastable optical clock with two cold-atom ensembles. *Nat Photon*, 11(1):48–52, 2016.

[5] McGrew WF, Zhang X, Fasano RJ, Schäffer SA, Beloy K, Nicolodi D, et al. Atomic clock performance enabling geodesy below the centimetre level. *Nature*, 564(7734):87–90, 2018.

[6] Takano T, Takamoto M, Ushijima I, Ohmae N, Akatsuka T, Yamaguchi A, et al. Geopotential measurements with synchronously linked optical lattice clocks. *Nat Photon*, 10(10):662–666, 2016.

[7] Oelker E, Hutson RB, Kennedy CJ, Sonderhouse L, Bothwell T, Goban A, et al. Demonstration of $4.8 \times 10^{-17}$ stability at 1s for two independent optical clocks. *Nat Photon*, 13(10):714–719, 2019.

[8] Huntemann N, Sanner C, Lipphardt B, Tamm C, and Peik E. Single-ion atomic clock with $3 \times 10^{-18}$ systematic uncertainty. *Phys Rev Lett*, 116(6):063001, 2016.

[9] Huang Y, Zhang BL, Zeng MY, Hao YM, Ma ZX, Zhang HQ, et al. Liquid-nitrogen-cooled Ca$^+$ optical clock with systematic uncertainty of $3 \times 10^{-18}$. *Phys Rev Appl*, 17(3):034041, 2022.

[10] Safronova MS, Budker D, DeMille D, Kimball DFJ, Derevianko A, et al. Search for new physics with atoms and molecules. *Rev Mod Phys*, 90(2):025008, 2018.

[11] Flambaum VV and Dzuba VA. Search for variation of the fundamental constants in atomic and molecular and and nuclear spectra. *Can J Phys*, 87(1):25–33, 2009.
[12] Rosenband T, Hume DB, Schmidt PO, Chou CW, Brusch A, Lorini L, et al. Frequency ratio of Al$^+$ and Hg$^+$ single-ion optical clocks metrology at the 17th decimal place. *Science*, 319(5871):1808–1812, 2008.

[13] Lange R, Huntemann N, Rahm JM, Sanner C, Shao H, Lipphardt B, et al. Improved limits for violations of local position invariance from atomic clock comparisons. *Phys Rev Lett*, 126(1):011102, 2021.

[14] Peik E, Zimmermann K, Okhapkin M, and Tamm C. Prospects for a nuclear optical frequency standard based on thorium-229. In Maleki L, editor, *Proceedings of the Seventh Symposium on Frequency Standards and Metrology*, pages 532–538. World Scientific, Singapore, 2009.

[15] Campbell CJ, Radnaev AG, Kuzmich A, Dzuba VA, Flambaum VV, and Derevianko A. Single-ion nuclear clock for metrology at the 19th decimal place. *Phys Rev Lett*, 108:120802, 2012.

[16] Wense L, Seiferle B, Laatiaoui M, Neumayr JB, Maier H, Wirth H Wirth H, Runke J, Eberhardt K, Düllmann CE, Trautmann NG, and Thirolf PG. Direct detection of the $^{229}$Th nuclear clock transition. *Nature*, 553:47–51, 2016.

[17] Seiferle B, Wense L, Bilous PV, Amersdorffer I, Lemell C, Libisch F, Stellmer S, Schumm T, Düllmann CE, Pálffy A, and Thirolf PG. Energy of the $^{229}$Th nuclear clock transition. *Nature*, 573:243–246, 2019.

[18] Sikorsky T, Geist J, Hengstler D, Kempf S, Gastaldo L, Ens C, Mokry C, Runke J, Düllmann CE, Wobrauschek P, Beeks K, Rosecker V, Sterba J H, Kazakov G, Schumm T, and Fleischmann A. Measurement of the $^{229}$Th isomer energy with a magnetic microcalorimeter. *Phys Rev Lett*, 125:142503, 2020.

[19] Beeks K, Sikorsky T, Schumm T, Thielking J, Okhapkin MV, and Peik E. The thorium-229 low-energy isomer and the nuclear clock. *Nat Rev*, 3(238):5025–5033, 2021.

[20] Flambaum VV. Enhanced effect of temporal variation of the fine structure constant and the strong interaction in $^{229}$Th. *Phys Rev Lett*, 97:092502, 2006.

[21] Berengut JC, Dzuba VA, Flambaum VV, and Porsev SG. Proposed experimental method to determine $\alpha$ sensitivity of splitting between ground and 7.6 ev isomeric states in $^{229}$Th. *Phys Rev Lett*, 102:210801, 2009.

[22] Fadeev P, Berengut J C, and Flambaum VV. Sensitivity of $^{229}$Th nuclear clock transition to variation of the fine-structure constant. *Phys Rev A*, 102:052833, 2020.

[23] Fadeev P, Berengut J C, and Flambaum VV. Effects of variation of the fine structure constant $\alpha$ and quark mass $m_q$ in mössbauer nuclear transitions. *Phys Rev C*, 105:L051303, 2022.

[24] Kozlov MG, Safronova MS, Crespo López-Urrutia JR, and Schmidt PO. Highly charged ions: Optical clocks and applications in fundamental physics. *Rev Mod Phys*, 90(4):045005, 2018.

[25] Raymond JC. Highly charged ions in astrophysics. *In Physics of Highly-Ionized Atoms*, MA:189–208, 1989.

[26] Gillaspy JD. Highly charged ions. *J Phys B: At Mol Opt Phys*, 34(19):R93, 2001.

[27] Prochaska JX, Howk JC, and Wolfe AM. The elemental abundance pattern in a galaxy at z=2.626. *Nature*, 423(6935):57–59, 2003.

[28] Webb JK, King JA, Murphy MT, Flambaum VV, Carswell RF, and Bainbridge MB. Indications of a spatial variation of the fine structure constant. *Phys Rev Lett*, 107(19):191101, 2011.

[29] Berengut JC, Dzuba VA, and Flambaum VV. Enhanced laboratory sensitivity to variation of the fine-structure constant using highly charged ions. *Phys Rev Lett*, 105(12):120801, 2010.

[30] Berengut JC, Dzuba VA, Flambaum VV, and Ong A. Electron-hole transitions in multiply charged ions for precision laser spectroscopy and searching for variations in $\alpha$. *Phys Rev Lett*,
[31] Berengut JC, Dzuba VA, and Flambaum VV. Transitions in Zr and Hf and Ta and W and Re and Hg and Ac and and U ions with high sensitivity to variation of the fine-structure constant. *Phys Rev A*, 84(5):054501, 2011.

[32] Berengut JC, Dzuba VA, Flambaum VV, and Ong A. Optical transitions in highly charged californium ions with high sensitivity to variation of the fine-structure constant. *Phys Rev Lett*, 109(7):070802, 2012.

[33] Berengut JC and Flambaum VV. Manifestations of a spatial variation of fundamental constants in atomic and nuclear clocks and oklo and meteorites and and cosmological phenomena. *Euro Lett*, 97(2):20006, 2012.

[34] Berengut JC, Dzuba VA, Flambaum VV, and Ong A. Highly charged ions with E1, M1 and E2 transitions within laser range. *Phys Rev A*, 86(2):022517, 2012.

[35] Dzuba VA, Derevianko A, and Flambaum VV. High-precision atomic clocks with highly charged ions: Nuclear-spin-zero $j^{12}$-shell ions. *Phys Rev A*, 86(5):054501, 2012.

[36] Dzuba VA, Derevianko A, and Flambaum VV. Ion clock and search for the variation of the fine-structure constant using optical transitions in Nd$^{13+}$ and Sm$^{15+}$. *Phys Rev A*, 86(2):054502, 2012.

[37] Yudin VI, Taichenachev AV, and Derevianko A. Magnetic-dipole transitions in highly charged ions as a basis of ultraprecise optical clocks. *Phys Rev Lett*, 113(23):233003, 2014.

[38] Safronova MS, Dzuba VA, Flambaum VV, Safronova UI, Porsev SG, and Kozlov MG. Highly charged ions for atomic clocks and quantum information, and search for $\alpha$ variation. *Phys Rev Lett*, 113(3):030801, 2014.

[39] Safronova MS, Dzuba VA, Flambaum VV, Safronova UI, Porsev SG, and Kozlov MG. Highly charged Ag-like and In-like ions for the development of atomic clocks and the search for $\alpha$ variation. *Phys Rev A*, 90(4):042513, 2014.

[40] Safronova MS, Dzuba VA, Flambaum VV, Safronova UI, Porsev SG, and Kozlov MG. Atomic properties of Cd-like and Sn-like ions for the development of frequency standards and search for the variation of the fine-structure constant. *Phys Rev A*, 90(5):052509, 2014.

[41] Dzuba VA, Flambaum VV, and Katori H. Optical clock sensitive to variations of the fine-structure constant based on the Ho$^{14+}$ ion. *Phys Rev A*, 91(2):022119, 2015.

[42] Dzuba VA and Flambaum VV. Highly charged ions for atomic clocks and search for variation of the fine structure constant. *Hyperfine Interact*, pages 79–86, 2015.

[43] Dzuba VA, Safronova MS, UI Safronova, and Flambaum VV. Actinide ions for testing the spatial $\alpha$-variation hypothesis. *Phys Rev A*, 92:060502(R), 2015.

[44] Yu YM and Sahoo BK. Scrutinizing Al-like $^{51}$V$^{10+}$, $^{53}$Cr$^{11+}$, $^{55}$Mn$^{12+}$, $^{57}$Fe$^{13+}$, $^{59}$Co$^{14+}$, $^{61}$Ni$^{15+}$, and $^{63}$Cu$^{16+}$ ions for atomic clocks with uncertainties below the $10^{-19}$ level. *Phys Rev A*, 94(6):062502, 2016.

[45] Yu YM and Sahoo BK. Selected highly charged ions as prospective candidates for optical clocks with quality factors larger than $10^{15}$. *Phys Rev A*, 97:041403, 2018.

[46] Yu YM and Sahoo BK. Investigating ground-state fine-structure properties to explore suitability of boronlike S$^{11+}$-K$^{14+}$ and galliumlike Nb$^{10+}$-Ru$^{13+}$ ions as possible atomic clocks. *Phys Rev A*, 99(2):022513, 2019.

[47] Porsev SG, Safronova UI, Safronova MS, Schmidt PO, Bondarev AI, Kozlov MG, Tupitsyn II, and Cheung C. Optical clocks based on the Cf$^{15+}$ and Cf$^{17+}$ ions. *Phys Rev A*, 102:012802, 2020.

[48] Beloy K, Dzuba VA, and Brewer SM. Quadruply ionized barium as a candidate for a high-accuracy optical clock. *Phys Rev Lett*, 125:173002, 2020.
[49] Beloy K. Prospects of a Pb$^{2+}$ ion clock. *Phys Rev Lett*, 127(1):013201, 2021.

[50] Yu YM, Pan D, Chen SL, Arora B, Guan H, Gao K, and Chen JB. Atomic structure of Nd$^{9+}$ for highly charged ion clocks. *Atoms*, 10(4):123, 2022.

[51] Allehabi SO, Brewer SM, Dzuba VA, Flambaum VV, and Beloy K. High-accuracy optical clocks based on group-16-like highly charged ions. *Phys Rev A*, 106:043101, 2022.

[52] Allehabi SO, Dzuba VA, and Flambaum VV. Atomic clocks highly sensitive to the variation of the fine-structure constant based on Hf II, Hf IV, and W VI ions. *Phys Rev A*, 106:1032807, 2022.

[53] Uzan JP. The fundamental constants and their variation: observational and theoretical status. *Rev Mod Phys*, 75(2):403, 2003.

[54] Srianand R, Chand H, Petitjean P, and Aracil B. Limits on the time variation of the electromagnetic fine-structure constant in the low energy limit from absorption lines in the spectra of distant quasars. *Phys Rev Lett*, 92(12):121302, 2004.

[55] Patrignani C and others (Particle Data Group). Review of particle physics. *Chin Phys C*, 90:100001, 2016.

[56] Tanabashi M and others (Particle Data Group). Review of particle physics. *Phys Rev D*, 98(3):030001, 2018.

[57] Zyla PA and others (Particle Data Group). Review of particle physics. *Prog Theor Exp Phys*, 2020(8):083C01, 2020.

[58] Overduin JM and Wesson PS. Kaluza-klein gravity. *Phys Rep*, 283(5-6):303–378, 1997.

[59] Salam A and Stratheee J. On kaluza-klein theory. *Ann Phys*, 141(2):316–352, 1982.

[60] Chodos A, Jaffe RL, Johnson K, Thorn CB, and Weisskopf VF. New extended model of hadrons. *Phys Rev D*, 9(12):3471, 1974.

[61] Marciano W and Pagels H. Quantum chromodynamics. *Phys Rep*, 36(3):137–276, 1978.

[62] Bronnikov KA. Scalar-tensor theory and scalar charge. *Acta Phys Pol B*, B4, 1973.

[63] Webb JK, Murphy MT, Flambaum VV, Dzuba VA, Barrow JD, Churchill CW, et al. Further evidence for cosmological evolution of the fine structure constant. *Phys Rev Lett*, 87(9):091301, 2001.

[64] Murphy MT, Webb JK, and Flambaum VV. Further evidence for a variable fine-structure constant from keck/hires qso absorption spectra. *Mon Not R Astron Soc*, 345(2):609–638, 2003.

[65] Wilczynska MR, Webb JK, Bainbridge M, Barrow JD, Bosman SEI, and Carswell RF. Four direct measurements of the fine-structure constant 13 billion years ago. *Sci Adv*, 6(17):eaya9672, 2020.

[66] Whitmore JB and Murphy MT. Impact of instrumental systematic errors on fine-structure constant measurements with quasar spectra. *Mon Not R Astron Soc*, 447:446–462, 2015.

[67] Dumont V and Webb JK. Modelling long-range wavelength distortions in quasar absorption echelle spectra. *Mon Not R Astron Soc*, 468:1568–1574, 2017.

[68] David Davis E. The oklo natural fission reactors and improved limits on the variation in the fine structure constant. *AIP Conf Proc*, 2160(1):070012, 2019.

[69] Peik E, Lipphardt B, Schnatz H, Schneider T, and Tamm C. Limit on the present temporal variation of the fine structure constant. *Phys Rev Lett*, 93:170801, 2004.

[70] Fortier TM, Ashby N, Bergquist JC, Delaney MJ, Diddams SA, Heavner TP, Hollberg L, Itano WM, Jefferts SR, Kim K, Levi F, Lorini L, Oskay WH, Parker TE, Shirley J, and Stalnaker JE. Precision atomic spectroscopy for improved limits on variation of the fine structure constant and local position invariance. *Phys Rev Lett*, 98:070801, 2007.

[71] Guéna J, Abgrall M, Rovera D, Rosenbusch P, Tobar ME, Laurent P, Clairon A, and Bize S. Improved tests of local position invariance using $^{87}$Rb and $^{133}$Cs fountains. *Phys Rev Lett*, 98:080801, 2012.
[72] Leefer N, Weber CTM, Cingöz A., Torgerson JR, and Budker D. New limits on variation of the fine-structure constant using atomic dysprosium. *Phys Rev Lett*, 111:060801, 2013.

[73] Godun RM, Nisbet-Jones PBR, Jones JM, King SA, Johnson LAM, Margoli HS, Szymaniec K, Lea SN, Bongs K, and Gill P. Frequency ratio of two optical clock transitions in $^{171}$Yb and constraints on the time variation of fundamental constants. *Phys Rev Lett*, 113:210801, 2014.

[74] Huntemann N, Lipphardt B, Tamm Chr, Gerginov V, Weyers S, and Peik E. Improved limit on a temporal variation of $m_p/m_e$ from comparisons of Yb$^+$ and Cs atomic clocks. *Phys Rev Lett*, 113:210802, 2014.

[75] Ashby N, Parker TE, and Patla BR. A null test of general relativity based on a long-term comparison of atomic transition frequencies. *Nat Phys*, 14:822–826, 2018.

[76] Lea SN. Limits to time variation of fundamental constants from comparisons of atomic frequency standards. *Rep Prog Phys*, 70(9):1473, 2007.

[77] Karshenboim SG. Some possibilities for laboratory searches for variations of fundamental constants. *Can J Phys*, 78(7):639–678, 2000.

[78] Micke P, Leopold T, King SA, Benkler E, Spieβ LJ, Schmöger L, et al. Coherent laser spectroscopy of highly charged ions using quantum logic. *Nature*, 578(7993):60–65, 2020.

[79] King SA, Spieβ LJ, Micke P, Wilzewski A, Leopold T, Benkler E, et al. An optical atomic clock based on a highly charged ion. *Nature*, 611(7934):43–47, 2022.

[80] Liang SY, Zhang TX, Guan H, Lu QF, Xiao J, Chen SL, Huang Y, Zhang YH, Li CB, Zou YM, Li JG, Yan ZC, Derevianko A, Zhang MS, Shi TY, and Gao KL. Probing multiple electric-dipole-forbidden optical transitions in highly charged nickel ions. *Phys Rev A*, 103:022804, 2021.

[81] Windberger A, Crespo López-Urrutia JR, Bekker H, Oreshkina NS, Berengut JC, Bock V, Borschevsky A, Dzuba VA, Eliav E, Harman Z, Kaldor U, Kaul S, Safronova UI, Flambaum VV, Keite CH, Schmidt PO, Ullrich J, and Versolato OO. Identification of the predicted $5s$-$4f$ level crossing optical lines with applications to metrology and searches for the variation of fundamental constants. *Phys Rev Lett*, 114:150801, 2015.

[82] Cheung C, Safronova MS, Porsev SG, Kozlov MG, Tupitsyn II, and Bondarev AI. Accurate prediction of clock transitions in a highly charged ion with complex electronic structure. *Phys Rev Lett*, 124:163001, 2020.

[83] Bekker H, Borschevsky A, Harman Z, Keitel CH, Pfeifer T, Schmidt PO, et al. Detection of the $5p$ – $4f$ orbital crossing and its optical clock transition in Pr$^{3+}$. *Nat Commun*, 10(1):1–7, 2019.

[84] Nakajima T, Okada K, Wada M, Dzuba V A, Safronova MS, Safronova UI, Ohmae N, Katori H, and Nakamura N. Visible spectra of highly charged holmium ions observed with a compact electron beam ion trap. *Nucl Instrum Meth B*, 408:118–121, 2017.

[85] Berengut JC, Flambaum VV, and Ong A. Testing spatial alpha-variation with optical atomic clocks based on highly charged ions. *EPJ Web of Conferences*, 57:02001, 2013.

[86] Davidson K and Netzer K. The emission lines of quasars and similar objects. *Rev Mod Phys*, 51(4):715, 1979.

[87] Tsamis YG, Barlow MJ, Liu XW, Danziger IJ, and Storey PJ. A deep survey of heavy element lines in planetary nebulae – I. Observations and forbidden-line densities and temperatures and abundances. *Mon Not R Astron Soc*, 345(1):186–220, 2003.

[88] Träbert E, Beiersdorfer P, Utter SB, Brown GV, Chen H, Harris CL, et al. Experimental M1 transition rates of coronal lines from Ar X, Ar XIV, and Ar XV. *ApJS*, 541(1):506, 2000.

[89] Träbert E, Beiersdorfer P, Brickhouse NS, and Golub L. High-resolution laboratory spectra on the $\lambda^{131}$ channel of the aia instrument on board the solar dynamics observatory. *ApJS*, 211(1):14, 2014.
[90] Brewer JM, Fischer DA, Valenti JA, and Piskunov N. Spectral properties of cool stars: extended abundance analysis of 1617 planet-search stars. ApJS, 225(2):32, 2016.

[91] Wahlgren GM, Nielsen KE, and Leckrone DS. High-resolution spectroscopy of the hot Am star HR 3383. Mon Not R Astron Soc, 500(2):2451–2460, 2021.

[92] Biémont E and Bromage GF. Transition probabilities for forbidden lines: the silicon isoelectronic sequence from S III in to Sn XXXVII. Mon Not R Astron Soc, 205(4):1085–1096, 1983.

[93] Biémont E and Hansen JE. Forbidden transitions in $3p^4$ and $4p^4$ configurations. Phys Scr, 34(2):116, 1986.

[94] Biémont E and Hansen JE. Calculations of transition probabilities for forbidden lines in $3p^n$ and $4p^n$ configurations. Nucl Instrum Meth B, 23(1-2):274–277, 1987.

[95] Biémont E, Cowan RD, and Hansen JE. Transition probabilities for forbidden lines in the ground-state configuration of the bromine isoelectronic sequence. Phys Scr, 37(6):850, 1988.

[96] Biémont E and Quinet P. Forbidden lines in $6p^k$ ($k = 1 − 5$) configurations. Phys Scr, 54(1):36, 1996.

[97] Sugar J and Musgrove A. Energy levels of copper and Cu I through Cu XXIX. J Phys Chem Ref D, 19(3):527–616, 1990.

[98] Shirai T, Nakagaki T, Nakai Y, Sugar J, Ishii K, and Mori K. Spectral data and grotrian diagrams for highly ionized copper, Cu X-Cu XXIX. J Phys Chem Ref Data, 20(1):1–81, 1991.

[99] Chou HS, Chan JY, Chang YH, and Huang KN. Energy-level scheme and transition probabilities of S-like ions. At Data Nucl Data Tables, 62(1):77–145, 1996.

[100] Bhatia AK and Doschek GA. Atomic data and spectral line intensities for Ni XIII. At Data Nucl Data Tables, 68(1):49–90, 1998.

[101] Träbert E, Saathoff G, and Wolf A. Ground configuration level lifetimes in S-like Ni and Cu ions (Ni XIII and Cu XIV) measured at a heavy-ion storage ring. EPJD, 30(3):297–302, 2004.

[102] Träbert E, Hoffmann J, Krantz C, Wolf A, Ishikawa Y, and Santana JA. Atomic lifetime measurements on forbidden transitions of Al-, Si-, P- and S-like ions at a heavy-ion storage ring. J Phys B: At Mol Opt, 42(2):025002, 2008.

[103] Torrettì F, Windberger A, Ryabtsev A, Dobrodey S, Bekker H, Ubachs W, et al. Optical spectroscopy of complex open-4d-shell ions Sn$^{7+}$-Sn$^{10+}$. Phys Rev A, 95(4):042503, 2017.

[104] Ralchenko Y, Draganić IN, Osin D, Gillaspy JD, and Reader J. Spectroscopy of diagnostically important magnetic-dipole lines in highly charged 3d$^0$ ions of tungsten. Phys Rev A, 83(3):032517, 2011.

[105] Safronova MS, Safronova UI, Porsev SG, Kozlov MG, and Ralchenko Y. Relativistic all-order many-body calculation of energies, wavelengths, and M1 and E2 transition rates for the 3d$^0$ configurations in tungsten ions. Phys Rev A, 97(1):012502, 2018.

[106] Si R, Guo XL, Brage T, Chen CY, Hutton R, and Fischer CF. Breit and qed effects on the 3d$^0$ $^2D_{3/2}$ → $^2D_{5/2}$ transition energy in Co-like ions. Phys Rev A, 98(1):012504, 2018.

[107] Biémont E and Hansen JE. Energy levels and transition probabilities in 3d and 3d$^0$ configurations. Phys Scr, 39(3):308, 1989.

[108] Ali MA and Kim YK. Electric quadrupole and magnetic dipole transition probabilities in the potassium isoelectronic sequence. Phys Rev A, 38(8):3992, 1988.

[109] Charro E, Curiel Z, and Martín I. Atomic data for M1 and E2 emission lines in the potassium isoelectronic sequence. A&A, 387(3):1146–1152, 2002.

[110] Träbert E, Beiersdorfer P, Brown GV, Chen H, Thorn DB, and Biémont E. Experimental M1 transition rates in highly charged Kr ions. Phys Rev A, 64(4):042511, 2001.
[111] Guise ND, Tan JN, Brewer SM, Fischer CF, and Jönsson P. Measurement of the Kr XVIII $3d^2D_{5/2}$ lifetime at low energy in a unitary penning trap. *Phys Rev A*, 89(4):040502, 2014.

[112] Liu JP, Li CB, and Zou HX. Theoretical investigation on forbidden transition properties of fine-structure splitting in $^2D$ state for K-like ions with $26 \leq Z \leq 36$. *Chin Phys B*, 26(10):103201, 2017.

[113] Biémont E and Quinet P. Recent advances in the study of lanthanide atoms and ions. *Phys Scr*, T105:38, 2003.

[114] Radžiūtė1 L, Gaigalas G, Kato D, Rynkun P, Kučas S, et al. Energy level structure of Er$^{3+}$. *J Quant Spectrosc RA*, 152:94–106, 2015.

[115] Clementson J, Beiersdorfer P, Magee EW, McLean HS, and Wood RD. Tungsten spectroscopy relevant to the diagnostics of ITER divertor plasmas. *J Phys B: At Mol Opt Phys*, 43(14):144009, 2010.

[116] Mita PM, Kato D, Murakami I, Sakaue HA, and Nakamura N. Identification of visible lines from multiply charged W$^{8+}$ and W$^{9+}$ ions. *Phys Rev A*, 102(4):042818, 2020.

[117] Radžiūtė L, Gaigalas G, Kato D, Rynkun P, and Tanaka M. Extended calculations of energy levels and transition rates for singly ionized lanthanide elements. II. Tb-Yb. *ApJS*, 257(2):29, 2021.

[118] Derevianko A, Dzuba VA, and Flambaum VV. Highly charged ions as a basis of optical atomic clockwork of exceptional accuracy. *Phys Rev Lett*, 109(18):180801, 2012.

[119] Madelung E. *E. Die mathematischen Hilfsmittel der Physikers*. Springer, Berlin, 1936.

[120] Kramida A,Ralchenko Y, Reader J, and NIST ASD Team. NIST atomic spectra database (ver. 5.8), 2020.

[121] Zainab A and Tauheed A. Revised and extended analysis of doubly ionized gold: Au III. *J Quant Spectrosc RA*, 237:106614, 2019.

[122] Safronova UI, Flambaum VV, and Safronova MS. Transitions between the $4f$-core-excited states in Ir$^{16+}$, Ir$^{17+}$, and Ir$^{18+}$ ions for clock applications. *Phys Rev A*, 92:022501, 2015.

[123] Liu YL, Wu CQ, Ding XB, Zhang FL, Zhang L, Yao K, Yang Y, Koike F, Murakami I, Kato D, Sakaue HA, Nakamura N, and Dong CZ. The M1 transitions and visible spectra of W$^{13+}$ ion. *Phys Lett A*, 454:128500, 2022.

[124] Nandy DK and Sahoo BK. Highly charged W$^{13+}$, Ir$^{16+}$, and Pt$^{17+}$ ions as promising optical clock candidates for probing variations of the fine-structure constant. *Phys Rev A*, 94(3):032504, 2016.

[125] Huo X, Jiang G, and Li X. Atomic properties and transition parameters of highly charged Sb-like isoelectronic ions. *Can J Phys*, 95:590–594, 2017.

[126] Lu Q, Fu N, Yan CL, Qu FH, Yang Y, Wang K, Chen CY, Zou Y, and Xiao J. Experimental and theoretical investigations of visible spectra of W$^{12+}$. *J Quant Spectrosc RA*, 279:108064, 2022.

[127] Singh N, Aggarwal S, and Mohan M. Extended atomic structure calculations for W$^{11+}$ and W$^{13+}$. *Atoms*, 8:92, 2020.

[128] Fu N, Lu Q, Yan CL, Xu GQ, and Wang K. Re-investigation and line identifications for W$^{11+}$ in the visible range. *J Phys B*, 2022.

[129] Lu Q, Yan CL, Fu N, Yang Y, Chen CY, Xiao J, Wang K, and Zou Y. Measurement and identification of visible lines from W$^{10+}$. *J Quant Spectrosc RA*, 262:107533, 2021.

[130] Safronova UI and Safronova MS. Correlation and relativistic effects for the $4f - nl$ and $5p - nl$ multipole transitions in er-like tungsten. *Phys Rev A*, 84:012511, 2011.

[131] Lu Q, Yan CL, Meng J, Xu GQ, Yang Y, Chen CY, Xiao J, Li JG, Wang JG, and Zou Y. Visible spectra of W$^{8+}$ in an electron-beam ion trap. *Phys Rev. A*, 103:022808, 2021.
[132] Koziol K and Rzadkiewicz J. Theoretical level energies, radiative lifetimes and transitions in W IX. *At Data Nucl Data Tables*, 137:101372, 2021.

[133] Visscher L and Dyall KG. Dirac-fock atomic electronic structure calculations using different nuclear charge distributions. *At Data Nucl Data Tables*, 67(2):207, 1997.

[134] Helgaker T, Jørgensen P, and Olsen J. *Molecular Electronic Structure Theory*. Wiley, Chichester, 2000.

[135] Dykstra CE et al. *Theory and Applications of Computational Chemistry: The First Forty Years*. Elsevier, Netherlands, 2005.

[136] Olsen J, Roos B, Jorgensen P, and Jensen HJA. Determinant based configuration interaction algorithms for complete and restricted configuration interaction spaces. *J Chem Phys*, 89(4):2185–2192, 1988.

[137] Fleig T, Olsen J, and Marian CM. The generalized active space concept for the relativistic treatment of electron correlation. I. kramers-restricted two-component configuration interaction. *J Chem Phys*, 114(11):4775–4790, 2001.

[138] Fleig T, Olsen J, and Visscher L. The generalized active space concept for the relativistic treatment of electron correlation. II. large-scale configuration interaction implementation based on relativistic 2- and 4-spinors and its application. *J Chem Phys*, 119(6):2963–2971, 2003.

[139] Fleig T, Jensen HJA, Olsen J, and Visscher L. The generalized active space concept for the relativistic treatment of electron correlation. III. large-scale configuration interaction and multiconfiguration self-consistent-field fourcomponent methods with application to UO$_2$. *J Chem Phys*, 124(10):104106, 2006.

[140] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC22 (2022), written by H. J. A. Jensen, R. Bast, A. S. P. Gomes, T. Saue and L. Visscher, with contributions from I. A. Aucar, V. Bakken, C. Chibueze, J. Creutzberg, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, T. Helgaker, B. Helmich–Paris, J. Henriksson, M. van Horn, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, N. H. List, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, J. M. H. Olsen, A. Papadopoulos, Y. C. Park, J. K. Pedersen, M. Pempointner, J. V. Pototschnig, R. di Remigio, M. Repisky, K. Ruud, P. Salek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. Sunaga, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, S. Yamamoto and X. Yuan (available at [http://dx.doi.org/10.5281/zenodo.6010450](http://dx.doi.org/10.5281/zenodo.6010450)), see also [http://www.diracprogram.org](http://www.diracprogram.org).

[141] T. Saue, R. Bast, A. S. P. Gomes, H. J. Aa. Jensen, L. Visscher, I. A. Aucar, R. D. Remigo, K. G. Dyall, E. Eliav, E. Faßhauer, T. Fleig, L. Halbert, E. D. Hedegård, B. Helmich–Paris, M. Iliaš, Ch. R. Jacob, S. Knecht, J. K. Lærdahl, M. L. Vidal, M. K. Nayak, B. Senjean, A. Shee, A. Sunaga, and J. van Stralen. The DIRAC code for relativistic molecular calculations. *J Chem Phys*, 152:204104, 2020.

[142] Sahoo BK and Das BP. Relativistic normal coupled-cluster theory for accurate determination of electric dipole moments of atoms: First application to the $^{199}$Hg atom. *Phys Rev Lett*, 120(20):203001, 2018.

[143] Li CB, Yu YM, and Sahoo BK. Relativistic coupled-cluster-theory analysis of energies and hyperfine-structure constants and and dipole polarizabilities of Cd$^+$. *Phys Rev A*, 97(2):022512, 2018.
[144] Berkel DJ, Miller JD, Bergquist JC, Itano WM, and Wineland DJ. Minimization of ion micromotion in a paul trap. *J Appl Phys.*, 83(10):5025–5033, 1998.

[145] Keller J, Partner HL, Burgermeister T, and Mehlstäubler TE. Precise determination of micromotion for trapped-ion optical clocks. *J Appl Phys.*, 118(10):104501, 2015.

[146] Dubé P, Madej AA, Tibbo M, and Bernard JE. High-accuracy measurement of the differential scalar polarizability of a $^{88}$Sr$^+$ clock using the time-dilation effect. *Phys Rev Lett.*, 112(17):173002, 2014.

[147] Huang Y, Guan H, Bian W, Ma L, Liang K, Li T, et al. A comparison of two $^{40}$Ca single-ion optical frequency standards at the $5 \times 10^{-17}$ level and an evaluation of systematic shifts. *Appl Phys B*, 123(5):1–18, 2017.

[148] Itano WM. External-field shifts of the $^{199}$Hg$^+$ optical frequency standard. *J Res Nat Inst Stan*, 105(6):829, 2000.

[149] Dubé P, Madej AA, Bernard JE, Marmet L, Boulanger JS, and Cundy S. Electric quadrupole shift cancellation in single-ion optical frequency standards. *Phys Rev Lett.*, 95(3):033001, 2005.

[150] Sobelman II. *Atomic spectra and radiative transitions*. Springer Science & Business Media, New York, 2012.

[151] Sahoo BK. Nuclear quadrupole moment of $^{43}$Ca and hyperfine-structure studies of its singly charged ion. *Phys Rev A*, 80(1):012515, 2009.